Farklı Mühendislik Yaklaşımlarıyla Kompozit Malzemeler IV

Composite Materials with Different Engineering Approaches IV

Editörler: Dr. Öğr. Üyesi Yalçın Boztoprak
Prof. Dr. Murat Yazıcı

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ÖZGÜR
YAYINLARI

Ön Söz

Sevgili okuyucular,

Hayatta kullandığımız her ürün bir malzemeden üretilmekte ve günümüz teknolojileri ile birlikte kompozit malzemeler hayatımızda önemli bir yer tutmaktadır. Bu kitap, kompozit alanındaki bilimsel çalışmaları farklı mühendislik perspektiflerinden incelemektedir. Kompozit malzemeler üzerinde çeşitli malzemeler kullanarak yeni ürünler ve yenilikçi teknolojiler geliştirmek ve sürdürülebilir çözümler sağlamak için bu çalışmaları farklı mühendislik yaklaşımlarıyla incelemek önemlidir ve bu kitapta kompozit malzemeler bu bakış açısıyla incelenmiştir.

Okuyucular, günümüzde kompozit alanında yapılan çeşitli çalışmalara erişebilecekler. Kitapta ayrıca farklı matris ve takviye elemanları kullanılarak polimer, seramik ve elastomer matrisli kompozit malzemeler üzerinde yapılan çalışmalar hakkında bilgiler yer almaktadır.

Bu kitap akademisyenler, mühendisler, araştırmacılar ve öğrenciler için bir kaynak olarak tasarlanmıştır. İleride kompozit malzemeler üzerine yapacağınız araştırma ve çalışmalara büyük fayda sağlayacağına inanıyorum.

Saygılarımla.

Preface

Dear readers,

Every product we use in life is manufactured from a material, and composite materials hold an important place in our lives with today's technologies. This book examines scientific studies in the composite field from different engineering perspectives. It's important to examine these studies with different engineering approaches to develop new products and innovative technologies using a variety of materials on composite materials and provide sustainable solutions, and composite materials are examined in this book from such a perspective.

Readers will be able to access the diverse work being done today in the field of composites. The book also includes information on studies carried out on polymer, ceramic, and elastomer matrix composite materials using different matrix and reinforcing elements.

This book is designed as a resource for academics, engineers, researchers, and students. I believe that it will highly benefit your research and work on composite materials down the road.

Yours sincerely.

İçindekiler

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Bölüm 1

Yapısal Kompozit Süperkapasitörler

Merve Ünal[1]

Çağatay Özada[2]

Behiye Korkmaz[3]

Murat Yazıcı[4]

Özet

Artan sera gazı emisyonları ve fosil yakıtların giderek tükenmesi nedeniyle, dünyada çevrenin korunması ve küresel enerji talepleri konusunda giderek artan bir endişe söz konusudur. Bu nedenle, yakıt ve enerji tüketimini azaltan çok fonksiyonlu kompozit enerji depolama teknolojileri son yıllarda oldukça dikkat çekmektedir. Potansiyel bir elektrokimyasal enerji depolama ve yapısal mekanik yük taşıma sağlayan yapısal süperkapasitörler, bu özellikleri tek bir yapıda gösterdiği için genel sistemin hacminin ve kütlesinin azaltılmasını sağlarlar. Bu üstün özelliği sayesinde yapısal süperkapasitörler elektrikli araçlar, havacılık endüstrisi ve taşınabilir cihazlar için cazip bir seçenek haline gelmiştir. Bu kitap bölümü yapısal süperkapasitörlerin, geliştirilmiş elektrokimyasal ve mekanik özelliklere sahip elektrotları, elektrolitleri ve ayırıcıları hakkında genel bir bakış açısı sunmaktadır.

1. Giriş

Elektrik enerjisi depolama cihazlarına olan talep, genişleyen yeşil enerji sektörü, elektronik ve elektrikli araç endüstrisinin hızlı gelişimi ile son yıllarda önemli ölçüde artmıştır [1]. Bununla birlikte elektrikli araçlar, hava taşıtları ve yapısal malzemelerde menzil ve çalışma süresini arttırmak için daha fazla

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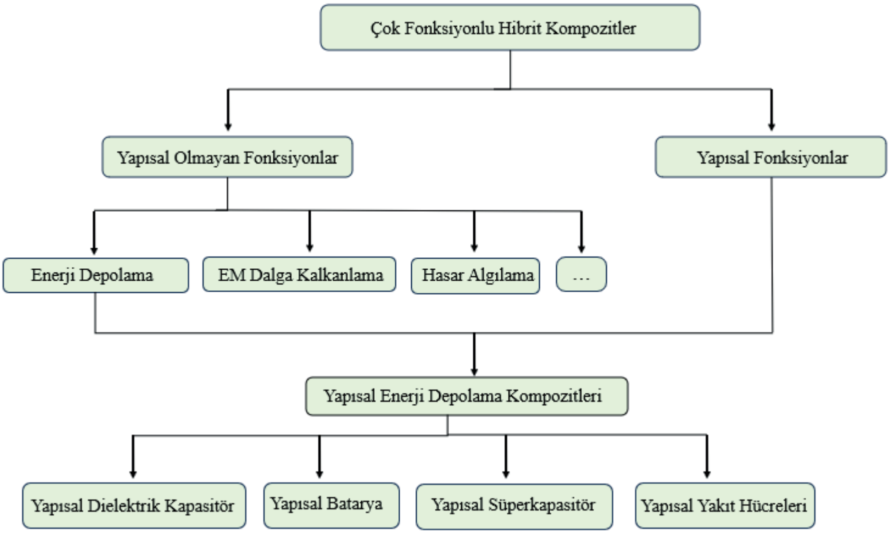
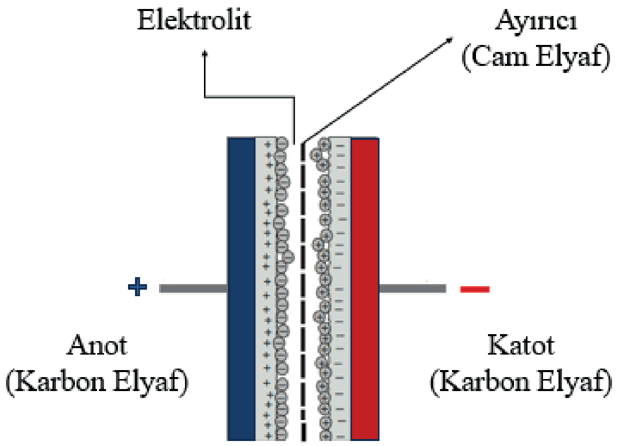
bataryaya ihtiyaç duyulmaktadır. Bu durum, yük taşıma kapasitesine katkıda bulunmayan [2] ağırlık artışlarına neden olmaktadır [3]. Bu bağlamda ağırlıkta iyileşme sağlayan çok fonksiyonlu hibrit kompozitler, son yıllarda oldukça dikkat çekmektedir. "Hibrit kompozitler" terimi iki veya daha fazla türde takviye elyafı içeren yük taşıyıcı yapısal kompozitleri tanımlamaktadır [4]. Ancak, karbon nanotüp ve grafen gibi nano yapıdaki katkıların geliştirilmesi hibrit kompozitlerin kapsamını büyük ölçüde genişletmiş ve elektriksel ve termal özellikler gibi yapısal olmayan fonksiyonları da mümkün kılmıştır [5]. Yapısal fonksiyonların ve yapısal olmayan fonksiyonların birbiri ile entegrasyonu ile son on yılda hibrit kompozit araştırmalarında çok önemli gelişmeler kaydedilmiştir. İlgili araştırmacıların sürekli elyaflar kullanarak sert, mukavim ve hafif yapısal kompozitler ile enerji depolama sistemini birleştirme çalışmaları yapısal enerji depolama kompozitlerinin oluşumunu sağlamıştır [6]. Yüksek mekanik rijitlik/mukavemet ve yeterli enerji depolama kapasitesini aynı anda sağlayabilen yapısal enerji depolama kompozit cihazları, elektrikli araçlar ve hava araçları da dahil olmak üzere birçok yapısal uygulama için ağırlık azalması ve hacim kazanımı ile birlikte sürdürülebilirlik stratejisi sunmaktadır [3,7]. Şekil 1'de gösterildiği gibi yapısal enerji depolama kompozitleri; yapısal dielektrik kapasitörler, yapısal piller, yapısal yakıt hücreleri ve yapısal süperkapasitörler olmak üzere çeşitli enerji depolama cihazlarını kapsamaktadır. Bu kitap bölümünün ana konusunu yapısal süperkapasitörler oluşturmaktadır.



Şekil 1: Çok fonksiyonlu hibrit kompozitlerin sınıflandırılması [6].

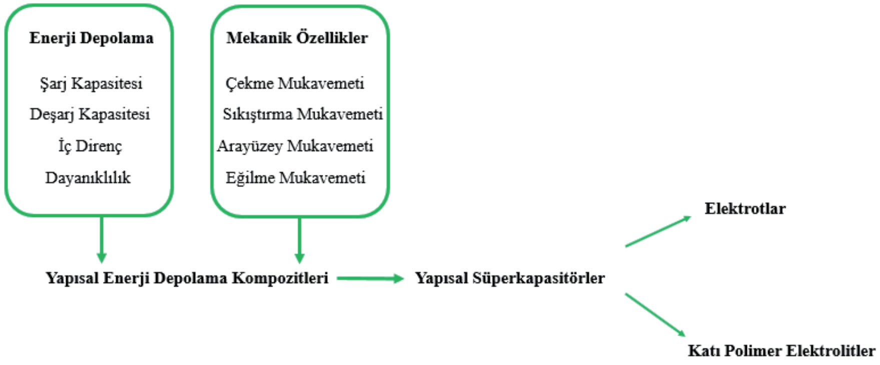
2. Yapısal Süperkapasitörler

Süperkapasitörler geleneksel bataryalara göre daha yüksek güç yoğunluğu, daha uzun çevrim ömrü ve daha iyi tersinirlik ve geleneksel kapasitörlere göre daha hızlı şarj/deşarj döngüsü gibi çeşitli avantajlar sunan bir enerji depolama cihazıdır [8–12]. Süperkapasitörlerde enerji depolama, elektrot/elektrolit arayüzünde elektrostatik yük birikimine dayanır. Geleneksel olarak bir membranla ayrılmış ve yüksek iyonik iletkenliğe sahip bir sıvı elektrolitin içine gömülmüş gözenekli karbon yapıda iki elektrottan oluşan bir sandviç yapıda gerçekleştirilir. Süperkapasitörler enerji depolama yöntemlerine göre elektriksel çift katmanlı kapasitörler (EDLC'ler), psödokapasitörler ve hibrit kapasitörler olmak üzere üç kategoriye ayrılır [11]. EDLC'lerde Şekil 2'de gösterildiği gibi, elektrotlar ve elektrolit arasındaki arayüzeyde iyon adsorpsiyonu yoluyla elektrik enerjisi depolamaktadır [3]. Psödokapasitörler için yaygın kullanılan elektrot malzemeleri Nikel (Ni), Rutenyum (Ru) ve Manganez (Mn) gibi geçiş metal oksitleri ve polipirol (PPy), polianilin (PANI) ve politiyofen (PTh) gibi iletken polimerlerdir [13–15]. Bu kapasitörlerde elektrik enerjisi, pillerin çalışma prensibine benzer şekilde elektrotların yüzeyindeki redoks reaksiyonu ile depolanır. Bu nedenle, şarj ve deşarj sürecinde iletken elektrotlarda kimyasal tükenmeler meydana gelebilmektedir. Bu durum psödokapasitörlerde elektrostatik enerji depolama sistemlerine kıyasla sınırlı bir kullanım ömrüne neden olmaktadır. Hibrit kapasitörlerde ise geleneksel bir EDLC'den daha yüksek enerji depolama, ancak bir bataryadan daha iyi güç sağlamak için hem bir elektro-çift katmanlı elektrodu hem de psödokapasitif tipi elektrodu birleştirir [11]. Süperkapasitörlerde kullanılan elektrolitler ise iyonik olarak iletken ancak elektriksel olarak yalıtkan malzemelerdir [16]. Süperkapasitörlerin sahip olduğu özellikleri, süperkapasitörleri cazip bir enerji depolama seçeneği haline getirmekte ve optimizasyonlarıyla ilgili çok sayıda araştırma yapılmasını sağlamaktadır.



Şekil 2: Elektriksel çift katmanlı kapasitörlerin şematik gösterimi [1].

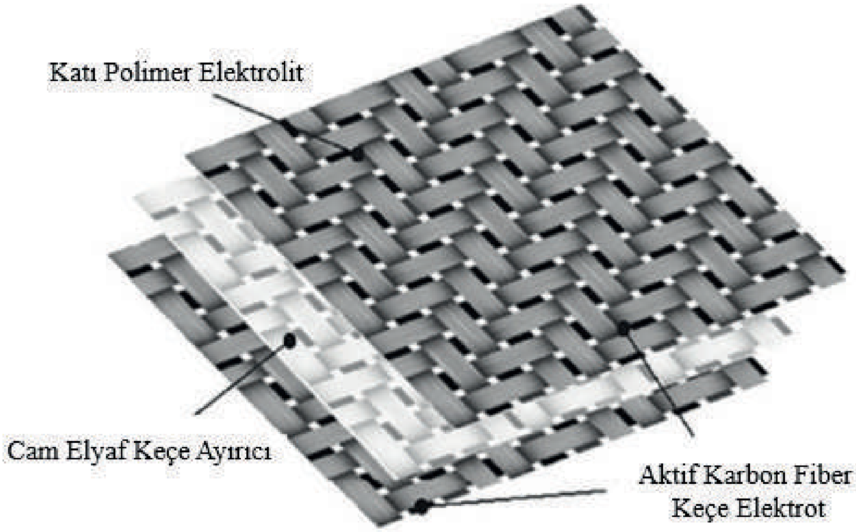
Son yıllarda, yapısal süperkapasitörler yeni bir süperkapasitör türü olarak ortaya çıkmıştır. Bu süperkapasitörler elektrik enerjisini depolarken aynı zamanda mekanik yükleri de taşıyabilmektedirler [1] (Şekil 3). Sahip oldukları üstün özellikler sayesinde yapısal süperkapasitörler; elektrikli araçlar, havacılık ve insansız hava araçları gibi çeşitli uygulamalarda kullanılabilmektedir [8,17].



Şekil 3: Yapısal enerji depolama kompozitlerinin çok fonksiyonelliği [18].

Tipik olarak yapısal süperkapasitörler Şekil 4'te gösterildiği gibi yapısal karbon esaslı elektrotlardan, ayırıcı olarak bir cam elyaftan (GF) ve yüksek mekanik mukavemete sahip katı hal polimer elektrolitinden (SPE) oluşur. Yapısal elektrolitlerdeki iyonların hareketi, iletken elektrotların her iki tarafına voltaj uygulanarak başlatılır ve elektrik alanının oluşmasına neden olur [16].

Bir süre sonra enerji, elektrot ile elektrolit arasındaki arayüzde iyonların çift katman şeklinde birikmesiyle depolanır. Yapısal elektrotların yüksek enerji depolama kapasitesine ve iyi mekanik özelliklere sahip olması gerekir. Bu elektrotların üretiminde karbon elyaf (CF), karbonun hem elektrotlar için hem de yüksek performanslı yapısal takviye olarak yaygın bir şekilde kullanılması nedeniyle cazip bir başlangıç noktasıdır [2]. Bununla birlikte, karbon nanotüp(CNT) ve karbon aerojel (CAG) yapısal süperkapasitörler için kullanılan ana elektrot malzemeleridir [19]. Yapısal elektrolitler, iyonik hareketi oluşturarak katı ve sert yapısıyla mekanik destek de sağlar. Polimerler hem yapısal matris hem de elektrolit olarak kullanılabilir. Ancak her iki özelliği aynı ayda gerçekleştirebilmek için dikkatli bir tasarım gereklidir [2]. Yapısal elektrolitler temel olarak matris polimerlerden, iyonik sıvılardan (IL) ve lityum tuzlarından oluşmaktadır [19].



Şekil 4: Yapısal süperkapasitörün şematik gösterimi [2].

3. Yapısal Süperkapasitör Elektrotları

Elektrot malzemeleri yapısal süperkapasitörlerde kritik öneme sahiptir. Süperkapasitörün yük depolama kapasitesini tanımlamaktadır. Bu kapasite elektrot malzemesinin porozitesine, özgül yüzey alanına ve dış etkenlere karşı gösterdiği yüksek kararlılığa bağlıdır. Yüksek enerji yoğunluğuna ulaşmak için yüzey alanın geniş olması beklenmektedir. Bu durum yüzeyde iyonların depolanmasını arttıracağı için Helmholtz çift katman yapısını olumlu yönde etkilemektedir.

Karbon bazlı elektrotların enerji depolama uygulamalarında kullanılmasını uygun kılan başlıca özellikleri; düşük maliyetleri, geniş yüzey alanları, kontrollü gözenek yapıları, yüksek iletkenlikleri, yüksek sıcaklık kararlılıkları ve kompozit malzemelerle uyumluluklarıdır. Ayrıca bu malzemeler iyi bir korozyon direnci sergilerler. Yüzey alanı ve elektrot malzemesinin gözenek boyutu, spesifik kapasitansı etkileyen en önemli faktörlerdir.

Aktif karbon, karbon nanotüpler (CNT) ve grafen gibi karbon bazlı malzemeler normalde EDLC'lerde çalışma elektrotları olarak kullanılır. Diğer aktif karbon formlarıyla karşılaştırıldığında, CNT'ler daha yüksek iletkenliğe sahiptir ve bu da yüksek güç yoğunluklarına katkıda bulunur. Karbon bazlı elektrotlar, kısmen çeşitli özelliklerini iyileştirmek için çok çeşitli yöntemlerin mevcut olması nedeniyle giderek daha popüler hale gelmektedir. Karbonun işlevselleştirilmesinin yanı sıra karbona kusurların eklenmesi ve kompozit elektrotlar yapmak için redoks-aktif malzemelerle birlikte kullanılmaları, bir süperkapasitörün performansını artırmaktadır.

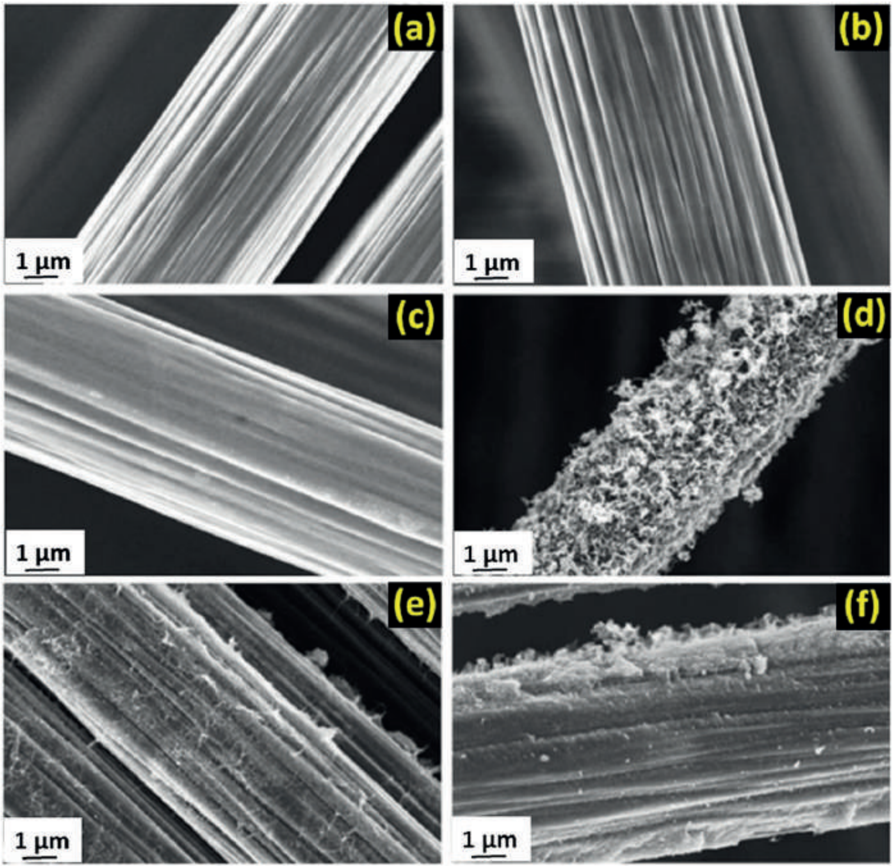
3.1. Karbon Elyaf

Karbon elyaf, çekme mukavemeti, basma mukavemeti, delaminasyon direnci ve çok iyi elektrik iletkenliği gibi olağanüstü mekanik özellikleri olduğu için mükemmel bir yapısal süperkapasitör elektrot malzemesidir. Karbon elyaf elektrot yüksek erişilebilir yüzey alanına, elektrokimyasal stabiliteye ve mekanik esnekliğe sahiptir. Bununla birlikte, aktif karbonlar, CNT'ler, grafen ve karbon aerojeller gibi diğer karbon bazlı malzemelerle karşılaştırıldığında, karbon elyaf yapısal elektrotlar düşük spesifik yüzey alanları (0,2 m^2 /g) nedeniyle daha düşük spesifik kapasitans (11 mF/g) göstermektedir [20]. Bozulmamış karbon elyaf pürüzsüz bir yüzeye ve kimyasal inertliğe sahiptir, bu da elektrolit iyonları ile arayüzey etkileşimi için düşük aktiviteye neden olur. Bozulmamış karbon elyaf genellikle şarj-deşarj işleminde çok düşük elektriksel çift katman kapasitansı gösterir.

Karbon elyaf üzerine uygulanan fiziksel, kimyasal veya elektrokimyasal aktivasyon işlemleri sayesinde fonksiyonel gruplar eklenebilmektedir. Bu fonksiyonel gruplar sayesinde karbon elyafların ıslanabilirliği elektrokimyasal performansının geliştirilmesi sağlanmaktadır [21]. Hidroksil ve karbonil gibi oksijen içeren fonksiyonel gruplar elektrokimyasal performans üzerinde önemli etkiye sahiptir. Bu nedenle, istenen fonksiyonel gruplara sahip iyi tasarlanmış karbon elektrot, süper kapasitör uygulamaları için uygulanabilir ve bu da elektrokimyasal aktiviteyi ve kapasitansı etkili bir şekilde artırabilir. Ayrıca, morfoloji ve mikroyapı elektrot malzemelerinin elektrokimyasal özelliklerini etkileyen önemli faktörlerdir.

Karbon elyafların farklı asitler, bazlar ve yüzey aktif maddeler ile yüzey modifikasyonu sağlanmaktadır. Özellikle, çok güçlü asitler veya bazlar elyaf kalitesini bozabilir ve kompozitlerin zayıf mekanik özelliklerine neden olabilir. Bu nedenle, kullanılan modifiye edici maddenin hacmini dikkatli bir şekilde seçmek ve ayarlamak önemlidir. Daha önceki araştırmalar potasyum hidroksit (KOH) ile işlemin mekanik özelliklerden ödün vermeden karbon elyafların yüzey alanını arttırdığını göstermiştir. Bununla birlikte, oksijen plazma ve büyük darbeli elektron ışını teknikleri de bulunmaktadır. Bunlar yüzey alanını ve matris arayüzeyinin yapışmayı iyileştirebilen tahribatsız yöntemlerdir.

Şekil 5, farklı yüzey işlemlerinden sonra karbon elyaf elektrotlarının taramalı elektron mikroskobu (SEM) görüntülerini göstermektedir. Brunauer-Emmett-Teller (BET) yüzey alanındaki ve özgül kapasitansındaki değişiklikler Tablo 1'de sunulmuştur.



Şekil 5 a)Karbon elyaf, b) Isıl işlem CF, c) KOH işlemli CF, d) CNT graft, e) CNT kaplama, f) Karbon aerojel modifiyeli CF SEM görüntüleri [22].

Tablo 1. CF/GF/CF kompozitinde farklı işlemlerle muamele edilen CF'lerin BET yüzey alanı ve özgül kapasitansı (3 M potasyum klorür (KCl) elektrolitinde 5 mV s-1 tarama hızında -0,2 ila 0,2 V arasında elde edilen döngüsel voltametri verilerinden hesaplanmıştır) [22].

Sıra	Karbon Elyaf Örnekler	BET Yüzey Alanı (m^2/g)	Özgül Kapasitans (F/g)
1	Karbon Elyaf (CF)	0,035	0,057
2	Isıl işlem CF	0,068	1,453
3	KOH işlemli CF	37,263	29,451
4	CNT kaplama	38,562	27,291
5	CF üzerinde CNT	41,027	30,783
6	Karbon aerojel modifikasyonu	165,252	156,462

3.2. Karbon Nanotüp

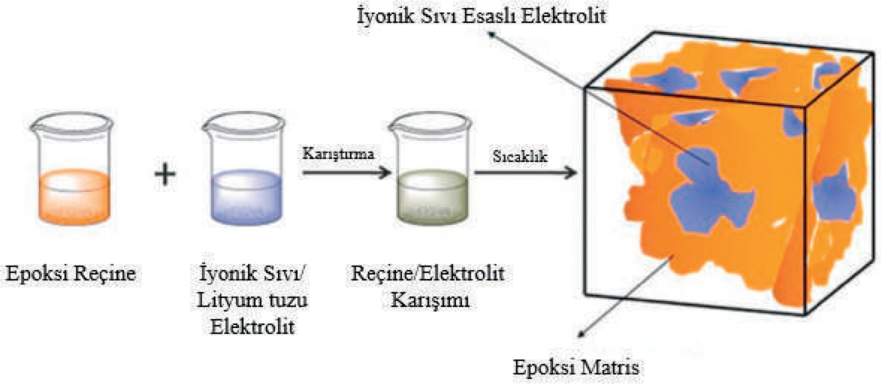
Benzersiz gözenek yapıları, olağanüstü elektriksel özellikleri ve iyi mekanik ve termal dayanıklılıkları nedeniyle, tek boyutlu ("quasi 1D") karbon nanotüpler son yıllarda süperkapasitör uygulamaları için büyük ilgi görmüştür. Karbon nanotüpler sırasıyla tek duvarlı karbon nanotüpler (SWCNT'ler), çift duvarlı karbon nanotüpler (DWCNT'ler) ve çok duvarlı karbon nanotüpler MWCNT'ler olarak üçe ayrılmaktadır [23]. Yüksek elektrik iletkenlikleri ve kolay erişilebilir yüzey alanları tek duvarlı karbon nanotüpün [(SWCNT) > 1600 m^2 /g], çok duvarlı karbon nanotüpten [(MWCNT) > 430 m^2 /g)] daha fazla olması [6] nedeniyle yüksek güçlü elektrot malzemeleri için uygundur. Ayrıca, karbon nanotüpler boru şeklindeki ağ ve yüksek mekanik esneklik nedeniyle aktif malzemeler için ideal takviyeler oluşturmaktadır.

3.3. Karbon Aerojel

Eşsiz üç boyutlu kafes yapısı, geniş spesifik yüzey alanı, düşük yoğunluğu ve mükemmel elektrik iletkenliği ile karbon aerojel, süper kapasitörler için ideal bir elektrot malzemesi olarak kabul edilir. Geleneksel karbon aerojeller fenolik reçineler, poliamidler ve poliüretanlar gibi polimerlerden elde edilir ve genellikle sol-jel, çözücü değişimi, süperkritik kurutma ve karbonizasyon süreçleriyle hazırlanır [24]. Karbon aerojellerin spesifik yüzey alanı 400-800 m^2 /g aralığındadır [25]. Mekanik özellikleri nispeten zayıf olduğundan, karbon aerojeller doğrudan yapısal uygulama için uygun değildir. Bu süreçler yüksek enerji tüketimine ve düşük verime sahip olma eğilimindedir ve bu da çeşitli çevre kirliliği sorunlarına yol açabilir. Biyokütleden karbon aerojel elektrot malzemelerinin hazırlanması, uygun maliyet etkinliğinin yanı sıra yeşil ve sürdürülebilir kalkınma için elverişlidir. Mevcut biyokütle karbon aerojel elektrotları, alg, bambu, şeker kamışı, odun, mısır samanı, muz vb. türetilen biyokütle polisakkaritlerine ve proteinlerine dayanmaktadır. Biyokütlenin doğal yapısı ile karbon aerojellerin hazırlanması benzersiz avantajlara sahip olmaktadır.

4. Yapısal Elektrolitler

Yapısal elektrolitler cihaz performansı için kritik öneme sahiptir ve yapısal süperkapasitör teknolojisinin en zorlu yönlerinden biridir [26]. Çünkü yüksek iyonik iletkenlik esnek bir yapı gerektirirken, iyi mekanik özellikler ise polimer zincirlerinin sertliğini gerektirir. Yapısal elektrolitler; elektrotlara iyon taşımasını sağlayan, diğer bileşenlerle kimyasal olarak uyumlu, işlenebilir, ölçeklenebilir ve arayüzlerinde iyi bir mekanik bağa ihtiyaç duyan yapılardır [27]. Bu elektrolitlerin etkili olabilmesi için 0,1 ila 1 GPa arasında bir sıkıştırma ve kesme sertliği sağlayabilmesi ve ortalama 1 mS/cm mertebesinde bir iyon iletkenliğini gerçekleştirmesi gerekir [3,26,28]. Yapısal süperkapasitörlerde sıklıkla kullanılan katı elektrolitler, bir tuzun polimer matris içine dağıldığı tek fazlı elektrolitlerdir. Bu elektrolitlerin avantajları, herhangi bir uçucu veya yanıcı bileşiğin olmaması ve iyi mekanik özelliklere sahip olmasıdır [3]. Epoksi reçine ve vinil esterler gibi yüksek performanslı kompozitler en yaygın kullanılan yapısal polimer matrisleridir. Bu bağlamda, bu matrislerin modifikasyonları da yapısal elektrolitlerin temelini oluşturmaktadır [27]. Literatürde yapılan çalışmada [29], iyon taşınımını arttırmak için matrise lityum iyon tuzu katılarak elektrolit oluşturulmuştur. Elde edilen elektrolitin $1.7 \times 10-3$ mS/cm iyonik iletkenlik değerine ve 15 MPa sıkıştırma sertliğine sahip olduğu görülmüştür. İyonik iletkenlik ve mekanik davranışları optimize edilen bir başka çalışmada [30] ise, $1.6 \times 10-5$ mS/cm iyonik iletkenliğe ve 560 MPa sıkıştırma sertliğine sahip katı elektrolitler bildirilmiştir. Polimerlere iyonik sıvıların ve batarya elektrolitlerinin eklenmesi, yapısal ve iyonik taşıma fazlarının iç içe geçtiği bir ağ sağlayarak daha umut vericidir. İyonik sıvılar, düşük sıcaklıkta veya oda sıcaklığında erimiş, yüksek iletkenliğe sahip tuzlardır [31]. Bu özelliklerinden dolayı, ideal sıvı elektrolitlerden farklı özellikler gösterirler. Literatürde katı elektrolitlerde en sık rapor edilen çalışmalar [32–35], epoksi matrisi ve iyonik sıvılardan oluşmaktadır. Bu elektrolitlerde, yüksek viskoziteli iyonik sıvı termal kararlılık ve iyonik iletken özelliği sağlarken [36], epoksi matrisi ise mekanik özelliklerin yanında kimyasal ve termal kararlılık [34] sağlar. Literatürde yapılan bir çalışmada [37], epoksi reçine ve Etil-3-metilimidazolyum bis(triflorometilsülfonil)imid (EMIM-TFSI) iyonik sıvısı ve lityum bis(triflorometan) sülfonimid (LiTFSI) tuzundan oluşan bir polimer elektrolit Şekil 6'da gösterildiği gibi geliştirilmiştir. Bu elektrolitin maksimum iyonik iletkenliği 8 × 10-3 S/cm ve Young modülü 0,18 GPa olarak bulunmuştur. Bir başka çalışmada [31] ise trimetilamonyum bis(triflorometansülfonil)imid iyonik sıvısı kullanarak hazırlanan epoksi esaslı polimer elektrolitlerin iyonik iletkenlik değerlerinin 1 × 10-3 S/cm'ten yüksek olduğu görülmüştür. Bununla birlikte, katı elektrolitlerde mekanik özelliklerin ve iyonik iletkenliğin optimum koşullarda beraber sağlanması güçlük oluşturmaktadır. Bu durumda, matris ve iyonik sıvı (IL) fazların oranları kontrol edilerek, mekanik ve elektrokimyasal performans arasındaki denge ayarlanabilir [27].



Şekil 6: Epoksi reçine/iyonik sıvı esaslı katı polimer elektrolitlerin üretim prosedürü şematik gösterimi [37].

Polimer matrisinin yüksek kristalinitesinin katı polimer elektrolitlerde iyon taşınmasına zarar verildiği yapılan bir çalışmada rapor edilmiştir [38]. Bu nedenle, matris yapıya SiO_2, TiO_2 ve Al_2O_3 gibi inorganik katkı maddelerinin eklenmesi polimerin kristalliğini azalmak için etkili bir yaklaşım olduğu bildirilmiştir [6,39]. Bu yaklaşım katı polimer elektrolit çalışmalarında ilgi görmüştür [40–42]. Dolgu maddelerinin boyutu ve yüzey alanı ile bunların polimer elektrolit içindeki dağılımı, katı polimer elektrolitlerin hem iyonik iletkenliğini hem de elastik modülünü etkileyen başlıca faktörlerdir [43,44]. Literatürde gerçekleştirilen bir çalışmada [41], Al_2O_3 inorganik katkı maddesi epoksi reçine/iyonik sıvı/lityum tuzu sistemine dahil edilmiş ve Young modülü 1 GPa ve iyonik iletkenliği 0.29 mS cm−1 olan bir katı polimer elektrolit geliştirilmiştir. Diğer bir çalışmada [40] ise, PEGDGE/iyonik sıvı elektrolitine mezogözenekli SiO_2 katkısının eklenmesi ile sıkıştırma mukavemeti ve iyonik iletkenliğinde artış görülmüştür. Ağırlıkça %7.5 SiO_2 mezogözenekli polimer elektrolitin iyonik iletkenliği 0.29 mS cm−1 ve Young modülünün 21.9 MPa'a ulaştığı bildirilmiştir. Elde edilen bu değerler, SiO_2 katkısı içermeyen elektrolite göre iyonik iletkenliğinin arttığı, mekanik özelliğin ise iyileştiği görülmüştür.

5. Ayırıcılar

Geleneksel enerji depolama cihazlarında, iyonların geçmesine izin veren, pozitif ve negatif elektrotlar arasındaki elektron geçişini önleyen gözenekli bir ayırıcı kullanılır [45,46]. İdeal bir separatör iyi elektrik yalıtımına, yüksek gözenekliliğe, iyon taşıma mesafesini ve ağırlığını en aza indirmek için düşük kalınlığa ve iyi mekanik stabiliteye sahip olmalıdır [6]. Gözenekli polipropilen ve selüloz membranlar genellikle ticari enerji depolama cihazlarında ayırıcı olarak kullanılır [47,48], ancak zayıf mekanik mukavemetleri ve katı polimer reçine elektrolitlere zayıf yapışmaları nedeniyle yapısal süperkapasitörler için uygun seçim değildir. Literatürde yapılan bir çalışmada [49] gelişmiş iyonik iletkenliğe ve gözenekli polipropilen membran ve selüloz ayırıcıya kıyasla %80 daha fazla gözenekli poli(viniliden florür) esaslı bir ayırıcı geliştirilmiştir. Bu ayırıcının yapısal uygulamalarda kullanılması için mekanik özellikleri açısından optimizasyon çalışmaları yapılması gereklidir. Yapısal süperkapasitörler ayırıcısı olarak iyi yalıtıma sahip olan cam elyaf kumaş, mükemmel bir seçimdir. Dokuma kumaş yapısı sayesinde, cam elyaf kumaş birden fazla iyon değişim kanalı sağlayabilir ve yalıtkan yapısı pozitif ve negatif elektrotlar arasındaki kısa devreyi önleyebilir [18]. Ayrıca elektrolitin yapısına nüfuz etmesine izin veren cam elyaf kumaş, iyi ıslanabilirlik sağlayarak ve reçine ile uygun bir bağlanma gösterir. Bu da önemli stres yüklemesine ve delaminasyonlara dayanabilmesine olanak sağlar [2,16]. Bununla birlikte, cam elyaf kumaşın en büyük dezavantajı, kumaşın her katmanının kalınlığının geleneksel ayırıcılara kıyasla nispeten büyük olması ve bu da iyon taşıma mesafesini artırmasıdır. Fakat genel performansı göz önüne alındığında, cam elyaf kumaş hala birçok yapısal süperkapasitörlerde ayırıcı olarak yaygın bir şekilde kullanılmaktadır.

6. Sonuç

Bu kitap bölümünde elektrikli araçlarda, taşınabilir elektroniklerde ve insansız hava araçlarına yönelik enerji depolama cihazlarında yaygın olarak kullanılabilecek çok fonksiyonel yapısal süperkapasitörlerin genel perspektifte bir anlatımı yapılmıştır. Çok fonksiyonelliğe sahip yapısal enerji depolama sistemleri, ilgili uygulamaların geleceği için umut vaat etmektedir. Bu enerji sistemleri, atomlar ve moleküller gibi maddi elemanların hem yük taşıma hem de enerji işlevi göstermesi ile kütle verimliliği için önemlidir [50]. Yapısal süperkapasitörlerde diğer yapısal enerji depolama sistemlerinden farklı olarak, enerji performansı gösterilirken yapısal bütünlüğü korumak daha basit olduğu için dikkat çekmektedir. Yapısal süperkapasitörlerin fonksiyonel özelliklerinin, geleneksel süperkapasitörlerin veya elyaf takviyeli polimer kompozitlerinin son teknoloji performansına ulaşılmasına gerek olmadığı değerlendirmesi yapılmıştır [51]. Kütle sisteminden tasarruf edilmesi ve enerji verimliliğinin artırılması, iki işlevin uygun bir şekilde dengelenmesiyle elde edilebilmektedir. Ayrıca, verimli bir yapısal süperkapasitörün polimerik elektrolitinde mekanik özelliklerin ve iyonik iletkenliğin birlikte sağlanması oldukça önemlidir. Elektrolit kısmında her iki özelliğin beraber sağlanması zorlu bir iştir çünkü polimer yapısının sertliğinin arttırılması, iyon taşınmasını kesintiye uğratarak iyonik iletkenliği azaltma eğilimindedir [9]. Bu bağlamda, yeni malzeme geliştirilmesi ve tasarım ile yapısal süperkapasitörlerin hem elektrokimyasal enerji depolama hem de mekanik performanslarını arttırmak için daha fazla çalışmaya ihtiyaç duyulmaktadır. Geliştirilen yapısal süperkapasitörlerin pratik uygulamalar için kolay üretilebilir ve maliyet açısından da verimli olması istenmektedir.

Teşekkür

Bu çalışma, Bursa Uludağ Üniversitesi Bilimsel Araştırma Projeleri (BAP) birimi tarafından desteklenen FOA-2022-1146 numaralı proje kapsamında gerçekleştirilmiştir. Yazarlar, Bursa Uludağ Üniversitesi BAP birimine verdiği destekten dolayı teşekkür etmektedir.

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Chapter 2

A Study on Synergizing Strength of Thermoplastic Composites Modified with Waste Ceramic and Metal

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Abstract

The realm of research and development in environmentally sustainable materials assumes a paramount role in contemporary industry, aligning with concerted environmental conservation initiatives. Within this landscape, thermoplastic composite materials, enriched with waste ceramics and laden with metallic fillings, command attention due to their unique amalgamation of superior mechanical attributes and an unwavering commitment to ecological integrity. The repertoire of waste ceramics encompasses industrial remnants or ceramics earmarked for recycling, embodying a conscientious approach to resource optimization. Analogously, the metal fillings are derived from recycling processes, reflecting a broader commitment to sustainable material sourcing.

The synergy achieved by combining waste ceramics and metal fillings represents a significant leap forward in resource efficiency, concurrently mitigating adverse environmental impacts. The introduction of ceramic additives imparts heightened resistance to elevated temperatures by mitigating the material's thermal expansion coefficient. In contrast, metal fillings contribute to augmented mechanical robustness, endowing the material with heightened tensile strength. These attributes render the materials particularly

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advantageous for diverse applications in industries such as automotive, aerospace, and construction.

Moreover, the recyclable nature and environmentally friendly composition of these composite materials underscore their pivotal role in environmental conservation, mitigating detrimental impacts. In essence, waste ceramic-added and metal-filled thermoplastic composite materials epitomize a harmonious blend of high mechanical prowess and ecological consciousness. Consequently, these materials emerge as an optimal choice for industrial utilization, offering a synthesis of robust mechanical properties and environmentally considerate structures.

1.Introduction

Thermoplastics, colloquially referred to as 'plastics,' represent a class of polymers distinguished by their capacity to undergo melting and reshaping upon exposure to heat. These materials, amenable to processes like injection molding and extrusion, exhibit unique properties during both their molten and solid states. During the cooling phase in manufacturing or molding, thermoplastic polymers typically evade the formation of an ordered crystal structure, primarily attributable to the intricate configuration of polymer chains predisposed to curling and contraction. The formation of a regular crystal lattice demands a considerable input of energy due to the complex nature of these chains.

The constituent chains of thermoplastics commonly manifest a semi-crystalline structure, amalgamating amorphous and crystalline attributes rather than adopting a pristine crystal lattice. This hybrid structure imparts elasticity from the amorphous regions and augments strength and rigidity through crystalline elements. The delineation of this semi-crystalline structure relies on the melting point (Te) within the crystallizing chains, while amorphous thermoplastics or segments within thermoplastics are characterized by the glass transition temperature (Tg). Beyond the melting point, the entire crystal structure within the polymer dissolves, leaving behind only the amorphous structure.

Thermoplastic polymers are characterized by specific glass transition temperatures (Tg) and an expansive melting temperature range in those encompassing crystal structures. The polydisperse nature of these polymers contributes to a broad melting curve, indicative of diverse defects or unit cells within the crystal lattice. Techniques such as X-ray analysis are employed to elucidate this intricacy. The chain architecture of thermoplastic polymers is typically linear or branched, with a notable absence of cross-links between chains. The capacity for melting and reshaping defines a thermoplastic, and any introduction of cross-covalent bonds resulting from external factors marks a departure from this classification, a transformation more commonly associated with thermosetting polymers (1–3).

In contrast to thermoset polymers, thermoplastic polymers lack covalent bonds between their chains but are intricately bound by a network of intra- and inter-chain interactions. These interactions include polar attractions, hydrogen bonding, London dispersion forces, and stacking of aromatic groups, which collectively contribute to the structural integrity of the material. Furthermore, intra-chain and inter-chain twists and entanglements play a crucial role in maintaining the cohesion of thermoplastic polymer chains. These intricate molecular arrangements, characterized by circulations and bends, exert a profound influence on the physical properties of thermoplastic polymers, particularly in terms of mechanical responsiveness.

Distinguishing themselves from elastomers, thermoplastics exhibit distinct mechanical properties. Elastomers demonstrate rapid elongation under tensile stress, reverting to their original position upon force removal, a phenomenon known as elasticity. In contrast, thermoplastics retain elasticity up to a certain point when stretched, ultimately undergoing permanent deformation or fracture. Notably, thermoplastics require higher forces for elongation compared to elastomers, indicating their heightened resistance to deformation.

The tensile strength and elastic modulus of elastomers, such as natural rubber, typically fall within the range of 15 MPa and 10 MPa. In contrast, thermoplastics display considerably higher values at 37 MPa and 800 MPa, respectively. An essential characteristic of thermoplastics is their capacity for enduring permanent deformation under load, facilitating a lasting change in shape under applied force, exemplified by thermoforming methods. The semi-crystalline structure inherent in thermoplastics enables a transition from a rigid to a pliable state at a specific temperature, determined by the amorphous regions within (glass transition temperature).

This thermal transition not only governs the applications of plastics but also influences the manufacturing processes. For instance, the choice of polymer with a high or low glass transition temperature dictates the suitability for specific uses, such as mobile phone cases requiring a rigid structure or electrical cables necessitating flexibility. Additionally, the glass transition temperature influences production processes, with the incorporation of plasticizer additives aimed at enhancing the formability of thermoplastics or reducing the required processing temperature to conserve energy.

Following the synthesis of thermoplastic polymers, the resultant materials are typically packaged and commercialized in the form of small granules. Purchasers possess the capability to employ diverse production techniques to melt, mold, or extrude these granules into various forms, exemplifying the versatility of thermoplastics. Commonly utilized in the production of items such as plastic cups, bags, packaging materials, and toys, thermoplastics find widespread application across diverse sectors. Importantly, the recyclability of these materials allows for their repeated use, aligning with sustainable practices.

In applications emphasizing transparency, preference is often given to amorphous thermoplastics, exemplified by materials such as PMMA (polymethyl methacrylate) or polycarbonate. Amorphous thermoplastics, characterized by their lack of a regular crystal structure, are well-suited for applications where clarity is paramount. However, it is crucial to note that amorphous thermoplastics typically exhibit lower resistance to chemicals and are susceptible to environmental stress cracking.

Conversely, semi-crystalline thermoplastics demonstrate enhanced resistance to solvents and chemicals but possess an opaque structure due to larger crystal sizes exceeding the wavelength of light. Consequently, they are not favored in optical applications. Prominent examples of thermoplastic polymers include polycarbonate, poly(vinyl chloride), polyethylene, polypropylene, and polystyrene. These polymers, distinguished by their diverse chemical compositions, cater to a broad spectrum of industrial applications, underlining their ubiquity and preference across various industrial domains(1,4,5).

1.1 Post-Synthesis Utilization of Thermoplastic Polymers: Applications and Characteristics

1.1.1 PC (Polycarbonate: An Insight into a High-Performance Thermoplastic)

Polycarbonate, a high-performance thermoplastic renowned for its low specific gravity, stands out as an engineering plastic distinguished by a myriad of exceptional properties. Characterized by high impact resistance, low moisture absorption, commendable thermal insulation, and stability in both molten and oxidative states, polycarbonate holds a significant position among commercial polymers. While it is commonly synthesized from bisphenol A (BPA), an alternative synthesis route involving phosgene is also feasible.

Polycarbonate derived from BPA exhibits notable impact resistance, making it a preferred choice for optical applications, notably in eyeglass lenses. Its transparency and superior light transmittance contribute to its prominence in optical items. However, its susceptibility to scratches necessitates the application of a thin protective film on its surface. Innovations in polycarbonate formulations, incorporating reactive compounds or epoxies, are being explored by eyeglass manufacturers as an alternative to traditional film coating methods.

In comparison to polymethylmethacrylate (PMMA) plastic, polycarbonate demonstrates heightened strength and a broader temperature range but comes with an elevated cost. The vitrification temperature of polycarbonate is approximately 150°C, with fluidity manifesting above 300°C. Commercial products are commonly fabricated through injection molding and extrusion methods, with the ease of production influenced by the molecular weight of the polycarbonate.

It's noteworthy that another variant of polycarbonate, specifically employed in ultralight optical devices, is synthesized from a carbonate monomer featuring allyl groups at both ends, rendering it a cross-linked thermoset polycarbonate. Unlike the BPA-based thermoplastic, this variant cannot be melted upon heating but undergoes decomposition. Despite this limitation, it boasts a higher refractive index than glass, facilitating the production of thinner components with robust mechanical properties and exceptional heat resistance.

The versatility of polycarbonate finds expression in an array of applications, particularly in the production of digital devices and electronic goods such as CDs and DVDs. Its application extends to items requiring resistance to shattering, including protective components for sports equipment, medical devices, as well as bottles and food storage containers. In summary, polycarbonate stands as a widely utilized material in the manufacturing landscape, particularly in the realm of digital technology and items demanding a combination of durability and transparency(4–7).

1.1.2 PVC (Polyvinyl Chloride: Composition, Characteristics, and Industrial Applications)

Polyvinyl chloride, commonly known as PVC, stands as the third-largest thermoplastic polymer in use, finding extensive applications across diverse industries ranging from toy manufacturing to the production of construction materials. The manufacturing of PVC predominantly employs the suspension polymerization method, involving the polymerization of vinyl chloride monomers to yield a polymer characterized by a low crystal structure. The incorporation of large chlorine groups results in a robust and resistant molecular arrangement, contributing to PVC's durability.

However, PVC exhibits sensitivity to light and heat, representing a notable drawback. Under conditions of elevated temperature or prolonged exposure to light, PVC may release hydrogen chloride (HCl) molecules into its surroundings, potentially leading to the decomposition of surrounding materials and posing health risks. The inherent instability of PVC and related halogenated polymers is mitigated through the incorporation of additives, and ongoing efforts focus on developing solutions to minimize or eliminate adverse environmental impacts.

PVC's intrinsic hardness and toughness, stemming from its favorable mechanical properties, contribute to its wide-ranging applicability. The incorporation of plasticizer additives further enhances its versatility, enabling the modification of PVC into a flexible form. Coupled with rubber plastics, PVC achieves increased impact resistance. Despite its colloquial reference as "vinyl," it is essential to recognize other polymers within the vinyl family, including polyvinyl acetate, polyvinylidene chloride, and polyvinyl alcohol.

Various plasticizing additives, such as diisooctyl phthalate, tritolyl phosphate, and epoxidized oils, play a crucial role in PVC modification. These additives interpose between PVC chains, facilitating their movement and functioning akin to an "internal lubricant." The role of these additives in PVC mirrors the functions performed by polystyrene copolymers and polymer blends in analogous manners, showcasing the intricate balance and chemical dynamics involved in tailoring PVC for diverse industrial applications(2,8–10).

1.1.3 PE (Polyethylene in the Commercial Polymer Landscape: A Overview)

Polyethylene holds a preeminent position among commercial polymers, boasting a global capacity and capital capacity of 134.11 million tonnes in 2022. This sector is poised for continued growth, with a projected Average Annual Growth Rate (AAGR) surpassing 7% until 2027. Key players in polyethylene production, including China, the USA, Saudi Arabia, South Korea, and India, collectively contribute to a substantial 100 million tons of the global output, constituting 53% of total polyethylene capacity by 2022. This prolific production is a driving force behind polyethylene's extensive applications spanning various sectors(11,12).

Originating from petroleum, polyethylene is a thermoplastic polymer broadly categorized into two main classes: Low Density Polyethylene (LDPE) and High Density Polyethylene (HDPE). LDPE, synthesized through radical chain polymerization, exhibits greater molecular branching compared to HDPE. These branchings, whether short or long, influence LDPE properties. The high degree of branching impedes the formation of a crystal structure, resulting in lower crystallinity (40-60%) compared to HDPE. Additionally, branching reduces density, with LDPE densities ranging from 0.9 to 0.93 $g.cm^{-3}$. LDPE, with a glass transition temperature (Tg) of approximately 120°C and a melting temperature around 110°C, demonstrates flexibility over a broad temperature range. Commercial (13–15) varies in number average molecular weight (20-100 $kg.mol^{-1}$) and molecular weight distribution (3-20), providing diverse properties determined by factors such as reactor type, polymerization temperature, and pressure.

In contrast, the production of High Density Polyethylene (HDPE) utilizes Ziegler-Natta and Philips-type reactive initiators, resulting in reduced branching and high polymer conversion. This reduction in branching facilitates the formation of an ordered crystal structure, leading to higher crystallinity (70-90%) and a crystal melting temperature of approximately 135°C for HDPE.

HDPE's versatility is evident in its widespread applications, with 40% attributed to plastic parts produced by air blow molding, 30% to parts manufactured through injection molding, and the remaining percentage to products created via the extrusion method. These applications span diverse industries, including beverage and food containers, kitchenware, pipes, tubes, cables, and cleaning product bottles. The unique properties and production methodologies of LDPE and HDPE enable tailored usage across an array of markets, solidifying polyethylene's position as a cornerstone in industrial materials(16–19).

1.1.4 PS (Polystyrene: An Economical and Versatile Thermoplastic Polymer)

Polystyrene, an economical and robust thermoplastic polymer, finds extensive utility across a diverse spectrum of applications. Characterized by an aromatic polymer chain, polystyrene is synthesized from the aromatic styrene monomer, a liquid hydrocarbon molecule derived from the petrochemical industry. Among the most encountered plastics in daily life, polystyrene holds the distinction of being the second most widely used plastic after polyethylene. Its thermoplastic nature allows for facile processing and molding through heating and cooling, contributing to its versatility. Solid at room temperature, polystyrene lends itself to the production of a myriad of products with desired shapes through molding and cooling at elevated temperatures. Notably, CD and DVD covers exemplify applications wherein polystyrene is molded to achieve specific shapes. Pure solid polystyrene is inherently transparent, yet the inclusion of pigments during production enables the creation of polystyrene in various colors. Additionally, the production of polystyrene foam, commonly seen in white water glasses and numerous daily-use products, is another testament to its adaptability. Expressed with the formula $(C_8H_9)n$, polystyrene is formed by attaching a phenyl group to every second carbon on a lengthy hydrocarbon chain. Its synthesis from a vinyl-based monomer involves free radical vinyl polymerization, yielding isotactic polystyrene (iPS). Despite the potential advantages of iPS, its industrial production is relatively uncommon due to the superior properties offered by other crystallizable polymers. Moreover, the cost-effectiveness of isotactic polypropylene or polyethylene synthesis tends to make them more favorable alternatives in industrial settings.

Polystyrene, recognized for its economical nature and robust thermoplastic attributes, presents a diverse range of applications. Its molecular structure, originating from the aromatic styrene monomer derived from the petrochemical industry, contributes to its status as one of the most commonly encountered plastics in daily life, following polyethylene in prevalence. As a thermoplastic polymer, polystyrene can be efficiently processed and molded through heating and cooling, enabling its utilization in various industries. While isotactic polystyrene (iPS) possesses a crystal structure, it tends to be brittle and challenging to process. Atactic polystyrene (atactic PS), the more commonly produced form, is amorphous due to the disorder introduced by atacticity, eliminating a melting point. Despite its inability to crystallize, atactic PS is crucial in engineering plastics. Copolymerization with polybutadiene during polymerization results in a copolymer known as high impact polystyrene (HIPS). The macro-phase separation in this copolymer, with polybutadiene globules enhancing impact resistance, transforms the traditionally brittle polystyrene into a more durable material. Polystyrene exhibits inertness to chemical reactions, showcasing resistance to alkali metals, halogen acids, and various reducing and raising compounds. However, exposure to certain solvents can compromise its integrity. While polystyrene has excellent optical properties, such as easy coloring, transparency, and clarity, its mechanical properties, including brittleness and low heat deflection temperature (HDT), make it less suitable for certain applications, such as those requiring sterilization for healthcare use. Copolymers of polystyrene, especially styrene-butadiene synthetic rubbers, find significant application, particularly in latex-based paints. Styrene-butadiene copolymers, often comprising 60% styrene and 40% butadiene by weight, play a crucial role in the thermoplastic elastomer market. Introducing copolymers like acrylonitrile and fumaronitrile enhances properties like heat and impact resistance while preserving styrene's desirable characteristics. Another notable development is the Acrylonitrile Butadiene Styrene (ABS) polymer, widely used in the automotive sub-industry. ABS resin integrates a rubber-reinforced polymer matrix with a glassy matrix containing polystyrene and styrene-acrylonitrile copolymer. The elastomeric rubber component is the styrene-butadiene copolymer, contributing to ABS's superior resistance to high temperatures and chemical solvents compared to High Impact Polystyrene (HIPS). Unlike other plastic materials, ABS can be cold-formed, akin to metals, marking it as an exceptional engineering plastic material. The production of polystyrene in a foamy form is accomplished through the suspension polymerization method, a technique that introduces a blowing agent into the system. In this transformative process, the high heat generated during the reaction serves a dual purpose: softening the polystyrene resin and evaporating the added blowing agent. This dual action results in the creation of a spongy or foam-like structure within the polystyrene resin, yielding a material with distinct properties conducive to various applications (20–26).

1.1.5 PA (Polyamides: A Fusion of Nature and Industry)

Polyamides, members of the polyamide class, arise from the bonding of monomers containing repeating units of acid and amine groups through amide bonds. While nature's polyamides encompass proteins, wool, and silk, synthetic counterparts, such as nylon and aramid, have been engineered in laboratories. Among synthetic polyamides, nylon stands out as a prominent engineering polymer with applications spanning the textile industry, musical instrument strings, and various other fields. Despite being thermoplastic polymers, polyamides are predominantly employed in the fiber industry, where their key properties shine. These properties include exceptional resistance to wear and tear, robust mechanical characteristics at elevated temperatures, low gas permeability, and resistance to chemicals. Notably, more than 60% of produced nylon is utilized in the form of fibers. The discovery of nylon by DuPont in 1935 marked a pivotal moment in polymer history. Initially employed as bristles in toothbrushes, nylon rose to commercial prominence in the 1940s when it began replacing silk in women's socks due to its silky texture. The scarcity of silk during World War

II further fueled the adoption of nylon, leading to significant advancements in polymer science and industry. Nylon played a crucial role in wartime applications, featuring in parachutes, military ropes, and tires.

Beyond its role in the fiber industry, nylon serves as a versatile polymer for the production of solid-state mechanical parts. It has become a preferred material over metals, particularly in components subjected to low and medium forces, such as impellers and screwed parts. In engineering-grade formulations, nylon undergoes processing through extrusion, pour molding, and injection molding methods. For applications requiring heightened structural strength, impact resistance, and stiffness, nylon composites enter the scene. Reinforced with glass particles or fibers, these composites enhance the material's overall performance. For instance, nylon composites, especially those fortified with 25% glass fiber, find application in the automotive industry, notably in components like engine semi-parts, thanks to their remarkable heat resistance. Aramid, a distinguished member of the polyamide class, stands out from nylons due to the presence of aromatic groups in its chain backbone. Renowned for exceptional strength, aramid fibers, known by brand names such as Kevlar and Nomex, find application, especially in ballistic scenarios, owing to their remarkable properties. These fibers not only exhibit outstanding strength and Young's modulus but also showcase excellent heat and fire resistance attributed to their aromatic groups. Polyamides, including aramids, are synthesized through the condensation polymerization mechanism. Unlike polyesters, strong acids are not utilized in the synthesis of polyamides, as the reaction rate is inherently high. The commonly employed method involves the direct amidation of diacids with diamine. For instance, Nylon6,6 polyamide is crafted through the reaction of hexamethylene diamine and adipic acid. The regular and symmetrical chain backbone of polyamides facilitates easy crystallization. While polyamides are semi-crystalline polymers with approximately 50% crystal structure in the standard production process, the application of mechanical tension increases the crystal structure ratio in resulting fibers. Nylon6,6, a noteworthy polyamide, boasts moderate crystallinity, combining sought-after properties such as strength, flexibility, toughness, wear resistance, colorability, low coefficient of friction (self-lubrication), low creep, and resistance to solvents. Despite its impressive attributes, the primary drawback of Nylon6,6 is its susceptibility to moisture, leading to a decline in dimensional and mechanical properties in humid environments. The mechanical strength of polyamides, including Nylon6,6, stems from the interactions between chains, specifically through hydrogen bonding. Though individually considered weak compared to covalent bonds, the multitude of interchain hydrogen bond interactions collectively forms a robust secondary force. These hydrogen bonds contribute to the crystallization of polymer chains, allowing polyamides to possess a highly crystalline structure and, consequently, high mechanical strength(27,28). However, the hydrogen bonds in polyamides are susceptible to disruption in humid environments, leading to a loss of interchain interaction. Water molecules, characterized by a polar structure akin to polyamide chains, possess the ability to disrupt interactions between polyamide chains, consequently increasing the mobility of these chains. Despite the disruptive influence of water molecules, polyamides do not dissolve in water. Instead, water induces swelling and softening in polyamides, effectively plasticizing them. Consequently, polyamides are susceptible to mechanical and dimensional degradation in humid environments. The recommended temperature range for the continuous use of polyamides is 65-75°C for pure polyamides and 100-115°C for polyamide composites reinforced with glass and other minerals. However, polyamides can retain their mechanical properties at temperatures up to 150°C. While commonly used polyamides such as nylon6 and nylon6,6 exhibit similar properties, nylon6 has a lower melting point at 223°C, while nylon6,6 boasts a melting temperature of approximately 255°C. Beyond nylon6 and nylon6,6, various polyamides have been developed, including Nylon6,9, Nylon6,10, Nylon6,12, Nylon11, Nylon12, Nylon12,12, and Nylon4,6. Polyamides with more methylene groups than nylon6 or nylon6,6 generally demonstrate increased moisture resistance, dimensional stability, and improved electrical properties. However, nylons with higher methylene groups often exhibit lower crystallinity and mechanical properties. Polyamides are typically insulating materials, yet they tend to generate static electricity at high voltage and frequency, potentially leading to hazardous sparks(29). As a result, the use of polyamides is generally restricted to low-frequency applications. To mitigate this electrical sensitivity, conductive particles such as carbon black or silver can be added to polyamides, enhancing their suitability in various settings(27,30,31).

1.1.6 PP (Polypropylene: A Versatile Thermoplastic Polymer)

Polypropylene, the preeminent commercial thermoplastic polymer, reached global production levels of 45 million tons in 2001, establishing a market valued at $65 billion. Isotactic polypropylene (iPP) boasts an exceptional strength-to-weight ratio, attributed to its low density and high strength. These properties render it the polymer of choice in diverse applications, ranging from automotive components to the textile and packaging industries(32).

Synthesized through the polymerization of propylene monomers derived from gases obtained in olefin facilities and oil refineries, polypropylene can adopt isotactic, syndiotactic, or atactic conformations, with each conformation influencing crystal structure, ratio, and density. While atactic polypropylene struggles to form a crystal structure, isotactic polypropylene can crystallize more effectively than LDPE but falls short of achieving the density of HDPE crystal structures. In essence, the crystal ratio of polypropylene fluctuates between 40% and 70%.

Polypropylene, known for its toughness and flexibility, has evolved into an engineering plastic, particularly when copolymerized with ethylene, often replacing ABS. The melting point of polypropylene crystals hovers around 160 degrees Celsius, with typical processing temperatures exceeding 200 degrees Celsius. Common production methods for polypropylene parts include injection molding and blow molding.

The melt flow index (MFI), a crucial parameter in the production phase, directly correlates with the molecular weight of polypropylene. MFI values provide insights into the ease of processing a plastic material, where higher MFI values indicate better mold-fillability. However, increasing MFI may compromise some physical properties, such as impact resistance.

Polypropylene exhibits sensitivity to UV rays and high temperatures during heat treatment. UV-absorbing additives, like carbon black, can extend the polymer's life by shielding it from UV rays. Additionally, antioxidant additives prevent polypropylene from degrading at elevated temperatures during molding processes.

Polypropylene is produced in three primary forms: homopolymer, copolymer, or block copolymer. Copolymers often incorporate ethylene as a co-monomer, yielding ethylene-propylene rubber. This copolymer significantly enhances impact resistance at low temperatures. Moreover, the random arrangement of ethylene monomers reduces the crystallinity of polypropylene, resulting in a more transparent plastic(33–35).

1.1.7 PET (Polyethylene Terephthalate: A Fundamental Thermoplastic Polymer)

Polyethylene terephthalate (PET), constituting 18% of global plastic production, ranks third after polyethylene and polypropylene. It is widely recognized and utilized in various daily applications, often referred to by the abbreviation PET but also designated as PETE, PETP, or PET-P. As a linear thermoplastic polymer belonging to the polyester group, PET finds applications in synthetic fibers, food packaging, and particularly bottling.

PET materials are shaped through thermoforming, comprising pure PET polymer or, in some instances, reinforced with glass fiber for engineering applications. PET, a significant commercial polyester, was introduced to the market in 1944. Its name originates from containing both an ethylene group and a terephthalate group in its repeating unit. The synthesis of high molecular weight polyesters, unlike polyamides such as nylon, involves the esterification reaction of a diacid and a diol. Commercially, the transesterification reaction is often followed, reacting dimethyl terephthalate with ethylene glycol to obtain bis-(2-hydroxyethyl) terephthalate and methanol. This is followed by further reactions to obtain PET and ethylene glycol products, with the latter being reusable. PET can be synthesized by various chemical methods or undergo different heat treatments post-synthesis, resulting in either a completely amorphous or semi-crystalline structure. PET with an amorphous structure yields transparency, while semi-crystalline PET can be transparent or opaque depending on crystal size and structure. Commercially synthesized PET may have a crystal structure of up to 60%, with an average melting temperature around 270 °C. Despite preferring a crystalline state, PET is not a polymer that crystallizes easily, impacting its inclusion among engineering plastics. Its long crystallization time increases molding costs, but additives are employed to expedite the process. With a high melting point of 270°C, PET exhibits a hard chain backbone, providing advantages such as high strength, toughness, and resistance up to 150°C. Its low specific gravity allows for variable hardness depending on thickness. PET is durable, impact-resistant, and offers good barrier properties against gases, solvent chemicals, and alcohols, albeit with less moisture resistance compared to some other plastics. the utilization of Polyethylene Terephthalate (PET) is extensive, particularly in the realm of plastic bottles due to its robust barrier properties. To enhance its barrier efficacy, PET can be compounded with poly(vinyl alcohol), offering superior barrier characteristics, especially in scenarios where oxygen permeability is of paramount concern. Notably, oriented PET films exhibit prominence in applications necessitating robust mechanical strength. These films, when oriented bidirectionally and aluminized, manifest an opaque and reflective surface, finding substantial application in the packaging industry for the fabrication of flexible packages. The versatility of PET extends to tape applications, leveraging its noteworthy mechanical strength. Instead of employing PET in its unadulterated state, a more rigid composite material can be derived by fortifying it with glass particles or fibers. While PET is commonly deployed as a linear thermoplastic homopolymer, its fortification can also be achieved through copolymerization. The introduction of the cyclohexane dimethanol group to the polymer backbone, as opposed to ethylene glycol, mitigates cohesion among PET chains and disrupts the crystal structure, leading to the advent of a novel copolymer known as PETG. By 2001, the global production of PET reached approximately 30 million tons, with 45% allocated to fiber applications. PET fibers exhibit remarkable resistance to wrinkles and abrasion, and their incorporation in textile products, particularly in tandem with cotton or cellulose-based fibers, imparts enhanced moisture resistance and a tactile sense of naturalness. In fiber form, PET finds application in diverse domains, encompassing curtains, clothing, upholstery fabrics, tire strips, and industrial filtration processes. Given its adeptness as a gas barrier, 10% of produced PET polymers are channeled into the food and beverage packaging sector, notably in bottling applications. PET's role extends to film applications, prominently featured in photographic films, magnetic and X-ray tapes, and electrical insulation contexts. Beyond these applications, PET emerges as a pivotal material in electronic devices, office equipment, and automotive components, progressively supplanting traditional metals like steel and aluminum in various engineering applications. PET's mechanical robustness and hardness undergo augmentation through compounding with materials such as glass fiber, silicone, graphite, or Teflon. Noteworthy examples include glass fiber-reinforced PET composites, well-suited for sustained use at elevated temperatures, reaching up to 150°C. This confluence of material science and engineering applications underscores the multifaceted significance of PET in diverse industrial landscapes(36–41).

1.1.8 PMMA (Molding the Future: Polymethylmethacrylate in Automotive, Optics, and Beyond)

Polymethylmethacrylate (PMMA), commonly recognized as acrylic glass or plexiglass in the market, stands out as a colorless and transparent thermoplastic polymer. Frequently employed as a viable substitute for glass and an alternative to polycarbonate due to shared properties, PMMA is valued for its economic efficiency and ease of processing, despite having a relatively fragile structure. Its synthesis from methyl methacrylate monomer primarily employs the radical chain growth polymerization method, although anionic polymerization is also feasible. The commercial form of PMMA is a linear polymer characterized by a 70-75% syndiotactic chain structure, yet its lack of complete stereo-regularity and the sizable methacrylate groups contribute to its amorphous nature, precluding crystallization. The glass transition temperature hovers around 105°C. PMMA's distinctive feature lies in its remarkable optical transparency, coupled with resilience to external weather conditions, rendering it suitable for applications emphasizing light transmittance. However, its susceptibility to scratches restricts its use in optical domains, despite attempts with various additives to address this issue resulting in a compromise on mechanical properties. Nevertheless, PMMA surpasses glass in transparency, maintaining its translucency even in thicknesses up to 35 cm. With a tensile strength reaching 70 MPa and impact resistance nearly comparable to High Impact Polystyrene (HIPS), PMMA is a machinable plastic. The heat-resistant variant of PMMA achieves a load bending temperature (HDT) surpassing 90°C, constituting a generally malleable plastic. While it exhibits resistance to many chemicals, it is not impervious to organic solvents. Injection-molded PMMA parts find application in diverse sectors, including automotive headlights, appliance covers, optical equipment, and home decoration products. Additionally, PMMA lends itself to the production of acrylic-based sheets. Beyond pure PMMA, copolymers involving ethyl acrylate and metal methacrylate monomers contribute to the production of thermoset resins. The industry predominantly employs acrylate/methacrylate copolymers synthesized from varying combinations, attesting to the versatility of acrylic plastics in industrial applications(42–48).

1.1.9 PEK-PEEK (High-Performance Polymers for Demanding Industrial Applications)

Polyketones belonging to the aromatic polyether class stand out as high-performance polymers of significant industrial importance. Predominantly represented by poly(ether ether ketone) (PEEK) and poly(ether ketone) (PEK), these polyketones find extensive utilization in critical sectors such as the aircraft and automotive industries, owing to their exceptional durability. Operating seamlessly within the temperature range of 240-280°C, these polymers exhibit robust resistance to elevated temperatures and chemical corrosion. Characterized by a semi-crystalline structure with a substantial 35% crystalline region, PEEK crystals undergo melting at 340°C, while PEK exhibits a higher melting point around 360°C. The vitrification point of PEEK is reached at approximately 140°C, whereas PEK requires heating to a higher temperature, up to 165°C, to surpass its vitrification threshold. The elevated glassification temperatures of these polyketones are attributed to their rigid structure, where phenyl groups impose constraints on molecular movement, facilitating crystal formation. The increased hardness of the carbonyl group in PEK, compared to the ether group, imparts reduced flexibility to the PEK chain, resulting in a higher glassification temperature. Both PEEK and PEK demonstrate remarkable resistance to high-temperature degradation and chemical influences, akin to polyamides and polysulfones in organic solvents and aqueous environments, respectively. However, PEEK exhibits solubility limitations, being soluble only to a restricted extent in specific high-evaporation-point polar organic solvents such as pyrene or benzophenone. The insolubility of PEEK in organic solvents constrains chemical modifications of its polymer chain. Notably, PEEK manifests sensitivity to halogens, Bronsted and Lewis acids, halogenated compounds, and aromatic hydrocarbons, necessitating cautious handling during chemical modification attempts. Literature reports indicate the use of sulfuric acid for modifying the PEEK chain through sulfonation, albeit with the awareness of potential polymer degradation. Polyketones' high melting point, while advantageous for end-use applications requiring elevated temperature resistance, can pose challenges during the manufacturing of parts. To mitigate this, additives can be introduced to reduce the viscosity of polyketones, facilitating a more manageable and efficient production process. As a relatively recent thermoplastic innovation, polyketones are prominently employed in environments demanding resistance to high temperatures and corrosion. Their applications span various sectors, including automotive components like piston parts and bearings, structural elements in aerospace, chemical applications involving pumps and compressor valves, and electrical uses such as cables(49–56).

1.1.10 TPE (Thermoplastic Elastomers: Properties, Structures, and Applications)

In the realm of polymer science, Thermoplastic Elastomers (TPEs) stand out as a distinctive polymer class manifesting elastomeric characteristics despite lacking chemical cross-linkages. Originating from the 1950s, their utilization in commercial applications only materialized in the 1970s, coinciding with the advent of styrene copolymers. While traditional elastomers employ chemical cross-links to impede chain slippage during deformation, TPEs employ physical bonds arising from a micro-heterogeneous, 2-phase molecular structure. The intricate terminology surrounding these molecular systems becomes more comprehensible through illustrative examples. Physical cross-links within TPEs interconnect pliable molecules, establishing a network-like structure. These materials demonstrate processability at elevated temperatures and manifest elastomeric traits upon cooling. Notably, the transition from a thermoplastic to elastomeric state is entirely reversible, distinguishing TPEs from conventional elastomers. This characteristic facilitates repetitive processing and recycling, underscoring the sustainability aspect of these materials. Defined by a dual-phase structure comprising an elastomeric and a thermoplastic hard phase, TPEs must exhibit three fundamental properties for classification: the ability to extend at high elongation rates, thermoplastic processability at elevated temperatures, and minimal mechanical creep. The conceptualization of this structure becomes clearer through the examination of thermoplastic polyurethane elastomers, exemplifying the presence of "physical cross-links" in the form of hard segments. In the realm of thermoplastic polyurethane elastomers, segmented copolymers emerge from the reaction of pre-polymer polyol-containing diisocyanate and short-chain diol. The resulting soft segments, composed of pre-polymer polyol, coexist with polyurethane hard segments formed by diisocyanate and diol interaction. These hard segments exhibit ordered crystal structures, forming hydrogen bonds and acting as physical cross-links, which, despite stability at ambient temperatures, disintegrate during processing or solvent interaction, facilitating malleability and thin coating applications. Another paradigmatic example within the TPE domain is the A-B-A type tri-block copolymers, involving three dissimilar monomers and characterized by phase separation and cluster formation based on the incompatibility of blocks with differing monomers. Commercially, TPEs categorize into six main classes, encompassing styrene-based block copolymers, polyolefin blends, elastomer-based alloys, thermoplastic polyurethanes, thermoplastic copolyesters, and thermoplastic polyamides. Recent academic and industrial explorations into TPEs include interpenetrating networks and competitive polymer network structures, scrutinizing their chemical compositions and physical interactions. While TPEs offer advantages such as recyclability, thermoplastic processability, minimal compounding requirements, and ease of coloring, they are countered by high costs, limited compatibility with inexpensive additives like carbon black, and susceptibility to temperature and chemical influences. The production landscape of TPEs involves methods such as extrusion and injection molding, alongside thermal molding, thermal welding, and blow-molding techniques. Notably, mass production, particularly via injection molding, stands out for its rapid and cost-effective nature(57–59).

1.2 Exploring the Lifecycles of Ceramics: Production, Applications, and Waste Management

Ceramics, inherently inorganic and characterized by their hardness and brittleness, exist in either crystalline or amorphous states. Typically derived from a composite of clay, quartz, feldspar, and other minerals, or synthesized through specialized processes, ceramics find extensive utility across diverse industries and daily life. The production of ceramics involves selecting and preparing raw materials, forming the material into the desired shape, drying it, and then firing it in a kiln at a lower temperature (bisque firing). After bisque firing, glazing (if desired) and a second firing at a higher temperature take place. The ceramics may undergo a final firing, followed by quality control inspections. The finished ceramics are then packaged for distribution. Advanced ceramics may undergo additional processes like powder processing and precision machining. The specific production process can vary based on the type of ceramic being manufactured. The taxonomy of ceramics encompasses various types, each tailored for specific applications. Building ceramics, instrumental in construction, constitute one category. Electrical ceramics, prized for their electrical insulating or piezoelectric properties, find application in electronic devices and sensors. Art ceramics, crafts, and artworks also form a distinct category, while advanced ceramics are engineered for high-performance industrial applications, boasting attributes such as high temperature resistance, friction resistance, and chemical resilience. The distinguishing properties of ceramics encompass durability, hardness, electrical characteristics, thermal conductivity, and fracture resistance. Notably, ceramics exhibit a notable resistance to high temperatures, abrasion, and chemicals, surpassing metals and plastics in hardness. The expansive applications of ceramics traverse numerous domains: construction and decoration benefit from tiles, tiles, and ceramic coatings, while the electronics and electrical industry relies on ceramics for insulators, capacitors, and sensors. In the medical and biomedical field, ceramics find application in prosthetics and dental implants. The realm of arts and crafts embraces pottery and ceramic sculptures. Additionally, ceramics play a pivotal role in aerospace applications, featuring prominently in spacecraft and missile aerosol components. This versatility, stemming from the diverse properties of ceramics, positions them as indispensable materials across a multitude of industries and applications(60–65).

1.2.1 Waste Ceramics: Recycling, Sustainability, and Environmental Impact

Waste ceramics encompass material residues arising from construction, ceramics industry activities, and various industrial production processes. This category encompasses distinct types of waste, including:

-Building Ceramics: Constituting materials like tiles, ceramic plates, and porcelain utilized in construction projects.

-Industrial Production Wastes: Encompassing by-products, defective productions, and waste components generated during ceramic industry manufacturing processes.

-Porcelain Wastes: Arising predominantly from kiln processes, this category includes broken or faulty products during porcelain production.

-Ceramic Coating Wastes: Encompassing residues from the production or installation of ceramic coatings applied to surfaces like kitchen countertops, bathroom sinks, or flooring.

These diverse forms of waste ceramics often lend themselves to recycling or alternative applications through various processes. The management of waste ceramics carries the potential to contribute significantly to sustainable construction and production practices. Recycling entails repurposing waste ceramics for the manufacture of new materials or construction components, thereby curbing reliance on natural resources and mitigating landfill accumulation. Several methodologies can be employed in the recycling of waste ceramics, including fragmentation through grinding or milling for use as granular material, which frequently finds application in construction projects. Certain waste ceramics can undergo recycling processes to yield new ceramic products, thereby conserving raw materials in subsequent manufacturing endeavors. Moreover, the restoration of waste ceramic materials for reuse in construction or landscaping projects is a viable option. Alternatively, these materials can serve as aggregates in concrete or asphalt mixtures, presenting an environmentally conscious alternative. However, the recycling of waste ceramics is not devoid of technical and economic challenges, necessitating ongoing efforts and advancements in research and technology to enhance the efficiency of recycling processes. Continued exploration in this domain holds the potential to yield more effective solutions for the recycling and utilization of waste ceramics(66–71).

1.2.2 The Role of Waste Ceramics in Enhancing Polymer Composites

The amalgamation of waste ceramics with polymers emerges as a promising domain within materials science and engineering, presenting substantial prospects for sustainable material production. A primary merit of these applications lies in the synthesis of composite materials through the integration of waste ceramic components into polymer matrices. These composite materials seamlessly integrate the robustness inherent in ceramics with the pliancy characteristic of polymers, thereby facilitating the creation of more resilient and versatile materials across various industries. Notably, the formulation of building materials by incorporating waste ceramics into polymer matrices holds the potential to enhance the properties of construction materials. This transformative integration can concurrently bolster energy efficiency through heightened durability and reduced material weight. The consequential impact is particularly significant in the construction industry, where the adoption of such composite materials contributes to the optimization of structural properties and overall efficiency. The development of these applications signifies a strategic initiative aimed at mitigating the environmental footprint associated with waste ceramics, concurrently augmenting their recycling potential. The synergy between waste ceramics and polymers, therefore, not only addresses the sustainability imperative but also capitalizes on materials engineering advancements. Consequently, the amalgamation of waste ceramics with polymers emerges as a crucial focal point in both environmental sustainability and the expansive field of materials engineering, ushering in innovative avenues for research and application(66,67,72–75).

1.3. An Overview of Metal Materials and Their Varied Applications in Composites

1.3.1 Metals: Properties, Applications, and Industrial Significance

Metals, characterized by their inherent luster, conductivity, and malleability, represent a category of materials renowned for their proficiency in conducting electricity and effectively dissipating heat. Noteworthy for their high strength, magnetic attributes, and versatile applications across industries, metals undergo extraction from ores through mining and subsequent metallurgical processes, ultimately serving as foundational raw materials in various manufacturing endeavors. Alloy formation stands as a common practice to enhance the properties of metals, with examples including iron-carbon alloys like steel and copper-zinc alloys exemplified by brass. The deliberate amalgamation of metals into alloys refines their mechanical and thermal characteristics, broadening their utility across diverse industrial applications. Integral to the principles of natural resource conservation and environmental sustainability, metal recycling assumes paramount importance. Recognized as generally recyclable materials, metals undergo systematic processes to reclaim and reintegrate them into new production cycles. This practice not only mitigates the depletion of finite resources but also aligns with broader environmental imperatives, rendering metals essential contributors to the circular economy and sustainable material management(76–80).

1.3.2 Exploring the Versatility of Metal Matrix Composites

Metal Matrix Composites (MMCs) are composite materials formed by incorporating reinforcing materials into a metal matrix. These reinforcing elements frequently include ceramics, carbon fibers, or organic fibers. The widespread utilization of MMCs spans diverse sectors, including aviation, space exploration, automotive, electronics, and construction materials. The selection of these materials is primarily driven by their notable advantages, including high-temperature resistance, lightweight characteristics, and exceptional strength.

Various production methodologies contribute to the fabrication of MMCs, encompassing powder metallurgy, liquid phase injection, infiltration, and metal plating. Each method imparts distinct qualities to the resulting composite material, offering flexibility in tailoring MMCs to specific application requirements. MMC adoption addresses multifaceted industrial challenges, particularly excelling in applications demanding heightened performance attributes. The amalgamation of a resilient metal matrix with reinforcing elements lends MMCs the versatility to navigate and excel in environments characterized by elevated temperatures and stringent mechanical demands. This adaptability positions MMCs as instrumental materials in overcoming the evolving challenges encountered across diverse industrial landscapes(76,81–84).

1.3.3 Classifying Metal Matrix Composites: A Spectrum of Reinforcement Strategies

Aluminum Matrix Composites (AMC) constitute composite materials where an aluminum alloy serves as the matrix, commonly strengthened with materials like carbon fiber, silicon carbide, or alumina.

Titanium Matrix Composites (TMC) are composites where a titanium alloy acts as the matrix, typically reinforced with materials such as carbon fiber or alumina.

Magnesium Matrix Composites (MMC) are composite materials featuring a magnesium alloy as the matrix, frequently enhanced with materials like carbon fiber, boron carbide, or silicon carbide.

Steel Matrix Composites (SMC) employ steel alloys as the matrix, often fortified with materials such as ceramics, carbon fiber, or alumina.

Nickel Matrix Composites (NMC) involve composite materials where nickel alloys serve as the matrix, commonly strengthened with materials like ceramics or carbon fiber. These metal matrix composites find extensive use across diverse industrial applications, offering advantages such as lightweight composition, high strength, low density, and favorable thermal properties(81–83,85,86).

1.3.4 Metallurgical Influence: Unveiling the Impact of Metals on Polymer Composites

Incorporating a metal layer into polymer matrix composites represents a strategic approach to bolstering mechanical strength and enhancing various material properties. This additional metal layer contributes to improved heat transfer through heightened thermal conductivity, governs electromagnetic characteristics by increasing electrical conductivity, and fortifies wear resistance. Beyond these mechanical enhancements, the metal layer serves to augment corrosion resistance and introduce functional properties, making it adaptable to a diverse range of applications. The inherent high strength and durability of the metal layer exert a positive influence on the overall performance of polymer matrix composites. This synergistic integration of metal and polymer imparts a multifaceted improvement in material attributes, rendering the utilization of a metal layer in such composite materials highly popular. The amalgamation of these materials not only diversifies the functional capabilities but also aligns with the growing demand for advanced composite materials that can thrive in varied and demanding applications(76–79,82,85,86).

2. Findings and Conclusions

Research focused on the mechanical properties of thermoplastic composites infused with waste ceramics and metal aims to assess and enhance the material's performance characteristics. These composites exhibit the potential for superior mechanical durability and strength compared to traditional thermoplastics. The inclusion of ceramic and metal additives offers advantages by bolstering overall material durability, particularly in applications subject to heavy loads and harsh environmental conditions. The lightweight nature of metal fillers, coupled with the thermal and electrical conductivity properties of ceramic additives, expands the utility of the material across a broad spectrum of applications.

However, alongside these advantages, it's crucial to consider potential drawbacks, including increased production costs, reduced machinability, and the potential impact on abrasion properties due to metal fillings. These factors may influence the material's widespread availability and its commercial success in industrial applications.

The significance of incorporating waste ceramics aligns with sustainability goals, emphasizing the conservation of natural resources and the efficient utilization of waste. This approach represents a pivotal stride toward developing environmentally friendly material alternatives and fostering more sustainable industrial processes.

In conclusion, the investigation into the mechanical properties of thermoplastic composites with waste ceramic and metal additions contributes to the pursuit of innovative solutions in materials science and engineering. Such studies play a vital role in advancing the development of materials that are not only more durable and lightweight but also sustainable for future use in various industrial applications.

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Chapter 3

In Examining the Wear Behavior of Polymer Composites Modeling Methods

Ayhan Aytaç[1]

Abstract

The wear behavior of polymer composites is an important issue in industrial applications. When examining the wear behavior of polymer composites, it is important to determine the relationship between parameters such as material properties, surface properties, temperature and wear mechanisms. Various modeling methods have been developed to determine the wear behavior of polymer composites. This article examines the modeling of the wear behavior of polymer composites and reviews existing methods. A general evaluation of studies on modeling the wear behavior of polymer composites is presented.

Studies in the literature generally address various mathematical approaches to describe the wear behavior of polymer composites. In particular, existing approaches to mathematically describe the friction and wear behavior of multicomponent systems are examined. In the studies to be carried out, setting up an experimental setup in a laboratory environment, mathematical modeling or computer-aided simulation modeling can be carried out. However, within the scope of the study, modeling using Finite Element Method (FEM), Artificial Neural Network (ANNs), experimental setup and mathematical modeling were examined. Additionally, the development of new hybrid polymer matrix composites and the study of their wear behavior are also discussed.

1. Introduction

Polymer composites are gaining traction in tribological applications because of unique material characteristics including excellent wear resistance and reduced friction (Abdelbary, 2015; N. K. Myshkin & Kovalev, 2017). Determining the link between characteristics including material

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qualities, surface properties, temperature, and wear processes is crucial for analyzing the wear behavior of polymer composites. To find out how polymer composites wear, several modeling techniques have been created. It is possible to do computer-aided simulation modeling, mathematical modeling, or experimental setup in a laboratory setting. This study looked at mathematical modeling, artificial neural networks (ANNs), finite element method (FEM) modeling, and experimental setting.

Wear in polymer composites is caused by the material in contact with the friction surface interacting with it. The characteristics of polymers indicate that factors including surface energy, elastic modulus, specific heat, thermal conductivity, and operating circumstances affect wear behavior (Abdelbary, 2015). In polymer composites, local fatigue rises with repeated contact during wear (Panda et al., 2017). Research and compilation will be done on studies that predict the wear behavior of polymer composites based on the parameters given in the literature, and the findings will be compared and presented.

2. Factors Affecting Wear Behavior of Polymer Composites

Factors affecting the wear behavior of polymer composites are:

1. Filler Material: The type, size and shape of filler particles can affect the wear resistance of polymer composites (Muhammad, D., & Asaduzzaman, M. 2012).

2. Loading Type: Normal load, sliding speed, vibration amplitude and frequency are important factors that determine the friction and wear behavior of polymer composites (Muhammad, D., & Asaduzzaman, M. 2012).

3. Surface Properties: Properties such as surface roughness, machining and post-machining treatment of polymer composites can affect the wear behavior (Muhammad, D., & Asaduzzaman, M. 2012).

4. Fiber Type: The type of fibers used in fiber-reinforced composites can affect wear resistance. For example, glass fibers can have different effects on wear behavior (Fig. 1) (Sarath et al. 2023).

5. Lubrication: Lubrication condition can affect the wear resistance of polymer composites. Proper lubrication can reduce friction and increase wear resistance.

In order to comprehend and maximize the wear behavior of polymer composites, several elements need to be considered. Researchers are making significant progress in modeling and enhancing the wear behavior of polymer composites in light of these considerations (Han. 1996, Fekete. 2021, Muhammad, D., & Asaduzzaman, M. 2012). The effective parameters influencing the wear behavior include sliding distance, sliding speed, load, volume ratio, and weight ratio, as shown by the analysis of the experiments.

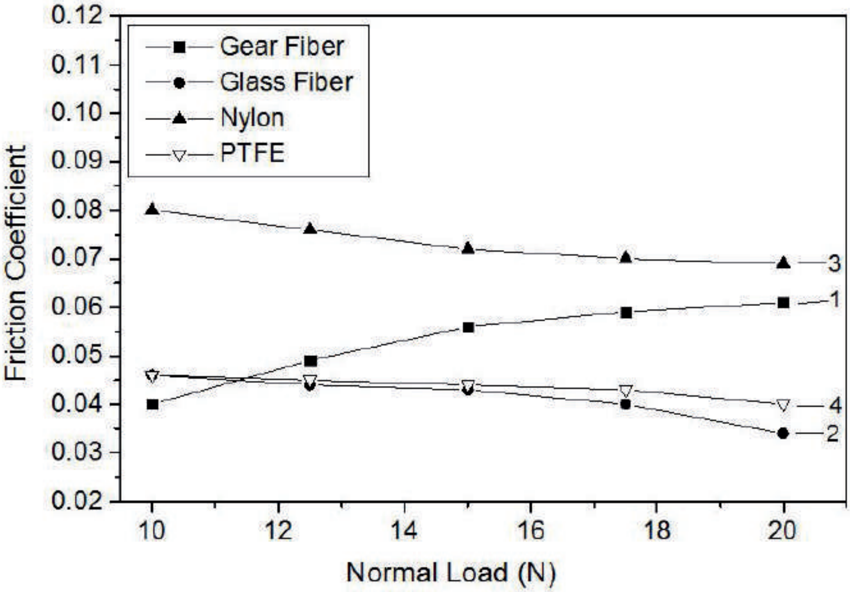

Figure 1. Polymer materials' load-friction coefficient graph, with a sliding speed of 1 m/s (Muhammad and Asaduzzaman, 2012).

Ashby provides a meaningful diagram that locates the polymeric materials with the lowest wear rate and scans the wear rate values (Figure 2). Furthermore, this diagram suggests that the wear rate domain can be expanded by using polymers in applications, especially towards lower values (Ashby. 2017).

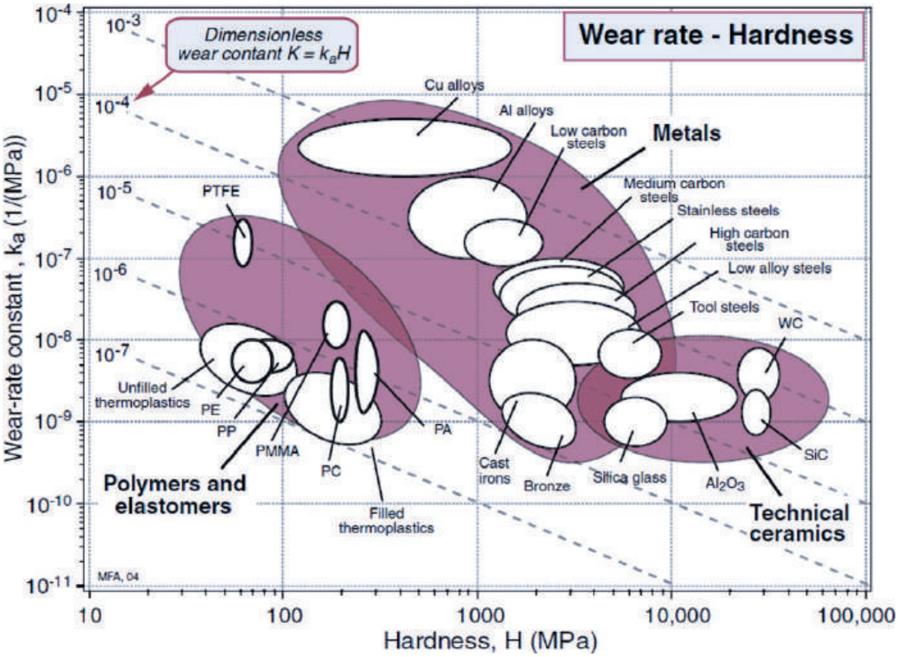

Figure 2. Polymer and polymer composite placement within the hardness-wear rate constant (Ashby, 2017).

3. Development and Wear Behavior of Hybrid Composite Polymers

When created efficiently, the new composite material has a more remarkable durability than it would if each constituent were used alone. Composites are employed in electrical, thermal, and environmental applications in addition to their structural qualities. In general, polymers' mechanical qualities are insufficient for a variety of structural uses. Different polymer matrix materials are used to form hybrid polymer matrix composites, and reinforcements like carbon, glass, or aramid fiber are frequently included as well. Studying the mechanical and wear properties of such composite materials is necessary for their development. (Fig. 3) (Fu et al. 2002).

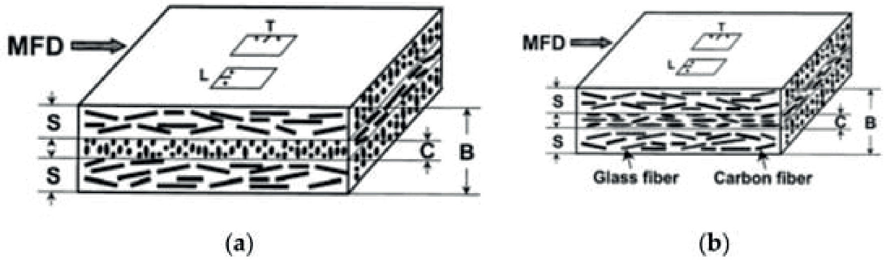

Figure 3. Diagram illustrating the three-layer architectures of hybrid composites with GFs/CFs and single-additive composites (a) *(Fu vd. 2002).*

To improve the mechanical characteristics and wear resistance of hybrid polymer matrix composites, researchers are experimenting with diverse combinations of matrix and reinforcing materials. These investigations span a broad spectrum, including material selection, production techniques, experimental testing, and modeling.

Karthik and colleagues conducted a study with the goal of creating new hybrid polymer matrix composites with Kevlar and epoxy resin as matrix materials. They used glass and carbon fibers for reinforcement. The hand lay-up method was utilized to prepare laminates made of fiber reinforced polymer matrix composite (FRP). To assess wear characteristics, the samples were put through a L9 Orthogonal Array pin-on-disc wear tester, which is part of Taguchi's Design of Experiments methodology. They used glass and carbon fibers for reinforcement. Increasing the hybrid polymer matrix composite laminate's thickness has improved its wear qualities. This material has numerous uses in the automobile sector and engineering structures (Karthik et al. 2020).

Numerous researchers have studied the following topics: carbon nanotubes (CNTs), rubber particles, nanodiamonds, titanium dioxide, wollastonite, tungsten carbide, graphene oxide, titanium carbide, silicon carbide, silica, and carbon. By adding filler particles like graphite and aluminum oxide, it strengthens epoxy. Researchers have worked on a number of projects to hybridize carbon fiber, polyamide, Kevlar, electrospun polysulfone nanofibers, and shape memory alloy fibers in order to improve the mechanical properties of glass fiber reinforced polymer composites. Better mechanical, thermal, and electrical conductivity characteristics are exhibited by carbon nanofibers and carbon fibers. (Gojny et al., 2006).

In conclusion, the discipline of materials engineering is still conducting research on the creation of hybrid polymer matrix composites and the analysis of their wear behavior. Research in this area helps the materials sector develop novel and cutting-edge applications.

4. Wear Modeling Approaches

4.1. Artificial Neural Network Approach (ANNs)

A computing system called an artificial neural network (ANN) mimics the architecture, or neurons, of a real nervous system. Every input to a neuron has a function that determines its contribution to the next neuron as well as its connectivity strength. For material research and modeling, this network system is recommended; however, it needs a specific amount of findings. (Friedrich et al., 2005). A review of works using the Artificial Neural Network model technique is provided below. Thermoplastics and thermosets augmented with unique fillers—including nanoparticles—are given specific consideration. Using artificial neural networks, attempts are undertaken to forecast wear characteristics and do systematic parameter assessments. ANNS is a new technology that can be used to forecast these materials' wear qualities based on test conditions and composition. Additionally, it makes systematic parameter studies for material optimization using computers possible. (Wear of polymer composites - K Friedrich, R Reinicke, Z Zhang, 2002, n.d.).

Three polymers' erosive wear data—polyethylene (PE), polyurethane (PUR), and an epoxy modified with hygrothermally decomposed polyurethane (EP-PUR)—have been handled by the artificial neural network technique (Zhang et al., 2003). It was shown that the friction coefficient and wear rate values decreased with an increase in the applied load in the study that examined the tribological properties, wear, and friction of ultra-high molecular weight polyethylene under dry sliding and Hank's balanced salt solution lubrication conditions. For the sliding speed values and applied load ranges examined in the study, the dry sliding condition produced the maximum friction coefficient and wear rate values, according to the findings. The study looked at how well artificial neural networks (ANNs) could forecast the material's wear rate values and friction coefficients under various sliding situations, and the findings were consistent with that. (Ermiş & Ünal, 2021).

4.2. Finite Element Method (FEM) Approach

The number of units, lines, regions, or volumes of the elements are initially defined depending on the properties of the tribological system when employing the finite element approach for wear modeling. For this, nodal points are employed. Nodes make it possible to display the amount of tribologically transferred stress. Nodes under a lot of stress also have large density. Linear or nonlinear functions are used to establish experimental conditions during wear. (Abdelbary, 2015). The studies that were done using the finite element method methodology are looked at below.

Finite element analysis has been applied to the study of stress and deformation properties during contact, as well as the determination of material properties. A macroscopic approach that assumes homogeneous, anisotropic material qualities derived from the rule of mixture-type relationships has typically guided the majority of these evaluations. This macroscopic approach's inability to accurately simulate the real-world interaction between the composite's fibers and matrix and its counterpart's asperities is a drawback (Friedrich et al., 2005). P-fiber orientation with respect to the shear direction was examined through the use of anisotropic half-space models. The contact simulation findings are used to approximate the stiffness basis for modeling each individual fiber as an infinite beam on an elastic foundation. These findings indicate a fiber stress brought on by shear and deformation (Ovaert & Wu, 1993). The contact and stress states created when a steel ball was driven into a fiber-reinforced composite were ascertained using a FE micromodel. For N- and P-fiber orientation, the position and distribution of subsurface stresses and strains were investigated. It was discovered that there is significant shear and compression on the surface in the case of N-fiber orientation. When P-fiber orientation is present, the matrix experiences stress of both the shear and compression types, yielding and local plastic deformation, while the fibers' typical deformations include compression and bending (Váradi et al., 1999). The frictional wear process in a polymer-metal contact pair: a numerical modeling approach The FEM model was made using the Abaqus software to show an integrated process and the construction of a numerical tool. The contact pair that serves as the foundation for this work is the contact between an elevator's thermoplastic polyurethane (TPU) guide shoe insert and the matching steel guide. A true simulation of these tests would need a very significant computing time because the tribometer tests required vast travel distances and a huge number of cycles in order to fit and verify the wear model. Thus, testing conducted over a suitable simulation period should be used to simulate the wear process comparable to the distances traveled (Martínez et al., 2012). The wear of polymer composites in friction joints is simulated by calculating temperature and using a mathematical model and an algorithm to solve a physically realistic stress-strain contact problem using a finite element method. The interaction processes at the PCM-counterbody interface, as well as the issue of non-stationary thermal conductivity, have been developed by developing an approach to wear process simulation based on temperature calculation in a surface layer of a polymer composite material (PCM), which takes into account the effect of ambient temperature and its influence on friction and wear process development. It was simulated by using the finite element technique (FEM) to solve a contact interaction problem. When the coefficient of friction for smooth and rough surfaces is compared, it can be shown that wear increases as surface roughness increases, but temperature essentially stays the same. (Bochkareva et al., 2018). Without making any additional heat exchange assumptions, the non-linearity of deformation and contact temperature in polymer composites was calculated by solving a non-stationary heat conduction issue in terms of mechanical-thermal energy conversion and heat loss through convection. The state of finite elements related to a polymer composite's attributes was examined, beginning with the computed temperature. (Bochkareva et al., 2020). At room temperature and a steady speed of 3 m/s, wear testing of three distinct laminated composites carbon fiber, woven glass fiber, and glass fiber reinforced epoxy was carried out on a pin-on apparatus under five different loads of 10, 20, 30, 40, and 50 N. constructed with a disc tribometer. Model of linear elastic finite elements The failure mode in the shear mode and the pin on the disk under dry lubrication were both simulated using FEM. The coefficient of friction can be numerically determined with the use of FEM in measuring friction force. One feature from FEM that is crucial for material description and analytical model work is tensile strength. As a result, an easy tensile test was used to determine it experimentally. The findings indicate that GFRP-R (Glass Fiber Reinforced Polypropylene R-Glass Prepreg) composites have a higher wear rate. (Abdellah et al., 2022).

4.3. Experimental and Mathematical Model Approaches

One can utilize wear behavior modeling developed using mathematical models or experimental setups directly, or one can use it to validate or contrast computer-aided simulations and models. Studies that used this model method were looked at.

A suggested model for abrasive wear of unidirectional fiber-reinforced polymer composites includes two models that illustrate the extremes of cyclic wear behavior, in contrast to steady-state wear, when various components wear at the same rate. This structure, which can be described as quasi-steady-state or cyclic, accommodates changes in the fiber and matrix wear rates. The underlying process has been explained, and it has been noted that this model yields more precise estimates of polymer composites' wear resistance than forecasts made using straightforward linear and inverse mixing rules based on the steady-state model. (Yen & Dharan, 1996). These predictions were compared with two engineering models to estimate the wear rates of thrust bearings made of polymers and dry friction rotating journal bearings. Additionally, it was shown how roughness, roughness orientation, and the development of transfer layers affect wear behavior (Franklin, 2001). The analysis of the study revealed a mathematical expression that uses dimensional analysis and similarity theory to calculate the temperature in the friction zone (T). In turn, the temperature acts as a reference point for forecasting wear. The established model states that it is possible to find the T value for every component in the friction pair. A thorough grasp of a polymer composite's mechanical and thermal properties, as well as its operating conditions, is necessary for the model to be applicable. If the operating parameters and fundamental data of the composites are known, then using the model makes it possible to determine the wear value of friction pairs made of polymer compositesIt is claimed that using models saves a substantial amount of time and money as compared to carrying out real friction wear trials under real conditions. (Tretyakov, 2004). The application of single-track and intersecting etching techniques is investigated to study abrasive wear in polymers. The results of earlier studies were confirmed through scratch and pin-on-disk wear tests on a variety of commercial polymers, indicating a relationship between scratch phenomena and abrasive wear. Interestingly, Sinha et al. found that the traditionally determined scratch hardness did not show any pattern with abrasive wear. (2007). Several influential parameters that could be analytically confirmed were included in a model that was developed in an attempt to create a comprehensive analytical model for predicting the wear of engineering polymers. The wear equations are divided into two categories: abrasive wear and fatigue wear. This is because the two mechanisms of wear work in separate ranges of roughness. It is important to note that, except in cases where melt wear predominates, the E/H ratio assumes a value at which wear is expected to be negligible in most parametric combinations. These predictions are useful in practice and match up well with various engineering polymer trials. (Chowdhury & Chakraborti, 2008). Small-scale roller-on-plate tests were used to compare the friction and wear behavior for polyoxymethylene homopolymers (POM-H) and teflon-doped polyethylene terephthalate (PET/PTFE). Four experimental models are presented to predict tribological data on contact pressure shear rate (pv-value), which is the parameter used to characterize tribological data. Sample geometries and contact deformation, as well as thermal effects (heat generation and dissipation), were taken into account with a new macroscopic geometry model that allows test results in small and large-scale tests. (Samyn & Schoukens, 2008). A description of the wear model, transfer, and their effects on friction is given. The creation and motion of particles as well as the friction-transfer relationship are both explained by the model's unknown parameters. In a linear reciprocating sliding tribometer, where a polymer-coated rod slides in a point contact configuration on a rough metallic roller under high pressure and a large sliding length of 10 mm, the parameters are obtained experimentally. It has been demonstrated that the developed model does a good job of describing how friction changes across multiple cycles. (Boissonnet et al., 2012). By merging Reye's wear model with elastohydrodynamic lubrication theory, a wear model under lubricated conditions was created. According to the wear simulation, HDPE wear rises with increasing sliding speed and normal load but falls with increasing lubricant viscosity and asperity height. The wear model can shorten the time required for wear testing and be used to forecast the long-term wear of polyethylene-based polymers in lubricated settings. (Xu et al., 2018). It has been demonstrated that temperature affects polymer-polymer sliding contacts, and that the choice of materials for static and rotating parts in polymer-polymer contact designs affects the sliding contact life. It has also been demonstrated that application temperature during operation significantly affects longevity. Lastly, a new design approach based on the deformation energy concept is offered, which suggests a wear model because this energy causes changes in the properties of the material. The suggested model is different from current models in that it uses the Peclet number to include the thermal characteristics of materials in contact (Ramesh et al., 2019). Hybrid natural fiber-reinforced polymer composites have emerged as an environmentally friendly alternative to traditional building materials due to their low cost and high strength-to-weight ratio. Response surface method (RSM) was used in the studies. RSM also provided a mathematical model for optimization of sliding wear of hybrid composites. The most suitable composite with optimum values for minimum sliding wear of hybrid composites was found. A fuzzy logic model was also developed for the prediction of sliding wear of hybrid composites based on experimental data. From the results obtained, it was seen that the developed fuzzy model could predict the sliding wear of hybrid composites with 87% accuracy. (A. K. Sinha et al., 2021).

5. Evaluation of Wear in Polymer Matrix Composites

The outcomes are typically assessed through a combination of theoretical modeling and experimental studies. As part of these investigations, material qualities are ascertained, wear resistance is tested, and mathematical models are created. Studies that look at polymer matrix composite materials' wear behavior experimentally exist. It is necessary to investigate the tribological and mechanical aspects of polymer matrix composites' wear and friction characteristics. These kinds of investigations are critical to comprehending how material components interact, assisting in the selection of materials, and assessing their application performance.

Mechanical modeling and the assessment of material parameters are commonly employed in calculations to assess wear in polymer matrix composites. These computations (Sudeepan et al., 2014):

- Friction and wear property calculation: Material properties and mechanical modeling are utilized to determine the friction and wear properties of polymer matrix composites. These models comprise the matrix element, the fibrous zone, and the material's wear outcome.
- Dry sliding wear behavior calculation: The following procedures are used in studies where the wear resistance, material characteristics, and dry sliding behavior of polymer matrix composites are calculated.
- Tribological and mechanical properties: The tribological and mechanical properties of polymer matrix composites are computed by means of mechanical modeling, which establishes the material-instek and coaxial properties and computes the parameters influencing the material's wear and friction properties.
- Polymer matrix composites: The structure and characteristics of these materials, such as reinforcing materials, thermosetting polymers, and other additive materials, are determined using a variety of techniques and computations. The performance of polymer matrix composites in various applications and areas of usage is assessed using this data.

These computations are used to assess polymer matrix composites' wear behavior and enhance their application performance. Furthermore, the performance of the materials in applications is assessed and material selection is guided by these computations (Sudeepan et al., 2014).

6. Conclusion and Evaluation

Low coefficients of friction, strong resistance to abrasion, ease of shaping, and resistance to oxidation or corrosion characterize polymeric materials. Polymer composites are stronger and more rigid than pure polymers because of the presence of reinforcing elements, which enables them to bear heavy loads and stresses. While many thermoset composites may deteriorate or lose their mechanical qualities at high temperatures, other polymer composites have good temperature resistance.

The use of polymeric materials has several benefits, such as low density, resistance to oxidation and tribocorrosion, non-toxic structure, easy shaping, and low cost. It does seem to have certain drawbacks, though, in addition to its positives. Negative temperatures affect polymeric materials differently, and even a slight variation in operating circumstances can have a substantial impact on their tribological characteristics.

Examining classical tribology reveals that it was first created as a discipline for metals. Polymer tribology is dominated by interfaces and various operating circumstances such as thermal heat, contact pressure, and the production of transfer films. Because of this, conventional experimental techniques in this area are modified for use with polymers rather than valid for polymers. The scale and complexity of the system under examination vary, and there are several methods in the literature for assessing the tribological behavior of a pair of polymer-based materials. This makes it evident that a distinct working area is created by a suitable kind of tribo test setup with the right parameters chosen to mirror the material/composite's real-time application.

Polymer composites, because of their special tribological characteristics, are very versatile, and can be customized, have many uses and great potential in the future. The capabilities of polymer composites will be further expanded by ongoing research and development activities and technical advancements, resulting in enhanced performance, sustainability, and new applications in a variety of sectors. Furthermore, the development of hybrid composites has opened up a significant area for tribological research.

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Chapter 4

Manufacturing of Ceramic Materials With 3D Selective Laser Melting and Analysis of Their Possible Applications for Ballistic Purposes

Ayhan Aytaç[1]

Abstract

Selective laser melting (SLM) or selective laser sintering (SLS) methods are part of additive manufacturing techniques that involve work on a wide range of materials, including ceramic materials. Moreover, SLM is known to be able to produce customized components of various materials such as metal, ceramics and polymers and hence is a popular manufacturing method. Studies emphasize that these techniques also have potential for analysis of possible applications for ballistic purposes. Just as there are studies examining the mechanical properties of ceramic materials produced by the selective laser melting method, there are also studies on the marginal compatibility of ceramics used in the creation of ceramic plates.

The development of advanced ceramic materials for ballistic applications has been a topic of interest in the defense industry. Metals, ceramics and composite materials are generally used in personnel and vehicle armor applications. However, today, composite or hybrid composite designs come to the fore as a result of evaluating the level of protection together with the weight parameter. When the literature is examined; It shows that additive manufacturing techniques can also be used in the production of ceramic materials and therefore are preferred in armor production. In the study where the literature is examined in detail, it is emphasized that the most popular materials of ceramics in recent years are alumina and zirconia, which are among the main engineering material groups. Al2O3 is widely used as ceramic material in various industrial sectors, exhibiting high strength, hardness and excellent dielectric properties. On the other hand, ZrO2 is often added to increase the toughness and wear resistance properties of

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ceramic composites, making it a valuable addition to ceramic formulations. The combination of Al2O3 and ZrO2 has demonstrated promising results in improving the mechanical and ballistic properties of functionally graded materials, increasing fracture resistance and wear properties. In this study, a general evaluation of the studies in the existing literature is presented on the production of ceramic materials by 3D Selective Laser Melting and the analysis of their possible applications for ballistic purposes.

1. Introduction

Ceramic materials are an important class of materials for ballistic protection applications in the defense industry due to their properties such as high temperature resistance, high hardness, high strength and low density. It has advantages such as relatively high mechanical and tribological properties, high specific strength and hardness. Reinforced composites have many advantages such as low density and high strength. However, the fiber could not be used independently due to low impact resistance and high cost. For this reason, applications such as strengthening composite hybrid laminated plates including ceramic plates, including intermediate layers, considering that they disrupt the piercing structure of the threat by absorbing the kinetic energy of the threat, are promising. The limitations of ceramic materials obtained by traditional production methods encourage the use of 3D printing technologies in the production of ceramic materials. In this context, the production of ceramic materials, especially Al2O3 (alumina) and ZrO2 (zirconia), by selective laser melting 3D printing method is of great importance to evaluate potential applications for ballistic purposes.

3D printing, also known as additive manufacturing, is a shaping method in which a 3D computer model is sliced into 2D sections to create a physical structure through the addition of material layer by layer. Within this general definition, there are many specific technologies that vary in raw material and forming/bonding method for specific materials and applications. This differs significantly from more traditional subtractive or equivalent manufacturing methods that have been used for hundreds of years and allows the fabrication of structures that would otherwise be impossible to create relatively quickly and efficiently. This has allowed different industries to create exciting new parts and products, while saving time and money and improving performance [1-5]. However, the main materials used for 3D printing so far are polymers and metals; Ceramics, on the other hand, are relatively less researched and developed. However, in recent years, there has been a significant increase in the interest and use of ceramic materials due to the many useful application areas of ceramic materials as well as 3D printing technologies. Characterized by excellent thermal, chemical and electrical durability and stability, high strength and hardness, and useful optical properties, ceramics are ideal materials for applications in aerospace, medical, military and defense, electronics and many other industries [6-8].

In recent years, the production of ceramic materials with 3D printing technologies has been developing rapidly. These technologies offer many advantages compared to traditional methods in the production of ceramic materials. In particular, the selective laser melting 3D printing method provides high precision in the production of ceramic materials, production of high-density parts, production of complex geometries and material savings. Therefore, the selective laser melting 3D printing method has significant potential in the production of ceramic materials for ballistic protection applications.

Selective laser melting (SLM) is a powder bed-based layer manufacturing technique that enables additive manufacturing of complex-shaped objects directly from 3D CAD data. SLM is based on the direct and complete melting of powder material with a laser beam. SLM for metallic materials is already used successfully in industry. A comparable additive manufacturing technique is not yet available for high-performance ceramic materials such as zirconia or alumina. For less challenging materials containing silica or glassy phases, there are laser-based additive manufacturing approaches and solid-state sintering-based approaches described in the literature [9].

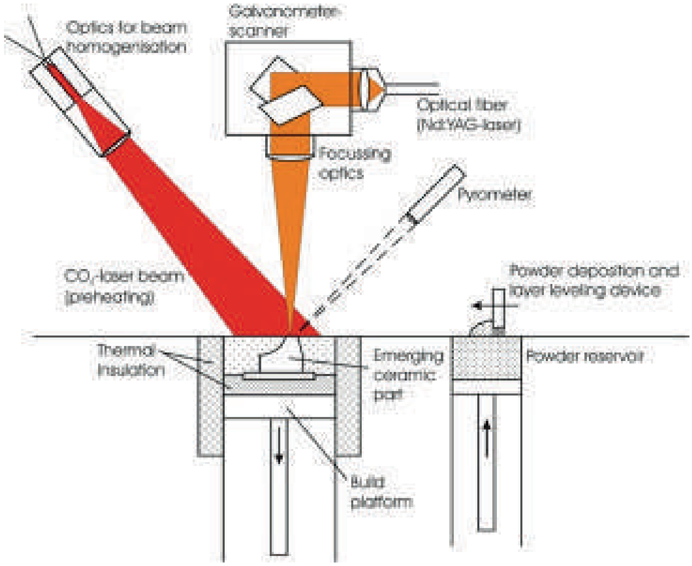

Figure 1. Schematic illustration of the experimental SLM system [10].

The SLM creation process consists of four main steps [10]: A thin layer of ceramic powder material is deposited on the build platform. Appropriate areas of the powder layer are selectively heated and melted by means of a focused laser beam. The building platform is lowered by a distance corresponding to the layer thickness. Steps are repeated until all layers are created (Figures 1,2 and 3).

Studies in this field include many researches on the production of ceramic materials by selective laser melting 3D printing method. For example, Wilkes et al. [10], a selective laser melting 3D printing method was developed for the production of high-strength oxide ceramics. Selective laser melting of a 1600°C preheated Zirconia and alumina ceramic materials was experimentally investigated. To reduce thermally induced stresses, the ceramic was preheated to a temperature of at least 1600°C during the forming process. Within the scope of the study, crack-free samples with bending strength over 500 MPa were produced. It is stated that the produced samples have a fine-grained, two-phase microstructure consisting of tetragonal zirconia and alpha-alumina. In the said study, it was stated that the production of high-strength ceramic components could be achieved by using Al2O3 and ZrO2 ceramic materials and that it would pioneer industrial applications.

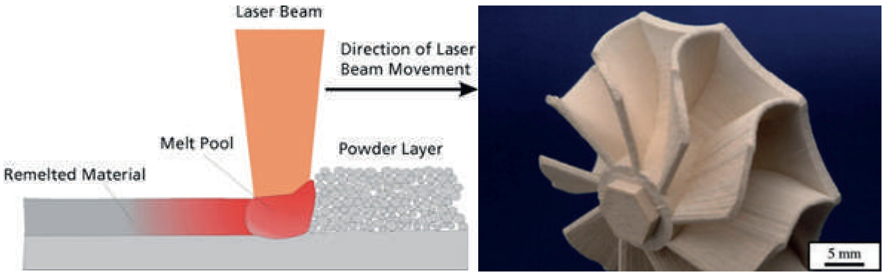

Figure 2. A- 3D Melting Method with SLM, B- Part made by SLM out of 80 wt.% zirconia/20 wt.% alumina (no preheating) [10].

In a review article by Lakhdar et al. on additive manufacturing (AM) of advanced ceramics; They emphasized the importance of minimizing the formation of residual porosity while preventing crack formation, which remains one of the main challenges of advanced ceramics in AM. Among currently available AM technologies, only a few processes allow the successful and reliable production of dense ceramic parts without any undesirable microporosity, while most technologies are only suitable for creating porous structures. Therefore, research and development efforts in the ceramic AM community have for several years been primarily focused on applications where porosity is beneficial, with a strong emphasis on porous components for biomedical applications and, in particular, scaffolds for tissue engineering [11]. Carloni et al. In their study, they produced transparent alumina ceramics using post-processing steps such as molding, vacuum sintering and polishing with an extrusion-based 3D printer. Within the scope of the study, manufacturable powder mixtures and 3D manufacturing parameters were optimized to produce quality bodies. They showed that two-stage vacuum sintering samples increased density while decreasing grain size, thus increasing the transparency of sintered alumina ceramics compared to single-step sintering samples. Two-stage vacuum sintered alumina ceramics stated that they achieved 70% total transmittance at 800 nm and relative density values higher than 99%. They demonstrated the ability of 3D AM manufacturing to compete with traditional transparent ceramic forming methods, as well as the additional benefit of freedom in the design and production of complex shapes [12]. Ceramics represent a new frontier for these LAM systems with many challenges and research needs. However, the material properties offered by ceramics compared to polymers and metals make the additive manufacturing of ceramic components an attractive engineering opportunity for many other technology fields such as aerospace and defense [13].

When the literature is examined in general, the studies on ceramics of the technology, which is quite new and has names such as Laser additive manufacturing and Laser 3D Printing, are limited. In the sintering of ceramics with this method, the problem of crack and pore formation caused by thermal stresses remains [14]. In addition, studies on the production of 3D ceramic materials with SLM and the determination of the energy absorption and damage behavior of hybrid sandwich composite panels produced with these materials under impact loads are very limited.

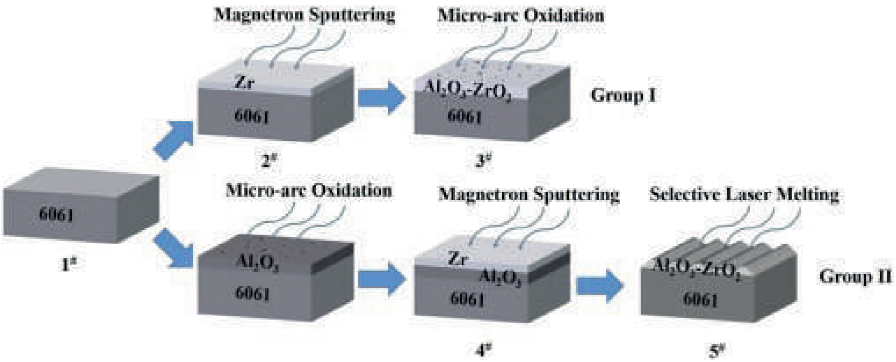

Figure 3. Schematic diagram of sample preparation used to test the mechanical properties of the structure formed by coating Al2O3 - ZrO2 layers with Micro-Arc Oxidation (MAO) and Selective Laser Melting (SLM) [14].

In conclusion; Ceramic products have been produced for decades using traditional techniques such as extrusion, kiln sintering and casting. However, these methods have several disadvantages in terms of possible shape and structure, which limit their range of application. The emergence of laser additive manufacturing (LAM) provides a significant opportunity to create ceramic components with much greater design freedom. This technology enables the creation of ceramic components that not only meet the increasing material requirements of aerospace applications but also offer new opportunities in terms of complex structures. The aim of this study is to investigate the usability of the production of ceramic materials such as Al2O3 and ZrO2 by selective laser melting 3D printing method for ballistic purposes. This study aims to increase ballistic protection capacity by offering a new approach in the production of ceramic materials used in the defense industry.

2. Ballistic Ceramics and Armor Applications

Focusing on the mechanical properties and performance criteria of the most commonly used ballistic ceramics, including alumina, silicon carbide and boron carbide, it can be seen that the main factors affecting the ballistic performance of ceramic materials are, in particular, hardness and fracture toughness. Additionally, the effect of functionally graded materials such as Al2O3-ZrO2 on the ballistic resistance capacity should also be examined. The effect of ceramic properties and penetration depth test parameters on the ballistic performance of armor ceramics are the most important critical factors that determine the effectiveness of ceramic materials in ballistic applications [15].

Dresch et al. A review conducted by provides a comprehensive analysis of the mechanical properties and ballistic behavior of ceramic materials and the suitability of these materials for armor applications (Figure 4). They also compared conventionally sintered and layered alumina and examined the ballistic behavior of these materials in detail. The research further emphasizes the development and optimization of ceramic-based ballistic protection systems [15].

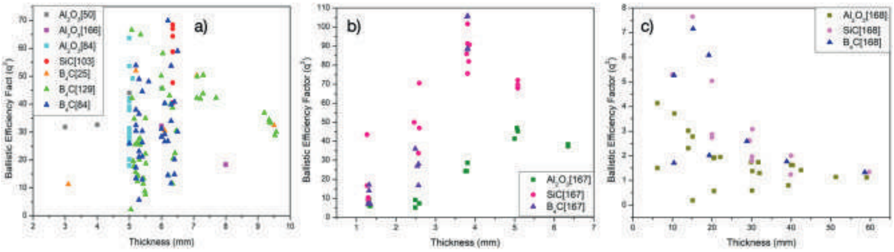

Figure 4. Relationship between ballistic efficiency factor and ceramic thickness. a) 7.62 AP; b) 0.30 AP M2; c) Rod. Data obtained from references [15].

Al2O3 is widely used as a ceramic material because it shows high strength and hardness. ZrO2 is often added to increase the durability of such a material. Huang et al. In a study by et al., they mixed Al2O3 and ZrO2 to formulate functionally graded materials (FGMs). Four-layer and eleven-layer Al2O3-ZrO2 FGMs were obtained from Al2O3 and ZrO2 mixtures by sintering at 1500 °C. They also designed experiments by mixing various ratios of Al2O3 and ZrO2 to analyze fracture toughness and hardness. As a result, they revealed that the 90% Al2O3 - 10% ZrO2 plate exhibited a hardness of 15.12 GPa, and the 50% Al2O3 - 50% ZrO2 plate achieved a fracture toughness as high as 4.7 MPa m0.5 [16].

2.1. Specific Properties of Al2O3 and ZrO2 Ceramic Materials for Ballistic Applications

Al2O3 (alumina) and ZrO2 (zirconia) ceramic materials have specific properties that make them suitable for ballistic applications. These features include:

1. Hardness: Alumina and zirconia ceramics exhibit high hardness, making them resistant to penetration and deformation when subjected to high-speed impacts. This feature is necessary to provide effective ballistic protection.

2. Impact Resistance: Combining the hardness of alumina with the durability of zirconia, zirconia-toughened alumina (ZTA) ceramic materials show excellent impact resistance. This property is very important to withstand the impact of high-speed bullets and fragments.

3. Wear Resistance: ZTA ceramic materials are known for their wear resistance, which is useful for maintaining the integrity and effectiveness of ballistic armor over time, especially in corrosive environments.

4. Fracture Toughness: The combination of zirconia and alumina in composite ceramics contributes to increased fracture toughness, allowing the material to absorb energy and resist crack propagation when exposed to ballistic impacts.

5. Microstructure: The microstructure of ZrO2-Al2O3 composite ceramics plays an important role in determining their mechanical properties, including hardness and fracture toughness. The microstructural properties of these ceramics are critical in terms of their ballistic resistance capabilities.

6. Mechanical Properties: The mechanical properties of alumina-based ceramics, including hardness and fracture toughness, are essential for their performance in ballistic applications. These properties are evaluated to evaluate the material's ability to withstand ballistic impacts.

In summary, the specific properties of Al2O3 and ZrO2 ceramic materials, such as hardness, impact resistance, wear resistance and fracture toughness, make them very suitable for ballistic applications. These properties enable ceramics to effectively resist penetration, absorb energy, and maintain their structural integrity when subjected to high-velocity impacts, making them valuable materials for ballistic armor and protective applications [16-18].

2.2 Ballistic Ceramics and the Importance of Developing These Ceramics as Armor Plates

Nowadays, the importance of ceramic materials developed for ballistic applications in the defense industry is increasing. These ceramics are preferred especially on the front surfaces of composite and hybrid composite plates due to their superior mechanical properties. The limitations of ceramic materials obtained by traditional production methods encourage the use of 3D printing technologies in the production of ceramic materials. In this context, the production of ceramic materials, especially Al2O3 (alumina) and ZrO2 (zirconia), by selective laser melting 3D printing method is of great importance to evaluate potential applications for ballistic purposes. Future research could focus on improving the surface quality of manufactured components, solving problems with cold powder deposition on pre-heated ceramics, further increasing mechanical strength, and transferring the technology from laboratory scale to industrial application.

Ballistic ceramics are the preferred materials for armor plates due to their high hardness and low density. Ballistic properties of ceramics such as boron carbide and alumina are examined by methods such as elemental analysis, phase analysis, microstructure analysis, density, pore analysis and three-point bending test [19]. The ballistic performance of ceramics depends on factors such as armor thickness, plate thickness and support plate. The armor thickness should be at least the radius of the bullet and the front ceramic plate thickness used should be 1/3 of the total armor thickness [20]. The ballistic performance of ceramic armor with concave and flat surface shapes is examined using numerical modeling methods. Modern armors are generally designed as a combination of a hard front surface with a ceramic layer and a fiber-reinforced back plate [21].

3. Comparison of Ceramic and Other Armor Plates in Terms of Ballistics

Ceramic-based armor plates offer many advantages in terms of ballistic performance compared to other types of armor plates. Ceramics such as boron carbide and silicon carbide are known for their high hardness, allowing them to effectively fragment or deform the core of an incoming projectile, dissipating its energy and stopping penetration. This feature makes ceramic armor plates highly effective against armor-piercing bullets designed to penetrate metal armor. Additionally, ceramic armor plates are lighter than traditional metal armor, providing the user with better mobility and reducing fatigue. However, a potential disadvantage of ceramic armor is its brittleness, which can be reduced by using a layered backplate to increase ballistic performance [22].

Research has shown that the ballistic efficiency of ceramic armor is affected by factors such as material composition, plate size, design and construction. For example, the hardness of the ceramic material, the depth of substrate deformation, and the resistance of the plates to brittle fracture are critical factors affecting the ballistic performance of the armor [23]. Additionally, it has been found that the layer structure of laminated ceramic plates significantly affects their ballistic performance, with studies showing the effectiveness of layered ceramic composites for body armor applications [24].

In summary, ceramic-based armor plates exhibit superior ballistic performance due to their high hardness, which allows them to effectively dissipate the energy of incoming bullets, and their lighter weight than metal armor. Ongoing research continues to focus on optimizing the design and structure of ceramic armor plates to further increase their ballistic efficiency and overall protective ability [25].

4. Feasibility of Ceramic Material Production with SLM

SLM (Selective Laser Melting) technology is a method whose usability is being investigated in the production of ceramic materials. This technology provides higher precision and control in the production of ceramic materials than traditional methods. The SLM method is based on the principle of melting the powders used in the production of ceramic materials with a laser and combining them layer by layer. This method provides less waste and higher efficiency in the production of ceramic materials. The mechanical properties of ceramic materials produced by SLM depend on factors such as hardness, density, porosity and thermal behavior. Therefore, the ballistic performance of ceramic materials produced by SLM depends on factors such as material properties and design. Since SLM technology provides higher precision and control in the production of ceramic materials, its usability in high-performance applications such as ballistic armor plates is being investigated.

Although the SLM method is a widely used method for 3D printing of metallic materials, some difficulties are encountered when working with ceramics. The high melting points and brittle nature of ceramics make it difficult to process ceramics with SLM compared to traditional metal 3D printing processes. Additionally, the high thermal conductivity of ceramics may affect the laser melting process and cause undesirable thermal stresses [15].

5. Conclusion and Evaluation

Selective laser melting (SLM) is a promising technology for ceramic 3D printing, but it also poses many challenges. One of the main challenges is the difficulty of obtaining high-density ceramic parts due to the high porosity of printed parts. This is because the ceramic powders of the SLM process have a high melting point, which can cause voids and defects in the printed parts. Another challenge is the limited number of ceramic materials that can be used in SLM. The process requires materials that can melt and solidify quickly, which limits the range of ceramic materials that can be used. Additionally, the high melting temperatures of some ceramic materials can cause thermal stresses during the printing process, leading to cracking and deformation of printed parts. Additionally, the SLM process for ceramic materials requires precise control of laser power, scanning speed, and powder bed temperature to achieve the desired properties of the printed parts. Optimization of these parameters is critical to obtaining high-quality ceramic parts with the desired properties. Despite these challenges, the potential benefits of SLM for ceramic 3D printing are significant. The technology offers the ability to produce complex ceramic parts with high precision and accuracy that are difficult to achieve with traditional manufacturing methods. Additionally, SLM can enable the production of customized ceramic parts with unique geometries and properties that can be tailored to specific applications.

In conclusion, while SLM presents several challenges for ceramic 3D printing, the potential benefits of this technology make it an attractive option for the production of high-performance ceramic parts. Further research and development is needed to overcome the challenges associated with SLM for ceramic materials and fully realize the potential of this technology for ceramic 3D printing. This study reveals the advantages of production of ceramic materials by selective laser melting 3D printing compared to traditional production methods and their potential applications for ballistic purposes. The main issues that need to be studied are the manufacturability of ceramic materials such as Al2O3 and ZrO2 by 3D printing, optimizing production conditions, their effect on material properties and their contribution to ballistic performance. The aim of the study is to present a new approach in the production of ceramic materials used in the defense industry. This new production technique, based on melting and solidifying high-performance ceramic material, has some significant advantages compared to laser sintering techniques or other production techniques based on solid-state sintering processes.

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Bölüm 5

Zirkonya Matrisli Seramik-Seramik Kompozitler

Arife Yurdakul[1]

Özet

“Seramik Çelik” olarak adlandırılan zirkonyum dioksit/zirkonya (ZrO_2) başta dental ve biyomedikal uygulamalar olmak üzere kesici uçlar, rulmanlar, zırh malzemeleri ve sensörler gibi çok geniş yelpazeye dağılmış birçok farklı kritik sayılabilecek alanlarda oldukça dikkat çekici bir ileri teknoloji seramik malzemesidir. ZrO_2’ya bu kadar çok uygulama alanında kendisine yer bulmasını sağlayan en önemli faktör, tıpkı çeliklerde olduğu gibi martensitik faz dönüşümü sergileyebilmesidir. Bu durum çoğunlukla, %3 mol itriyum oksit ile oda sıcaklığında kararlı kılınmış tetragonal zirkonya polikristalin (3Y-TZP) seramikleri için karakteristik olup, 3Y-TZP seramiklerinin yüksek mekanik (sertlik, tokluk ve eğilme mukavemeti vb.) ve tribolojik özelliklerinin sebebi olarak gösterilmektedir. Ancak gelişen teknoloji ve ihtiyaç duyulan uygulama alanlarından beklenen mühendislik özelliklerinin sürekli güncellenmesi nedeniyle, yeni malzeme arayışları hız kesmeden devam etmektedir. Bu noktada, 3Y-TZP esaslı seramik malzemelerinde mukavemet değerlerinden ödün vermeden hem tok hem de sert olarak üretebilmek bu alanda çalışan bilim insanları için önemli bir araştırma konusu olmuştur. Böylece, 3Y-TZP matris faz olarak düşünülerek sırasıyla alümina (Al_2O_3), silisyum karbür (SiC), titanyum diborür (TiB_2), zirkonyum diborür (ZrB_2) ve silisyum nitrür (Si_3N_4) gibi oksit, karbür, borür ve nitrür grubu ileri teknoloji seramiklerinin takviye ikincil faz olarak kullanıldığı seramik-seramik kompozit üretimleri gerçekleştirilmiştir. Bu kitap bölümünde, sertlik, tokluk, eğilme mukavemeti ve aşınma karakteristikleri gibi mekanik ve tribolojik özelliklerin 3Y-TZP/Al_2O_3, 3Y-TZP/SiC, 3Y-TZP/TiB_2, 3Y-TZP/ZrB_2 ve 3Y-TZP/Si_3N_4 kompozitlerinde nasıl optimize edildiği anlatılmaktadır. Burada bahsedilen hususların araştırmacılar tarafından iyi bir şekilde anlaşılması, 3Y-TZP matris esaslı ancak farklı yeni takviye fazlarla güçlendirilmiş yeni kompozitlerin üretilmesinde öncü olacağı ve bu alanda yeni kapılar açacağı değerlendirilmektedir.

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1. Giriş

Yüksek eğme mukavemeti, üstün biyouyumluluğu ve yüksek kimyasal direnci nedeniyle zirkonyum oksit [zirkonya (ZrO_2)], bugüne kadar birçok farklı fonksiyonel ve yapısal amaçlar için yaygın olarak kullanılmıştır. Diş, kalça ve diz implantları gibi biyomalzemeler, kesme takımları, balistik zırh, rulmanlar ve seramik burç gibi uygulamalar en önemli kullanım alanlarına örnek olarak gösterilebilir [1-2]. Saf ZrO_2, sıcaklık aralığına bağlı olarak çeşitli polimorfik fazlarda bulunabilir. Monoklinik (m-ZrO_2; oda sıcaklığından 1170°C'ye kadar), tetragonal (t-ZrO_2; 1170-2370°C arasında) ve kübik (c-ZrO_2; 2370°C'den ergime noktası 2680°C'ye kadar)[3-4]. Tetragonal form, monoklinik formdan daha yoğundur ve faz dönüşümü sırasında (yaklaşık 1000°C), yapılarında çatlakların oluşmasıyla birlikte hacimde önemli bir değişiklik meydana gelir. Bu nedenle, birçok yüksek sıcaklık uygulamasında saf ZrO_2'nin kullanımı sınırlıdır. Ancak, ZrO_2 kısmen veya tamamen stabilize edilebilir ve bu nedenle birçok uygulamada başarıyla kullanılmaktadır. ZrO_2 bazlı yapısal seramikler üç gruba ayrılır: (a) dönüşümle toklaştırılmış ZrO_2, (b) kısmen stabilize edilmiş ZrO_2 (PSZ) ve (c) tetragonal ZrO_2 polikristalleri (TZP). Yüksek sıcaklıklarda, çeşitli oksitler (örneğin MgO, CaO ve Y_2O_3) ZrO_2 ile katı çözeltiler oluşturur ve bu da yüksek sıcaklıktaki kübik fazın daha düşük bir sıcaklıkta stabilize edilmesini mümkün kılar. PSZ, ZrO_2 modifikasyonlarının (kübik ve tetragonal) bir karışımıdır ve yetersiz kübik faz oluşturan katkılar (kararlaştırıcı) eklendiğinde oluşur. Tamamen kararlaştırılmış ZrO_2, uygun miktarlarda MgO, Y_2O_3 ve CaO gibi oksitlerin katkılanmasıyla üretilebilir. Bu durumda, kübik yapıya sahip katı bir çözelti elde edilir. Kararlaştırıcının türüne bağlı olarak temelde iki farklı mikro yapı oluşur. Örneğin, MgO ilavesi nispeten iri tanelerin oluşmasına yol açarken, itriyum oksit (Y_2O_3) ilavesi ise ince taneli bir mikroyapı ile sonuçlanır [5].

t-ZrO_2 kristal yapısına 3 mol % Y_2O_3 katkılandırıldığında, oda sıcaklığında ortaya çıkan ürüne itriyum stabilize tetragonal ZrO_2 polikristalin (3Y-TZP) seramik adı verilmektedir. Ayrıca 3Y-TZP'ler biyo-esaslı seramiklerde mekanik özellikleri geliştirmek için kullanılan en popüler malzemedir. 900 ila 1100 MPa arasında yüksek eğilme mukavemeti sergilerler. Bununla birlikte, 8–12 $MPa.m^{1/2}$ civarında düşük veya orta derecede kırılma tokluğuna sahiptir. Ancak nispeten düşük sertlikleri (HV-20°C, 1120 kg/mm^2) tribolojik uygulamalarda kullanımlarını kısıtlamaktadır [3,4,6].

Literatür araştırmasına dayanarak, stres kaynaklı tetragonal kristal yapıdan monoklinik yapıya (t-ZrO_2 $\rightarrow$m-ZrO_2) faz dönüşümü, önemli bir hacim değişikliğine (~%4-5) neden olarak ilerleyen çatlağın yakınında oluşan baskı neticesinde yüksek kırılma tokluğu ve mukavemeti kazanmada anahtar bir rol oynar. Böylece 3Y-TZP seramiklerinde oluşan çatlakları engellemek için dönüşüm toklaşması meydana gelir [7-9]. Bununla birlikte, 3Y-TZP'lerin bu mükemmel mekanik özellikleri, t-ZrO_2 →m-ZrO_2 faz dönüşümü nedeniyle nemli ortamda düşük sıcaklıkta (150–400°C) bozunmadan dolayı zarar görmektedir. Bu yüzden dönüşüm toklaşmasının keşfinden günümüze kadar yapılan çalışmalarda, Y-TZP monolitik malzemelerin mekanik özelliklerini geliştirmek amacıyla, ZrO_2 matrisine oksit ve oksit olmayan faz takviyesi ile kompozit formunda üretim yapmanın mümkün olduğu görülmüştür [10-11].

3Y-TZP seramiklerinin kırılma tokluğunu iyileştirmeye yönelik çalışmalar incelendiğinde, ilk olarak Y_2O_3'in kararlaştırıcı olarak %3'ten daha az mol oranında (örn. %1,5-2 mol) kullanıldığı dikkat çekmektedir. Başta Al_2O_3 olmak üzere karbon nanotüpler (CNT), grafen vb. birçok farklı ikincil takviye malzemesi ilave edilerek, 3Y-TZP'nin kırılma tokluğu geliştirilmeye çalışılmıştır. Ayrıca kıvılcım plazma sinterleme (SPS), mikrodalga sinterleme gibi farklı yeni sinterleme tekniklerinin ve iki aşamalı sinterlemenin 3Y-TZP seramiklerinin mekanik özelliklerinin geliştirilmesine etkileri rapor edilmiştir. Bu araştırmalar bilimsel açıdan çok önemli katkılar sağlasa da, tam yoğun kütlelerin elde edilememesi, ikincil fazların 3Y-TZP içerisinde tam olarak dağılamaması ve önerilen yeni sinterleme tekniklerinin sanayileşmeye uygun olmaması bilinen dezavantajlar olarak değerlendirilebilir [10]. Bu nedenle 3Y-TZP'lerin kırılma dayanımını iyileştirmek için hala daha pratik, endüstriyel ve uygulanabilir yeni yaklaşımlara ihtiyaç vardır. Bu doğrultuda, seramik-seramik kompozit yapıların geliştirilmesi ile birlikte nitelikli malzeme üretimi önem kazanmıştır.

1.1. Alümina (Al_2O_3) ile Toklaştırılmış Zirkonya (ATZ) Kompozitleri

Alümina (Al_2O_3) ile toklaştırılmış zirkonya (ATZ) kompozitleri, yüksek mukavemet, sertlik, tokluk ve aşınma direnci gibi olağanüstü mekanik özellikleri nedeniyle birçok endüstriyel alanda yaygın olarak kullanılan çekici bir yapısal seramik olarak karşımıza çıkmaktadır. Bu özellikler, ZrO_2 fazının dışarıdan uygulanan stres tarafından tetiklenmesi ile tetragonal fazdan monoklinik faza dönüşümünden etkilenmektedir. ATZ kompozitlerinde sinterleme işlemi sırasında oluşan kalıntı gerilim ile oluşan bu faz dönüşüm, mikro yapı tasarımı ile kontrol edilebilmektedir [12].

Al_2O_3 içeren seramikler, mükemmel mekanik performansına bağlı olarak en yaygın kullanılan yapısal seramiklerden birisidir. Ancak düşük kırılma tokluğu, mühendislikte geniş uygulama alanını sınırlamaktadır. Bu noktada, birçok araştırmacının konu üzerinde iyileştirici yöntemler sunduğu bilinmektedir. Çatlak ucu çevresindeki alanlarda elastik olmayan tahribat nedeniyle, Al_2O_3 seramiklerinin kırılma tokluğunu geliştirmek için stresle tetiklenmiş yarı-kararlı t-ZrO_2'nin t→m dönüşümünü kullanan faz dönüşüm toklaşması, burada geleneksel ve etkili bir yöntem olarak dikkat çekmektedir [13].

Saf ZrO_2'deki martensitik dönüşüm sırasında fazın neden olduğu hacimsel değişim (%4'ün üzerinde) nedeniyle, kararlı sinterlenmiş ZrO_2 seramiklerini elde etmek zordur. Böylece ZrO_2'ye 3 mol % itriyum oksit gibi az miktarda katkı elementinin ikame edilmesiyle, oda sıcaklığında tetragonal faz (3Y-TZP; tetragonal zirkonya polikristalin) kararlaştırılmış olur. Az miktarda Al_2O_3 parçacıkları içeren ZrO_2; yani alümina ile toklaştırılmış zirkonya (ATZ) kompoziti, Al_2O_3'ün yüksek mukavemeti, sertliği ve kimyasal kararlılığı ile tokluk ve biyouyumluluk gibi dikkate değer mekanik özelliklerin bir kombinasyonunu sergiler. Bu ATZ kompoziti, aşınmaya ve korozyona dirençli malzemeler gerektiren birçok endüstriyel parçalarda yaygın kullanılan çekici bir yapısal seramiktir. Ayrıca, ATZ kompozitleri son zamanlarda biyouyumlulukları ve estetik, fiziksel ve mekanik özellikleri nedeniyle ortopedik cerrahi, diş hekimliği ve biyomedikal implantlarda (ortopedik kalça protezleri, endoosseöz implantlar ve seramik kronlar gibi) uygulama için talep görmektedir [12].

ATZ kompozitlerinin mekanik özellikleri paslanmaz çelikler ile karşılaştırılabilir. Ancak ATZ metalik malzemelere göre daha düşük tokluk nedeniyle kırılgandır. Yüzey taşlama işlemi ve nemli ortamda yaşlanma, ATZ kompozitinin özelliklerini bozabilir. ATZ ile ilişkili bu dezavantajlar, ZrO_2 matrisinin tane boyutu ve matris içindeki Al_2O_3'ün parçacık boyutunu içeren mikro yapı özelliklerinin tasarlanması ve stabilize ZrO_2'de gözlemlenen faz dönüşüm toklaşmasının maksimuma çıkarılmasıyla azaltılabilir. Tane büyümesi kontrol edildiğinde, faz dönüşümünün (t→m) daha az olduğu bilinmektedir. Ayrıca ZrO_2'nin tane boyutu faz dönüşümünü etkileyen önemli bir faktördür. Bu nedenle ZrO_2'nin faz dönüşümünü sınırlandırmak için tane büyümesini optimize etmek önemlidir. Kompozitteki ZrO_2 matrisinin kalıntı stresi, stresle tetiklenmiş faz dönüşümü için çok önemlidir. Çünkü bu durum, çatlak tarafından absorbe edilen stresle ilişkilidir. Özellikle ATZ kompozitlerindeki artık gerilmeler, ZrO_2 ve Al_2O_3'ün çekme ve basmaya maruz kalmasına bağlı olarak, ATZ bileşenlerinin (ZrO_2 matrisi ve Al_2O_3 parçacıkları) elastik özellik uyumsuzluğu ve farklı termal genleşme katsayıları nedeniyle yüksek sıcaklıkta sinterleme sonrasında soğutma işlemi sırasında ortaya çıkabilir. Bununla birlikte, ATZ kompozitlerinin yüksek sıcaklıklarda sinterlenmesinden sonra soğuma hızının kontrol edilmesi ile bu kalıntı gerilmeler kontrol edilebilmektedir [12].

Yapılan bir çalışmada [12], 1550°C'de ATZ kompozitleri sinterlendikten sonra farklı soğutma hızının mekanik özellikleri, mikroyapısal gelişimine ve matris fazının kalıntı gerilimine etkisi araştırılmıştır. ATZ kompozitlerinin mekanik özellikleri özellikle de kırılma tokluğu, yüksek sıcaklıklarda sinterleme sonrası soğutma işlemi sırasında oluşan kalıntı gerilmelere bağlı olduğu belirtilmiştir [12].

En yaygın kullanılan seramik biyomalzemeler mükemmel biyouyumluluklarından dolayı Al_2O_3 ve ZrO_2'dir. Al_2O_3'ün ana avantajları yüksek sertliği ve aşınma direncidir. ZrO_2 ise daha düşük Young modülünün yanı sıra daha yüksek mukavemet ve kırılma tokluğu sergiler. Diş implantları için seramik bileşenler geliştirmek amacıyla, sinterleme sıcaklığı, sinterleme süresi ve Al_2O_3 içeriğinin ZrO_2–Al_2O_3 kompozitlerinin mekanik özellikleri ve sitotoksisite üzerindeki etkisi araştırılmıştır. Bu amaçla 3 mol % Y_2O_3 içeren t-ZrO_2 seramikleri değerlendirilmiştir [14].

Al_2O_3 miktarının artması ile birlikte kompozit malzemelerin sertliğinde lineer bir artış gözlemlenmiştir. Ağırlıkça %30 oranında Al_2O_3 ilavesi ile sertlik 1600 HV değerine ulaşmıştır. Öte yandan, kompozitlerin yaklaşık 8 MPa.$m^{1/2}$ olan kırılma tokluğu Al_2O_3 içeriğinden etkilenmemiştir. Görünüşe göre, düşük t-ZrO_2 içerikleri, ZrO_2 matrisi ile Al_2O_3 taneleri arasındaki termal uyumsuzluktan kaynaklanan gerilmeler tarafından telafi edilmektedir. Ağırlıkça %20 Al_2O_3 içeren ve 1600°C'de 120 dakika sinterlenen numunelerin eğilme dayanımı 690 MPa'a yakın olup, Young modülü 200 GPa'dır. Ayrıca, biyouyumluluk ön testi, ZrO_2-Al_2O_3 kompozit malzemenin sitotoksik olmayan olarak sınıflandırılabileceğini ve bu nedenle implant bileşenleri olarak olası uygulamalar için büyük potansiyele sahip olduğunu göstermiştir. Bu çalışmada, ZrO_2-Al_2O_3 kompozitinin estetik özelliklerinin yanı sıra mükemmel mekanik özellikleri ve biyouyumluluğu nedeniyle, dental implant uygulamalarında biyoseramik malzeme olarak kullanılabileceği gösterilmiştir [14].

Upadhyaya ve arkadaşlarının yapmış olduğu bir çalışmada, 3Y-TZP matris fazı için tane büyümesini engelleme potansiyeli gösteren Al_2O_3 dispersiyonları kullanılmıştır [15]. Tek fazlı seramik-seramik kompozit sistemlerin toz prosesi kritik bir adımdır. Küçük tane boyutlu partikül takviyelerinin matris fazında dağılımı için sentez gerçekleştirilmiştir. Mekanik alaşımlama, çözeltilerin buharlaştırılarak ayrıştırılması, birlikte çöktürme ve sol-jel vb. gibi çeşitli yöntemler ile çalışılmıştır. Mevcut çalışmada, yaş kimyasal metot olan birlikte çöktürme ile üretilen, iki gelişen fazın karşılıklı etkileşimi anlatılmıştır. 3Y-TZP ve Al_2O_3 için kristalleşme davranışı XRD analiz ile incelenmiştir. TG-DTA ve XRD analizleri, kristalleşmenin Al_2O_3 takviyesi ile engellendiğini ortaya koymuştur [15].

Basu ve arkadaşları [16], ZrO_2-Al_2O_3 kompozitlerini üretmek amacıyla, ağırlıkça %20 (hacimce %28) Al içeren itriyum oksit ile stabilize edilmiş tetragonal zirkonya (Y-TZP) polikristallerini kullanmışlardır. Kompozitler (%28 hacim içerikli) Al_2O_3 ile 1450°C'de 1 saat süreyle vakumda sıcak presleme yoluyla üretilmiştir. Mikroyapı ve mekanik özellikler ticari ZrO_2-%20 Al_2O_3 seramiği ile de karşılaştırılmıştır. Elde edilen toklukta gözlenen farklılık, itriyum oksit içeriği ile dağılımı ve Al_2O_3 partiküllerinden kaynaklanan kalıntı gerilimler nedeniyle açıklanmıştır. Karıştırma metodu ile oluşturulan homojen olmayan itriyum (Y) dağılımı ve azaltılmış toplam itriyum oksit içeriği ile yeni geliştirilen kompozitlerin tokluk değeri ~10 $MPa.m^{1/2}$'a kadar artış göstermiştir. Böylelikle ticari ZrO_2'nin, ağırlıkça %20 Al_2O_3 içeren seramiklerden iki kat daha fazla tokluk değerine sahip olduğu görülmüştür. Araştırma sonuçlarına dayanarak, TZP-Al_2O_3 kompozitlerinin tokluğunu uygun değerlere getirmek için basit bir yaklaşım önerilmiştir [16]. Dönüşüm toklaşmasının, ana toklaşma mekanizması olduğu gözlemlenmiştir. Dönüşüm sıcaklığının ZrO_2'nin tane boyutunun artmasına bağlı olarak artış göstereceği, baskılanmış t-ZrO_2'nin dönüşüm davranışı ve kararlılığın tane boyutuna bağlı olduğu, yüzey ve gerinim enerjisi, kimyasal serbest enerji ve matriste monoklinik fazın çekirdekleşme zorluğu açıklanmıştır. ZrO_2 matrisinin mükemmel tokluğu korunurken, Y-TZP/Al_2O_3 kompozitlerinde sertlik ise önemli ölçüde artmıştır. Kompozitlerde dönüşüm toklaşmasının artışına katkıda bulunan diğer mikroyapısal değişkenler, mekanik karıştırma ile üretilen kompozitlerin mikroyapısında geniş ve homojen olmayan bir itriyum oksit dağılımının olmasıdır.

ZrO_2, Al_2O_3 ve Al_2O_3-ZrO_2 (ATZ) kompozitleri farklı teknikleri optimize etmek ve değerlendirmek için kullanılmaktadır. Bu malzemeler biyouyumluluk, mukavemet, yorulma ve aşınma direnci özelliklerinden dolayı biyomedikal endüstri için çok caziptir. Diş, protez ve implant endüstrisi, eklemeli imalat (Eİ) teknolojisinin odak noktalarından üçüdür. Işığa duyarlı çamur süspansiyonların geliştirilmesi, 3D baskı sırasında en önemli noktalardan biridir ve bu nedenle, mikro yapıda iyi bir homojenlik sağlamak ve genel kusurları azaltmak için kolloidal prosesin kullanılması gereklidir. Son zamanlarda bazı araştırmacılar, katı madde içeriği, çözücü, dağıtıcı vb. gibi farklı parametrelere dikkat çekerek çamur süspansiyonların gelişimine odaklanmışlardır. Borlaf ve arkadaşları tarafından yapılan çalışmada, litografi esaslı seramik üretimi (LCM) ve dijital ışık prosesi (DLP) tekniğinde UV kürlenebilir süspansiyonların geliştirilmesi için bir ve iki adımda uygulanan proses sonuçlarının karşılaştırmaları yapılmıştır. Sinterlenmiş bünyelerde %99 civarında ortalama yoğunluk değerleri ile birlikte mikro gözenekler tespit edilmiştir. Her iki yöntem ile benzer özelliklere sahip ZrO_2 numuneleri üretilmiştir. Tek adımda hazırlanan UV takviyeli süspansiyondan hazırlanan ATZ için 781 MPa eğme mukavemeti değerine sahipken, iki adımda hazırlanan numunelerde delaminasyon oluştuğu belirtilmiştir [17].

1.2. Zirkonya (ZrO_2)-Silisyum Karbür (SiC) Kompozitleri

Dönüşümle toklaştırılmış ZrO_2 sisteminde, sadece dönüşümle toklaştırma yoluyla hem mukavemeti hem de tokluğu iyileştirmenin zor olduğu yapılan çalışmalarda belirtilmiştir. Bu mükemmel özellikler, sadece ortam sıcaklığında elde edilen tetragonal (t-ZrO_2) fazdan monoklinik (m-ZrO_2) faza stresle tetiklenmiş faz dönüşümünden kaynaklanmaktadır. Bu özellikler artan sıcaklıkla önemli ölçüde azalmaktadır. Çünkü daha yüksek sıcaklıklarda t-ZrO_2 faz kararlılığının artmasıyla t-ZrO_2'den m-ZrO_2'ye dönüşüm toklaşması etkisi azalır. Ayrıca, düşük sıcaklıklarda, yaklaşık 200°C'de tavlama esnasında da mekanik özellikleri bozulur [18].

Kompozit tekniği ve özellikleri iyileştirmek için çeşitli yöntemler uygulanmaktadır. Visker, levha, fiber veya partikül gibi ikincil takviye fazlarının matris içinde dağıtıldığı kompozit tekniği en etkili yöntemlerden biridir ve yaygın olarak kullanılmaktadır [19]. Son araştırmalar, matris taneleri içinde veya tane sınırlarında nano boyutlu partikül içeren seramik kompozitlerin (nanokompozitler olarak adlandırılır) yüksek sıcaklıklarda bile mükemmel mekanik özelliklere sahip olduğunu bildirmiştir. Matris malzemesi ve takviye arasındaki termal genleşme katsayılarının (CTE) uyumsuzluğuna dayanan artık gerilmeler ve dağıtılan faz tarafından yüksek sıcaklıklarda çatlak sapması ve tane sınırı kaymasının engellenmesi sebep olarak gösterilmiştir. Bu nedenle nanokompozit teknikleri 3 mol % Y_2O_3 katkılı ZrO_2 (3Y-TZP) için uygulanmış ve hem mukavemeti hem de tokluğu artırmak için 3Y-TZP/SiC nanokompozitleri üretilmiştir. SiC partikülü, 3Y-TZP'den çok daha düşük termal genleşme katsayısına, yüksek Young modülüne ve yüksek sıcaklıklarda mükemmel mekanik özelliklere sahip olduğu için bu çalışmada ikinci faz olarak kullanılmıştır. Ayrıca, düşük ve yüksek sıcaklıklarda ısıl işlem ile mekanik özelliklerin azalmasının yanı sıra, termal iletkenlik ve termal kararlılıkta da iyileşmeler beklenmektedir [18]. Bamba ve arkadaşları tarafından, Y-TZP/SiC nanokompozitleri sıcak presleme kullanılarak başarılı bir şekilde üretilmiştir. Nano-kompozitlerin mikroyapısı ve mekanik özellikleri değerlendirilmiş ve SiC partikülünün 3Y-TZP'nin özellikleri üzerindeki etkileri araştırılmıştır. SiC partikülü yoğunlaşma ve tane büyümesini engellemiş ve böylece nanokompozitler ince ve homojen bir mikro yapıya sahip olmuştur [18]. Ding ve arkadaşları, hacimce %20 'ye kadar SiC partikülleri içeren, basınçsız sinterlenmiş ve ardından sıcak izostatik preslenmiş Y-TZP seramiklerin mikroyapısı ve mekanik özelliklerini incelemiştir. ZrO_2 matrisinin tane büyümesi SiC ilavelerinden önemli ölçüde etkilenmemiştir. Sertlik, Young modülü ve kırılma tokluğu (K_{IC}) değerinin arttığı ve eğilme mukavemetinin (σ_b) artan SiC içeriği ile azaldığı bulunmuştur. Maksimum K_{IC} ve σ_b sırasıyla 7-8 MPa.$m^{1/2}$ ve 849 MPa hesaplanmıştır. SiC ilaveleri, çatlak boyutlarının artmasına ve düşük sıcaklıkta yaşlandırma sırasında t-ZrO_2'nin termal kararlılığının azalmasına neden olmuştur. Baskın toklaştırma mekanizması mikro çatlak olarak belirlenmiştir. Stres kaynaklı faz dönüşümü yalnızca ikincil bir rol oynamıştır [20].

SiC-visker takviyeli 3Y-TZP (SiCw/3Y-TZP) kompozitlerinin döngüsel yorulma çatlak büyümesinin ilk incelemesi Zhan ve arkadaşları tarafından [21] gerçekleştirilmiştir. Visker takviyeli bir seramik üzerinde elde edilen yeni deneysel sonuçlar, toklaştırılmış seramiklerin döngüsel yorulma davranışı hakkındaki bilgi birikimine katkıda bulunacaktır. Deneyler, sabit tepe yükü koşulu altında döngüsel olarak gerilim altında dört nokta eğme numuneleri kullanılarak gerçekleştirilmiştir. Dört noktalı eğme numuneleri kullanılarak yapılan uzun çatlak deneylerine dayanarak, döngüsel yorulma çatlak büyüme oranlarının (10^{-10}- 10^{-5} (m /döngü) aralığında) maksimum gerilme yoğunluğu faktörüne ve yük oranına duyarlı olduğu bulunmuştur. Diğer seramik malzemelere benzer şekilde, uzun çatlak yorulma eşiğinin (ΔK_{TH}), indentasyon kırılma tokluğunun (Kıc) %45'i mertebesinde olduğu ve artan kırılma tokluğu ile arttığı bulunmuştur. Çalışma ile SiCw/Y-TZP kompozitlerinde yorulma çatlak büyümesinin mekanik olarak indüklenen döngüsel bir süreç olduğu gösterilmiştir. Ayrıca, sonuçlar hem tokluğun hem de çatlak büyüme direncinin visker içeriğine bağlı olduğunu göstermektedir. Kompozitlerde yorulma çatlağı büyümesinin mikroplastikle ilişkili bir mekanizma izlediği öne sürülmektedir. Mikro çatlama, mikroplastisite için makul bir genel açıklama olarak kabul edilmektedir [21].

1.3. Zirkonya (ZrO_2)-Titanyum Diborür (TiB_2) Kompozitleri

Uzun yıllar boyunca titanyum diborür (TiB_2) hafif zırh için ilgi çekici malzemelerden biri olmuştur. Bu bileşik nozul, conta, kesici takım, kalıp ve aşınmaya dayanıklı ürünler için geniş ticari uygulamalar içermektedir. TiB_2 ayrıca, erimiş alüminyuma karşı mükemmel ıslanabilirliği ve korozyon direnci nedeniyle alüminyum üretiminde elektrot yapımında potansiyel uygulama alanı bulmuştur [5,23].

TiB_2 mükemmel bir sertliğe (1800-2700 kg/mm^2) sahip olmasına rağmen, ancak kırılma tokluğu çok yüksek olmamakla (5-7 MPa.$m^{1/2}$) birlikte, ayrıca orta düzeyde de bir eğilme mukavemetine sahiptir. Bu nedenle, TZP-TiB_2 kompozitlerinin tribolojik uygulamalar için umut verici kompozit malzemeler olduğu düşünülmektedir. TiB_2-ZrO_2 kompozitinin bir başka avantajı da, özellikle kübik fazda ilave edilecek ZrO_2 durumunda, termal genleşme katsayısı uyumsuzluğunun düşük olmasıdır. Oda sıcaklığında, TiB_2 ve c- ZrO_2 için termal genleşme katsayıları sırasıyla 7.19x10^6 ve 8.0x10^6 K^{-1} 'dir. Yapılan çalışmada [5], ZrO_2 ve itriyum oksit ile yakılarak sentezlenen TiB_2'nin mikroyapı görüntülerinde, gelişmiş TiB_2 kristallerinin ZrO_2 fazına iyi bağlandığı gözlemlenmiştir. Ortalama küçük partikül boyutuna sahip kompozit tozlar elde etmek için, yanma sıcaklığının azaltılması gerektiği belirtilmiştir. Bu durumda, çeşitli miktarlarda ZrO_2 eklenerek farklı bileşimlere sahip ürünler elde edilmektedir. Şaşırtıcı bir şekilde, yapılan deneylerde oluşan TiB_2 kristallerinin, yanma sıcaklığının ve ortalama parçacık boyutunun geniş aralıkta (ağırlıkça %35'e kadar) ZrO_2 ilavesinden etkilenmediğini göstermiştir. Ancak seyreltme, yanma cephesi hızını etkilemiştir. ZrO_2'yi tam olarak stabilize etmek için, yeterli miktarda itriyum oksit reaksiyona giren karışıma ilave edilmiştir. Eklenen itriyum oksit miktarına bağlı olarak, tetragonal $((ZrO_2)_{0.91}(Y_2O_3)_{0.09})_{0.917}$ veya kübik oksitler $((ZrO_2)_{0.88}(Y_2O_3)_{0.12})_{0.893}$ elde edilmiştir. ZrO_2 ilaveli, titanyum ve bor tozlarının yakma tekniği (CS) ile doğrudan sentezlenerek kompozitlerin üretimi gerçekleştirilmiştir [5].

Parçacık takviyeli seramik matrisli kompozitlerde, ikincil bir fazın varlığı genellikle termal genleşme katsayısı uyumsuzluğu nedeniyle kalıntı stres oluşturur. Artık gerilmenin büyüklüğü, farklı fazlar arasındaki E-modülü uyumsuzluğuna da bağlıdır. Yapılan bir çalışmada, artık gerilimin ve farklı ZrO_2 başlangıç tozlarının ZrO_2-TiB_2 kompozitlerindeki tetragonal ZrO_2'nin dönüşümü ve tokluğu üzerindeki etkisi araştırılmıştır [22]. Aynı zamanda, çalışmalarda yüksek toklukta malzemeler geliştirmek için TiB_2 gibi çeşitli kırılgan matrislere t-ZrO_2 fazının ilavesi de gerçekleştirilmiştir. Ancak TiB_2 gibi sert bir faza sahip, Y-TZP kompozitlerinin tokluğunu kontrol eden farklı mikroyapısal değişkenler ile ilgili kapsamlı bir çalışma yapılmamıştır.

ZrO_2 matrisindeki katkılama dağılımının, Y-TZP seramiklerinin tokluğu üzerinde büyük bir etkisi olduğu gözlemlenmiştir. Çalışmada, ticari olarak temin edilebilen farklı Y_2O_3 ile kararlaştırılmış ZrO_2 tozlarının, hacimce %30 TiB_2 katkılı ZrO_2 kompozitlerinin mekanik özellikleri üzerindeki etkisi açıklanmıştır. ZrO_2 başlangıç tozlarının yapısal farklılıkları ve kalıntı stresin, TiB_2 kompozitlerinin mekanik özellikleri üzerindeki etkisi bildirilmiştir. Ayrıca ZrO_2 matrisindeki itriyum dağılımının, Y-TZP bazlı kompozitlerin tokluğuna etkisi açıklığa kavuşturulmuştur. Hacimce %30 TiB_2 içeren tam yoğun t-ZrO_2 kompozitleri 1450°C'de vakumda sıcak presleme ile üretilebilmiştir. Kompozitlerde, kırılma tokluğu 10 $MPa.m^{1/2}$ ve sertlik değerleri 13 GPa olarak tespit edilmiştir. ZrO_2-TiB_2 kompozitlerinin ZrO_2 matrisindeki kalıntı çekme gerilmesinin, t-ZrO_2 matrisinin dönüşebilirliği ve kompozitlerin genel tokluğu üzerinde önemli bir etkiye sahip olduğu bulunmuştur.

Kalıntı streslerin faz dönüşümü üzerine etkileri, itriyum oksit ile kaplı ZrO_2 tozları ile kıyaslandığında, birlikte çöktürme yöntemi ile üretilmiş ZrO_2 tozlarında daha belirgin olduğu saptanmıştır. TiB_2 fazı tarafından oluşan çatlak sapması, aktif ve önemli bir toklaştırma mekanizması olarak tespit edilmiştir. Tetragonal fazın tane boyutunun elde edilen tokluk üzerinde herhangi bir etkisi yok gibi görünse de, ZrO_2 matrisindeki itriyum dağılımı, t-ZrO_2 fazının dönüşebilirliğini ve dönüşüm tokluğunu kontrol etmede ek bir değişken olarak tanımlanmıştır. Bu nedenle, ZrO_2 matrisindeki kalıntı gerilmelerle birlikte bu faktörün, Y-TZP içeren dönüşümle toklaştırılmış malzemelerin geliştirilmesinde tasarım parametreleri olarak dikkate alınması gerektiği ifade edilmiştir [22].

Basu ve arkadaşları tarafından [23], yüksek tokluğa sahip itriyum oksit ile kararlaştırılmış tetragonal zirkonya polikristalin (Y-TZP) kompozitlerini geliştirmek için sert TiB_2 parçacıkları ile takviye yapılmıştır. Deneysel sonuçlar, hacimce %30 TiB_2 içeren tam yoğun Y-TZP kompozitlerinin 13 GPa sertlik değerinde, 1280 MPa'a kadar yüksek mukavemet ve 1450°C'de vakumda sıcak presleme ile 10 $MPa.m^{1/2}$'a kadar mükemmel bir indentasyon kırılma tokluğu ile elde edilebileceğini ortaya koymuştur. Saf monoklinik ve 3 mol % Y_2O_3 ile çöktürülmüş ZrO_2 başlangıç tozlarının karıştırılmasıyla elde edilen toplam 2,5 mol % itriyum oksit içeriğine sahip bir ZrO_2 matrisi için optimum kompozit tokluğu elde edilmiştir. Geleneksel 3 mol % itriyum oksit ile çöktürülmüş ZrO_2 tozları ile karşılaştırıldığında, 3 mol % itriyum oksit kaplı ZrO_2-TiB_2 (70/30) kompozitlerinde elde edilen üstün tokluğun, ZrO_2 başlangıç tozundaki %3 mol itriyum oksit stabilizatör dağılımı ile elde edildiği vurgulanmıştır. TiB_2 katkılı %3 mol itriyum oksit içeren Y-TZP ile 3 mol % Y-TZP ve m- ZrO_2 toz karışımına sahip monolitik fromlarda tamamen tetragonal faz elde edilirken, 2 mol % itriyum oksit içeren TiB_2 katkılı kompozitlerde önemli oranda tetragonalden monoklinik faza dönüşüm (m-ZrO_2 %67,4) gözlemlenmiştir. Ayrıca, 2,5 ve 3 mol % itriyum oksit ile kararlaştırılan ZrO_2-TiB_2 (70/30) kompozitlerinde t-ZrO_2 fazının dönüşebilirliği, saf ZrO_2 matris malzemelerinden daha yüksektir. Bu durum, TiB_2 ilavesinin t-ZrO_2 fazına dönüşebilirliğini artırdığını göstermektedir. Aynı zamanda böylesi seramiklerde baskın toklaştırma mekanizmasının dönüşüm toklaşması olduğu da aşikardır. Kompozitlerin genel tokluğuna yönelik dönüşüm toklaşmasının büyük ölçüde ZrO_2 matris bileşimine ve TiB_2 katkısı ile meydan gelen artık gerilmelere bağlı olduğu oldukça açıktır. TiB_2 ilavesi, ZrO_2 matrisinde t-ZrO_2'ya dönüşebilirliğini artıran termal artık çekme gerilmelerine neden olur. Dönüşüm toklaşmasının 2,5 ve 3 mol % itriyum oksit içeren ZrO_2-TiB_2 kompozitlerinde ana mekanizma olduğu tespit edilirken, çatlak sapmasının da aktif olduğu gözlemlenmiştir [23].

TiB_2'nin yüksek sertliğe sahip birkaç borürden biri olarak, yüksek sıcaklıklarda ZrO_2 ile kimyasal olarak uyumlu olması beklenmektedir. Hacimce %50'den daha az TiB_2 içeren, Y-TZP bakımından zengin kompozitler hakkındaki mevcut bilgiler literatürde sınırlıdır. 1,94 mol % Y_2O_3 ile kararlaştırılmış ZrO_2 nanotozlardan üretilen, ağırlıkça %80'den fazla ZrO_2 içeren ZrO_2-TiB_2 kompoziti 1500°C'de hazırlanmıştır. Saf ZrO_2 ve TiB_2'den oluşan kompozitler (TiB_2- ağırlıkça %30 ZrO_2) için 800 MPa'dan daha yüksek mukavemet ve 7-9 $MPa.m^{1/2}$ tokluk değeri, yüksek saflıkta 1800-1900°C'de sinterlenmiş numunelerden elde edilmiştir. m-ZrO_2 ile hazırlanan TiB_2-ZrO_2 sistemindeki deneysel sonuçların, tane boyutu incelmesinin yanı sıra Ti'nin ZrO_2'ye difüzyonu ve bir $(Ti,Zr)B_2$ katı çözeltisinin oluşumu sonucunda t-ZrO_2 fazının kısmi bir stabilizasyonunun gerçekleşmesi ile ilişkili olduğunu açıklamışlardır [24].

Deneysel sonuçlardan Ti'nin her zaman ZrO_2 tanelerinde, TiB_2 tanelerinde de her zaman Zr konsantrasyonunun bulunup bulunmayacağı konusunda kesin sonucuna varmanın mümkün olmadığı yapılan benzer çalışmalardan gözlemlenmiştir. Bu durum Sarbu ve arkadaşları tarafından yapılan çalışmada, ZrO_2/TiB_2 (70/30) kompozit numunelerinin EDS ile yapılan ilk mikrokompozisyon incelemesi sırasında da ortaya çıkmıştır. Ti'nin, TiB_2 taneciklerinden ZrO_2 taneciklerine difüzyonunun enerji dağılımlı x-ışını spektroskopisi (EDS) mikroanaliz verilerine dayanarak kesin olarak tespit edilemeyeceği kanaatine varılmıştır. Bu nedenle, X-ışını floresans tekniği yerine mevcut çalışmada yalnızca elektron enerji kaybı spektroskopisi (EELS) kullanılmıştır. ZrO_2/TiB_2 (70/30) kompozitleri için detaylı mikroyapı incelemesi, Y-TZP matrisine hacimce %30 TiB_2 eklenmesinin kompozitin sertliğinde önemli ölçüde iyileşme sağlamadığını gösteren deneysel sonuçların uygun bir şekilde açıklanmaması nedeniyle gerçekleştirilmiştir. Ti, ne ZrO_2 taneciklerinin içinde nede ZrO_2 taneleri arasındaki üçlü bağlantıları dolduran amorf taneler arası faz içeren bölgelerde tespit edilmemiştir. Ti yalnızca büyük titanyum borür taneleri ile BN aglomeratı arasındaki amorf fazda tespit edilmiştir. Zr hiçbir zaman amorf tanecikler arası fazda veya titanyum borür tanelerinin içinde tespit edilmemiştir. Literatürde önerildiği gibi, $(Ti,Zr)B_2$ katı çözeltisinin oluşumunun yanı sıra Ti interdifüzyonu ile t-ZrO_2 fazının stabilizasyonu, 1450°C'de sıcak preslenen ZrO_2-TiB_2 kompozitleri için hariç tutulmaktadır [24].

1.4. Zirkonya (ZrO_2)-Zirkonyum Diborür (ZrB_2) Kompozitleri

IVB grubu metal borürlerinden olan zirkonyum borürler, ultra yüksek sıcaklık malzemesi olarak birçok alanda kullanım yeri bulmakta olup, ileri teknoloji refrakter seramik malzemeler olarak adlandırılırlar [25]. Güçlü kovalent bağ nedeniyle, geçiş metal borürleri yüksek ergime noktası (3245°C), yüksek sertlik, yüksek elastik modül, elektriksel ve termal iletkenliğin (60-130 W/m.K) yanı sıra, ergimiş metallere ve bazik olmayan cüruflara karşı olan inert kimyasal davranışları ve üstün termal şok direnci olan bir malzemedir [26-27]. Zr-B ikili faz diyagramına göre, zirkonyum borür fazları olarak, ZrB (927°C'ye kadar), ZrB_{12} (1720-2030°C aralığında) ve ZrB_2 (3227°C'ye kadar) bileşikleri mevcuttur ve bunlar arasında en kararlı faz ZrB_2'dir [25].

ZrB_2'nin süperiletkenlik davranışları literatürde incelenmiş ve güncel olarak da incelenmeye devam etmektedir. Çeşitli oksit ya da karbür katkıları ile geliştirilen zirkonyum borür esaslı kompozit malzemeler (ZrB_2-ZrC, ZrB_2-ZrO_2, ZrB_2-SiC, ZrB_2-SiO_2, ZrB_2-B_4C, vb.) mükemmel fiziksel ve mekanik özellikler göstermektedir [25].

Bununla birlikte, düşük kırılma tokluğu ve mukavemeti, zayıf sinterlenebilirlik ile birleştiğinde, monolitik borürlerin yapısal malzemeler olarak uygulamasını sınırlamaktadır [26]. Literatürde, 3 mol % itriyum oksit içeren ZrO_2 ve ZrB_2 kompozitler ile ilgili olarak Basu ve arkadaşları [26] tarafından, hacimce %30 ZrB_2 içeren itriyum oksit ile kararlaştırılmış Y-TZP kompozitleri, 1450°C'de 1 saat boyunca vakumda sıcak presleme ile hazırlanmıştır. Kompozit üretimi için farklı ticari ZrO_2 başlangıç tozlarının yanı sıra, birlikte çöktürme yöntemi ile üretilen ZrO_2 toz karışımları kullanılmıştır. Elde edilen kompozitlerin mekanik özelliklerinde ölçülen farklılıkların mikroyapı, ZrB_2 katkısından kaynaklanan kalıntı stres gerilmeler, kararlaştırıcı içeriği ve dağılımı nedeniyle meydana geldiği açıklanmıştır. Stabilizatör içeriği ve dağılımı önemli olurken, ZrO_2 matrisindeki kalıntı gerilmenin t-ZrO_2'nin dönüşebilirliğini etkileyen önemli bir ek faktör olduğu bulunmuştur. ZrB_2 fazı tarafından çatlak sapması, kompozitlerde aktif bir toklaştırma mekanizması olarak tanımlanmıştır. Mekanik özellikleri incelendiğinde, 9MPa.$m^{1/2}$ kırılma tokluğu ve 13 GPa sertlik değeri elde edilmiştir. İtriyum oksit kaplı tozların kullanımı ile 10 MPa.$m^{1/2}$ maksimum kompozit tokluğu ayrıca sağlanabildiği kaydedilmiştir. ZrO_2-ZrB_2 kompozitlerinin tokluğunu optimize etmek için basit bir 'toz karıştırma' yönteminin etkili olduğu bulunmuştur. Mevcut çalışmada matrisin tokluğu, 2 mol % Y içeriği ile en yüksek değer elde edilirken, kompozitlerin tokluğunun 2,5 mol % Y kullanıldığında maksimum olduğu ve daha sonra itriyum seviyesinde azalma ile birlikte tokluğun azaldığı bulunmuştur. Bu durum, ZrO_2 esaslı kompozitlerin geliştirilmesinde son derece önemlidir [26]. Burada dönüşüm toklaşması, optimize edilmiş kompozitlerde baskın toklaşma mekanizması olarak gözlemlenmiştir. ZrO_2-ZrB_2 kompozitlerinin ZrO_2 matrisindeki kalıntı çekme gerilmesinin, t-ZrO_2 matrisinin dönüşebilirliğini ve kompozitlerin dönüşüm tokluğu üzerinde önemli bir etkiye sahip olduğu bulunmuştur. Deneysel sonuçlar, kalıntı gerilmenin kompozitlerin dönüşüm tokluğunun optimize edilmesinde dikkate alınması gerektiğini açıkça göstermektedir. ZrO_2 matrisindeki genel itriyum içeriği ve dağılımı, t- ZrO_2 dönüştürülebilirliğini ve buna eşlik eden dönüşüm tokluğunu kontrol etmede kilit faktörler olarak tanımlanmıştır. Dolayısıyla tüm bu faktörler, Y-TZP bazlı dönüşüm tokluğu kazandırılmış malzemelerin geliştirilmesinde önemli tasarım parametreleri olarak dikkate alınmalıdır. Ayrıca, ZrB_2 fazı tarafından meydana gelen çatlak sapması aktif ve ek bir toklaştırma mekanizması olarak tanımlanmıştır.

Tribolojik uygulamalar için, yüksek toklukta ve sertlikte seramiklerin geliştirilmesi her zaman büyük bir itici güç olmuştur. Bu nedenle tribolojik özellikleri değerlendirmek ve anlamak için kapsamlı araştırma çabaları ortaya konulmuştur. Bakshi ve arkadaşlarının yapmış olduğu çalışmada [28], argon (Ar) atmosferi altında 110 MPa basınçta 1400^{o}C'de 1 saat boyunca sinterleme-HIP işleminden sonra yoğun, hacimce %30 ZrB_2 içeren TZP kompozitlerinin üretilebileceği bildirilmiştir. İnce tane boyutunda ZrB_2 takviyeleri ile Y-TZP malzemelerin mekanik özelliklerini önemli ölçüde artırdığı ve bu kompozitlerde yüksek sertlik (16 GPa) ve mükemmel tokluk (18 $MPa.m^{1/2}$) gibi mekanik özellikler tespit edilmiştir. Kompozitlerin sürtünme ve aşınma özellikleri ise malzeme parametrelerine (matris ile takviye fazın içeriği ve hacmi, sertlik, tokluk vb.) ve çalışma parametrelerine (kayma hızı, yük, nem vb.) bağlıdır. Aşınma mekanizması, kayma temaslarındaki tribokimyasal reaksiyonlar tarafından kontrol altına alınmaktadır. Burada, ZrO_2 faz dönüşümünün rolü ihmal edilebilir düzeyde bulunmuştur. Tüm kompozitler, incelenen sürtünme koşulları altında çeliğe karşı düşük aşınma oranı (107-108 mm^3/Nm) sergilemektedir. Ayrıca, kompozitlerin aşınma oranı artan toklukla birlikte azalmakta ve %2 mol Y ile stabilize edilmiş ZrO_2 matrisli kompozitlerde daha yüksek aşınma direnci ölçülmüştür. Birlikte çöktürülmüş 3 mol % itriyum oksit ile stabilize edilmiş ZrO_2 kompozitlerinde nispeten daha yüksek aşınma oranı (107 mm^3/Nm) kaydedilmiştir. Bu durum, tokluğun tribolojik uygulamalar için önemli malzeme parametrelerinden biri olarak kritik bir şekilde dikkate alınması gerektiğini göstermektedir. Fenomenolojik aşınma modeli üzerine yapılan bu çalışmada, sinter-HIP olmuş ZrO_2-ZrB_2 kompozitlerinin gevrek kırılma ve şiddetli aşınmaya karşı yüksek direncinin öncelikle mükemmel kırılma tokluğundan kaynaklandığını ortaya koymaktadır [28].

Bakshi ve arkadaşları tarafından [29], sıcak izostatik pres (sinter-HIP) yöntemi kullanılarak üretilen hacimce %30 ZrB_2 partikülleri ile güçlendirilmiş sert ve tok ZrO_2 kompozitlerinin mikroyapısı ve özellikleri incelenmiştir. Sinter-HIP kompozitlerinin mikroyapısı ve mekanik özellikleri üzerine ZrO_2 matris bileşiminin (Y_2O_3 içeriği) etkisi araştırılmıştır. Tamamen yoğun sinterHIP mikroyapısında; mikron altı ZrO_2 matrisindeki ZrB_2 partiküllerinin (1-3 μm) dağılımı dikkat çekmiştir. Bu çalışmanın önemli bir sonucu, ZrO_2 bazlı kompozitlerde ilk kez mükemmel bir sertlik (20 GPa) ve tokluk (18 MPa.m$^{1/2}$) değerinin elde edilmiş olmasıdır. Kırılma yüzeyindeki m-ZrO_2 içeriği, dönüşüm toklaştırma mekanizmasının tokluk artışı için aktif bir mekanizma olduğunu göstermektedir. Ek olarak, ZrB_2 partikülleri tarafından meydana gelen çatlak sapması da kompozitin toklaşmasına katkıda bulunmuştur. İndentasyon çatlak uzunluğu ölçümlerine ve aynı zamanda ZrO_2 ve ZrB_2 için teorik elastik modül değerlerine dayanarak indentasyon tokluğu, Anstis'in formülasyonuna göre değerlendirilmiştir. Tokluk değerleri 7-18 MPa.m$^{1/2}$ gibi geniş bir aralıkta değişmektedir [29]. Tokluktaki bu büyük değişimin, ZrO_2 matrisindeki Y_2O_3 stabilizasyonundaki değişimden kaynaklanmaktadır. Ayrıca, daha düşük % mol itriyum oksit içeriğine sahip ZrO_2 matrisli kompozitler için tokluğun daha yüksek olduğu bulunmuştur.

Elde edilen tokluk değerlerinin diğer ZrO_2 içerikli kompozitler ile karşılaştırıldığında, sıcak izostatik preslenmiş ZrO_2-ZrB_2 kompozitlerinin, TiB_2 [30], Al_2O_3 [16] veya ZrB_2 [29] ile takviye edilmiş sıcak preslenmiş ZrO_2 kompozitlerinden önemli ölçüde daha yüksek tokluğa sahip olduğu, takviye içeriğinin ise hacimce %30 civarında olabileceği söylenmektedir. Taramalı elektron mikroskobu (SEM) mikroyapı görüntülerinde mikroçatlak izine rastlanılmamıştır. t-ZrO_2 fazının HIP ile sinterlenmiş mikroyapıda bulunmasına bağlı olarak, stresle tetiklenmiş dönüşüm toklaşması mekanizmasının baskın toklaştırma mekanizması olduğunu göstermektedir [29]. Basınçsız sinterleme yöntemiyle üretilen hacimce %30 ZrB_2 içeren ZrO_2-ZrB_2 kompozitlerinde [30] ise, sinterleme 1400-1600^{o}C sıcaklık aralığında Ar atmosferinde 1 saat süreyle gerçekleştirilmiştir. Çalışmada, başlangıç tozu olarak 3Y-TZP ve itriyum içermeyen m-ZrO_2 tozları kullanılmıştır. ZrO_2 matrisindeki itriyum içeriğinin yanı sıra sinterleme sıcaklığının kompozitlerin yoğunlaşması, mikroyapısı ve mekanik özellikleri üzerindeki etkisi araştırılmıştır. Deneysel sonuçlar incelendiğinde, 1400^{o}C ve 1500°C'de üretilen kompozitlerin mükemmel sertlik (12 GPa) ve kırılma tokluğu (10-15 MPa.$m^{1/2}$) değerleri elde edilmiştir. Bununla birlikte, 1600°C ve üzerindeki sıcaklıklarda sinterlemenin mekanik özellikleri olumsuz etkilediği gözlemlenmiştir.

1.5. Zirkonya (ZrO_2)-Silisyum Nitrür (Si_3N_4) Kompozitleri

Gelişmiş bir yapısal seramik olan silisyum nitrür (Si_3N_4), yüksek eğilme mukavemeti, iyi sürünme direnci ve yüksek sertlik gibi birçok mükemmel özelliğe sahiptir. Aslında, Si_3N_4 aşırı düzeydeki termal şok ve termal değişimlere dayanabilen birkaç önemli monolitik seramik malzemeden biridir. Bu ilginç özellikleri nedeniyle gaz türbini motorları, termokupl tüpleri ve ergimiş metallere yönelik potalar gibi yüksek sıcaklıktaki yapısal uygulamalar için uygun bir ileri teknoloji seramik malzemesidir. Bu özellikler temel olarak Si ve N iyonları arasında oluşan güçlü kovalent kimyasal bağlar nedeniyle ortaya çıkmaktadır. Bununla birlikte, çoğu seramik gibi, geleneksel Si_3N_4 seramiği de zayıf kırılma tokluğuna sahiptir. Bu durum da düşük hasar toleransına ve zayıf güvenilirliğe, yani küçük Weibull modülüne yol açar [31-33]. Literatür araştırması, sıcak preslenmiş Si_3N_4'ün kırılma tokluğunun 3-5 MPa.$m^{1/2}$ aralığında olduğunu ve bu değerlerin beklenen uygulamalar için kabul edilebilir bir noktada olmadığını göstermektedir [32]. Monolitik Si_3N_4 seramiklerinin işlevsel ve mekanik özelliklerini iyileştirmek için bir takviye bileşeni olarak yüksek performanslı nanolif ve nanopartiküller kullanılarak kompozit malzemeler geliştirilmeye çalışılmıştır. Takviye olarak partikül ZrO_2 ilavesinin, stres kaynaklı martensitik t→m dönüşüme ve mikro çatlak toklaştırmasına dayanan toklaştırma mekanizmalarıyla seramiklerin kırılma tokluğunu artırdığı bildirilmiştir [31]. Cain ve arkadaşları sıcak preslenmiş ZrO_2-SiAlON kompozitlerinin kırılma tokluğunu araştırmıştır. Sistemin kırılma tokluğunun ZrO_2 içeriğinin artmasıyla iyileştiği ve hacimce %30 ZrO_2 içeren SiAlON kompoziti için 7,5 MPa.$m^{1/2}$'ye ulaştığı bulunmuştur. Ayrıca, Hirano ve arkadaşları ağırlıkça %5 Y_2O_3-ZrO_2 ilavesinin sadece β-Sialon kompozitinin kırılma tokluğunu ve sertliğini iyileştirmekle kalmadığını, aynı zamanda bu bileşiğin sinterlenmesine de büyük ölçüde yardımcı olduğunu göstermiştir [31]. t-ZrO_2'nin takviye bileşeni olarak kullanılması Si_3N_4 seramiklerinin kırılma tokluğunun iyileştirilmesinde etkili olsa da, ZrO_2 bileşeni ve Si_3N_4 matrisi arasındaki yüksek sıcaklık etkileşimi, özellikle 1600°C'nin üzerindeki sıcaklıklarda sinterleme sırasında ZrN veya ZrON fazlarının oluşumuna yol açtığı gözlemlenmiştir. Si_3N_4-ZrO_2 kompozitlerinin hava atmosferinde 500°C'nin üzerindeki sıcaklıklarda, zirkonyum nitrür ve zirkonyum oksinitrür fazları kolayca oksitlenir ve kompozit gövdelerin yapısal bozulmasına yol açan %4-5'lik bir hacim artışı ile birlikte m-ZrO_2'ye dönüşür [31]. Sayyadi-Shahraki ve arkadaşları tarafından yapılan çalışmada [31], ZrO_2 içeriğinin hacimce % 0 -30 arasında değiştiği tam yoğun Si_3N_4-ZrO_2 nano-kompozitleri, 10 dakika boyunca 30 MPa basınç altında 1600°C'de kıvılcım plazma sinterleme (SPS) yoluyla üretilmiştir. Sinterlenmiş nano-kompozitlerin XRD grafikleri, ZrO_2 bileşeninin tamamının tetragonal kristal yapıda kararlı olduğunu, kıvılcım plazma sinterleme (SPS) işlemi sırasında ne m-ZrO_2 ne de istenmeyen ZrN/ZrON fazının oluşmadığını göstermiştir. t-ZrO_2 partiküllerinin Si_3N_4 matrisi içinde homojen dağılımı SEM analizi ile gözlemlenmiştir. Mekanik özellikleri değerlendirildiğinde, Si_3N_4 bazlı kompozitlerin sertliğinin 16,6 GPa'dan 13,2 GPa değerine düştüğünü, kırılma tokluğunun ise ZrO_2 içeriğinin hacimce %0'dan %30'a çıkarılmasıyla 5,8 MPa.$m^{1/2}$ 'dan 7,1 MPa.$m^{1/2}$ değerine yükseldiğini göstermiştir. Bu durum, sırasıyla β-Si_3N_4'ün yerinde oluşumuna ve stres kaynaklı t-$ZrO_2 \rightarrow$m-ZrO_2 faz dönüşümüne bağlı olmasıyla açıklanmıştır. Ayrıca Si_3N_4 seramiklerinin biyo-aktif olduğu ve kolayca osteointegre olabildiği kanıtlanmıştır [34]. ZrO_2 seramikleri üzerinde in-vitro ve in-vivo testler mutajenik veya kanserojenik etkiler için bulgu gösterilmemiştir. ZrO_2'nin biyolojik aktivitesini iyileştirmek ve mevcut biyolojik dokulara entegrasyonunu sağlamak için hidroksiapatit gibi aktif fazlarla alaşımlama, kaplamalar, yüzey lazer modifikasyonları ve tekstüre etme gibi birçok farklı işlem önerilmiştir. Hem mekanik dayanıklılığa hem de estetiğe sahip olsa da, kendine özgü biyo-kararlılığa genellikle biyolojik entegrasyon eksikliği ile sonuçlanmaktadır. Yapılan çalışmada [34], osteointegrasyonu geliştirmek amacıyla biyomedikal ZrO_2, biyolojik yanını iyileştirmek için Si_3N_4 tozu ile lazerle kaplama işlemi geliştirilmiştir. Proses, nano-kristalin/amorf silikon içinde dağılmış Si_3N_4 partikülleri ile kompozit kaplama oluşumu ile sonuçlanmıştır. Mikroskobik gözlem, tabakanın alt tabakaya yapıştığını göstermiştir. Lazer kaplama işleminin uygulanması, pürüzlülüğün artmasına neden olarak biyolojik dokularla etkileşim olasılığını ve dolayısıyla biyoaktiviteyi daha da artırmıştır. Lazer kaplama, en yüksek ergime noktalı seramikleri bile eritebilen yüksek yoğunluklu bir lazer kaynağı ve genellikle tel veya toz şeklinde bir hammaddeden oluşan güçlü ve çok yönlü bir tekniktir. Eritilen malzemeler daha sonra kaplama üretmek ve aynı zamanda hasarlı bileşenleri onarmak için kullanılabilir.

Sonuç

Bu çalışmada, ileri teknoloji seramikleri alanında çalışan araştırmacılara bir kılavuz olması açısından oksit esaslı zirkonya (ZrO_2) seramikleri göz önünde bulundurularak, ZrO_2'nin alümina (Al_2O_3), silisyum karbür (SiC), titanyum diborür (TiB_2), zirkonyum diborür (ZrB_2) ve silisyum nitrür (Si_3N_4) gibi sırasıyla oksit, karbür, borür ve nitrür grubu ileri teknoloji seramikleri ile gerçekleştirilen seramik-seramik kompozit üretimlerine örneklemelerden detaylı bir şekilde bahsedilmiştir. Burada, ilgili alanda çalışmak isteyen araştırmacılar mevcut yazın taramasını incelediklerinde, özellikle 3 mol % Y_2O_3 ile kararlı kılınmış tetragonal ZrO_2 polikristalin (3Y-TZP) matris içerisine değişen ağırlıkça ve hacimce % miktarlarda Al_2O_3, SiC, TiB_2, ZrB_2 ve Si_3N_4 takviyesi sayesinde oluşturulan 3Y-TZP/Al_2O_3, 3Y-TZP/SiC, 3Y-TZP/TiB_2, 3Y-TZP/ZrB_2 ve 3Y-TZP/Si_3N_4 kompozitlerinin hem üretim hem de fiziksel, mekanik ve tribolojik özelliklerinin istenilen uygulama alanlarına bağlı olarak nasıl uygun hale getirilebileceklerini görmeleri mümkün olabilecektir. Özellikle mekanik ve tribolojik özelliklerin ayarlanmasında, ZrO_2'nin stres kaynaklı t→m dönüşüm toklaştırması ile katkı ilavelerinin çatlak sapması gibi temel mekanizmaların etkin rol oynadığı anlaşılabilecektir. Mevcut kitap bölümünün burada bahsedilen 3Y-TZP esaslı zirkonya seramiklerinin mühendislik özelliklerinin iyileştirilmesi ve/veya geliştirilmesinde burada bahsedilen bileşiklerden farklı yeni takviye fazlarla güçlendirilmesinde öncü olacağı ve yeni kapılar açacağı değerlendirilmektedir.

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Chapter 6

Nano Reinforced Metal Matrix Composites

Adem Onat[1]

Abstract

Nano Reinforced Metal Matrix Composites (NRMMCs) combine the strength and stiffness of metals with the exceptional properties of nanoscale reinforcements, such as nanoparticles or nanofibers. This chapter will inquire into the world of nano reinforced MMCs, exploring their properties, manufacturing techniques, characterization methods, and potential applications. Furthermore, it will discuss the challenges and limitations associated with their development, providing valuable insights into the future prospects of these innovative materials.

INTRODUCTION

Nano Reinforced Metal Matrix Composites (NRMMCs) are a new class of materials that combine the high strength and stiffness of metals with the superior properties of nano-sized reinforcements. The development of NRMMCs can be traced back to the early 1990s when researchers started exploring ways to enhance the properties of metal matrices by incorporating nano-sized reinforcements. The groundbreaking discovery of carbon nanotubes in 1991 opened up new possibilities for strengthening and improving the performance of metals. Since then, significant progress has been made in the synthesis and manufacturing techniques, leading to the widespread application of NRMMCs in various sectors today **[1, 2]**. In recent years due to their superior properties and potential applications in various fields, these composites have attracted a lot of attention by researchers.

Some of the common matrix materials used in NRMMCs are Aluminum, Magnesium, Nickel, Titanium, and Copper **[3-6].** These metals have high strength, toughness, ductility, thermal conductivity, and good corrosion

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resistance. However, they also have some limitations such as low wear resistance. In order to overcome these drawbacks, metal matrices can be reinforced with nano-particles or nano-fibers that have different physical and mechanical properties from the matrix.

The nano-sized reinforcements can be made of a variety of materials, including ceramics, metals, and polymers of various shapes and sizes, but their dimensions are generally less than 100 nm, which is about 1/100,000 the width of a human hair **[2].**

Nanomaterials can be broadly categorized into two main types based on the carbon content, i.e., organic and inorganic nanomaterials. Owing to the versatile applications and huge number of studies, carbon-based nanomaterials are considered as a separate class of nanomaterial with a broad range of spectroscopy [7]**.** The basic classification of nanomaterials is given in Fig. 1.

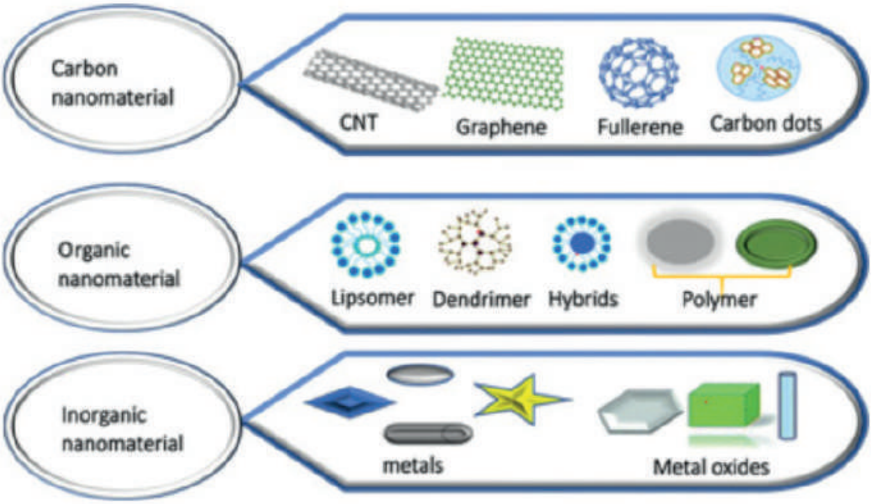

***Fig.1. Basic classification of nanomaterial reinforcements** [7].*

As can be seen Fig. 1, the most recent nanomaterials can be classified into three material-based categories:

***Carbon-based nanomaterials*:** Due to the unique property of catenation, carbon can form covalent bonds with other carbons in different hybridization states such as Sp, Sp2 and Sp3 to form a variety of structures of small molecules and longer chains. Carbon-based nanomaterials are found in morphological forms such as ellipsoids, hollow tubes, or spheres. Graphene (Gr), carbon nanotubes (CNTs), Fullerenes (C60), carbon nanofibers, carbon onions, and carbon black are the different categories of carbon-based nanomaterials.

Inorganic-based nanomaterials: These nanomaterials include metal-based nanoparticles, metal oxide/hydroxide nanoparticles, and transition metal chalcogenide (TMC) nanoparticles. These nanomaterials can be synthesized into metals like Ag, Au, Fe nanoparticles, and metal oxides such as ZnO, $TiO_{2,}$ and Fe_3O_4, CeO_2.

Organic-based nanomaterials: These nanoscale materials are made mostly from organic matter, aside from inorganic-based or carbon-based nanomaterials. The use of noncovalent interactions for self-assembling and molecular designing helps to transform the organic nanomaterials into coveted structures such as micelles, dendrimers, ferritin, micelles, compact polymers, and liposomes nanoparticles. These types of nanomaterials are usually biodegradable and nontoxic, and, therefore, considered environmentally friendly materials.

The most common nano-reinforcements used in NRMMCs are various types of nano-particles, such as carbides, nitrides, oxides, and carbon nanostructures, such as carbon nanotubes (CNTs), graphene, and graphene oxide **[8, 9]**. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) images of the nano reinforcements using for NRMMCs are given Fig.2 **[2].**

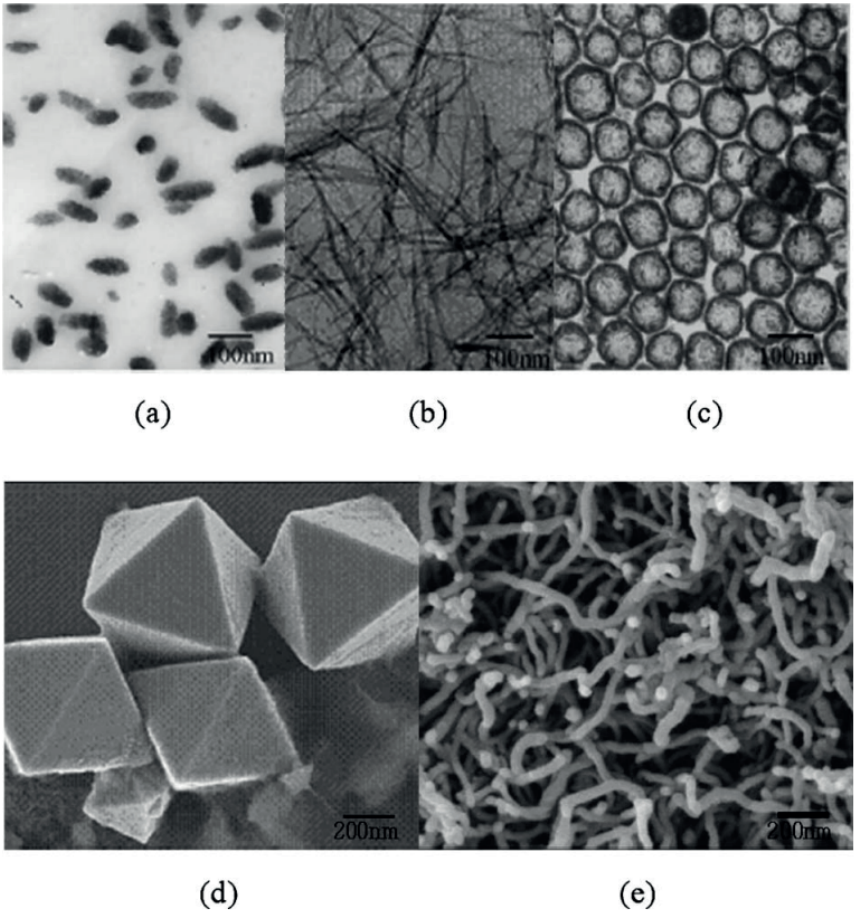

Fig. 2. TEM/SEM pictures of nanoparticles/nanotubes

a) Elliptical Nano particles, b) Nano fibers, c) Hollow nanoparticles, d) Octahedral nano particles and e) Carbon nanotubes. [2]

The nano-reinforcements have high surface area to volume ratio so they can improve the coefficient of thermal expansion (CTE) and mechanical properties of matrix material by grain refinement and by pinning dislocations. They can also improve the toughness of the matrix by deflecting cracks and promoting crack bridging, and improve the wear resistance and corrosion resistance of the matrix. These nano-particles have high hardness, high modulus, and high thermal stability. They can also interact with the dislocations in the metal matrix, resulting in additional strengthening effects **[3, 10, 11]**.

Fig. 3 shows carbon-based nanomaterials used as reinforcement for NRMMCs. Single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs) have a high aspect ratio and a large surface area [12]. Carbon nanotubes (CNTs) have also been intensively researched due to their excellent electrical, thermal and mechanical properties. These include an extremely high modulus of elasticity (0.9-2 TPa), a tensile strength of almost 63 GPa, extremely high thermal conductivity (3000 W/mK), high electrical conductivity of 106 S/m for SWCNTs and 105 S/m for MWCNTs [13] as well as non-corrosive properties towards acidic and alkaline media. [6]. These properties make them ideal candidates for the reinforcement of metal matrices [4].

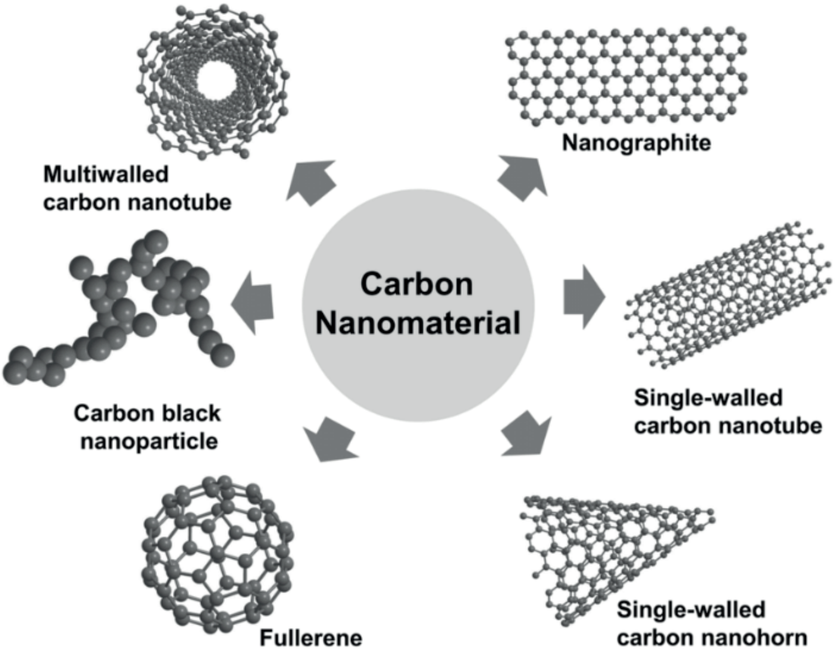

Fig. 3. Carbon nano materials used in NMMRCs [3]

For example, CNTs can increase the tensile strength of aluminum by more than 100% **[14],** graphene can improve the wear resistance of copper by more than 50% **[15]** , and graphene oxide can enhance the corrosion resistance of magnesium by more than 10 times **[16].**

ADVANTAGES of NRMMCs

NRMMCs offer a number of advantages over traditional metal matrix composites, which are reinforced with micro sized particles **[17, 18]:**

1. Nano reinforcements can provide greater strengthening and toughening effects.
2. Nano reinforcements can be dispersed more uniformly throughout the matrix, which can lead to improved properties.
3. Nano reinforced MMCs can be fabricated with lower reinforcement volume fractions, which can reduce weight and cost.

The properties of NRMMCs depend on the type and amount of reinforcement and the processing method used to produce the composite. In general, however, NRMMCs offer a number of advantages over conventional metal alloys, including:

- **Higher strength and stiffness:** Nanoparticles can significantly increase the strength and hardness of the metal matrix even in low volume fractions by forming grain refiners and dislocation barriers **[8].**

Grain refiners reduce the grains in the metal matrix, making the material stronger and more resistant to deformation. This is because the nanoparticles interact strongly with the metal matrix, creating a barrier to dislocation motion. Dislocation barriers prevent dislocations from passing through the metal matrix, making the material stronger.

For example, the tensile strength of aluminum can be increased more than 100% by carbon nanotubes **[14].**

- **Improved toughness:** Nanoparticles can also improve the toughness of MMCs by preventing crack propagation. This is because nanoparticles can deflect and pin cracks, making it more difficult for them to grow **[19].**
- **Improved wear resistance:** Nanoparticles can also improve the wear resistance of a metal matrix by forming a hard and protective layer on the surface of the material. This is because they are hard and abrasion-resistant **[13, 18].**
- **Increased corrosion resistance:** Nanoparticles can also increase the corrosion resistance of a metal matrix to oxidation and chemical attack than conventional metal alloys, which makes them suitable for applications that require high stability and longevity, such as marine structures **[1, 18].**

For example, graphene oxide can enhance the corrosion resistance of magnesium by more than 10 times . This is because they can form a protective layer on the surface of the metal matrix **[16].**

- **Reduced weight**: NRMMCs can be made lighter than traditional metal alloys by using nanoparticles with a low density. Nanoparticles can provide significant strengthening and stiffening effects at low volume fractions. This is important for applications where weight is a critical factor, such as aerospace and automotive applications **[20].**
- **Higher design flexibility:** NRMMCs can be tailored for specific applications by adjusting the type, amount, and distribution of nano-reinforcements in the metal matrix. This allows engineers to optimize the properties of NRMMCs for different needs and environments **[20].**

For example, an alloy can be designed to be strong and ductile or hard and brittle depending on the application.

APPLICATIONS of NRMMCs

NRMMCs are still at an early stage of development, but they have the potential to become one of the most important classes of engineering materials in the 21st century. NRMMCs have a wide range of potential applications in a variety of industries. Some of the specific applications of NRMMCs are **[4, 21, 22, 23]:**

- **Aerospace:** Nano-reinforced MMCs are being developed for use in aircraft and spacecraft components to reduce weight and improve performance. For example, NRMMCs are used in aircraft components, such as engine parts, landing gear, airframes and wings. This could lead to more fuel-efficient aircraft with longer ranges **[23].**
- **Military applications:** NRMMCs can be used to fabricate armor plating, ballistic missiles, and other defense-related components. The use of NRMMCs in military applications can lead to improved ballistic protection and performance **[23].**
- **Automotive:** NRMMCs are used in automotive applications to reduce weight and improve fuel efficiency. For example, NRMMCs are used in engine components, such as pistons, connecting rods, and cylinder heads. This could lead to more fuel-efficient and environmentally friendly cars **[13].**
- **Energy:** Nano-reinforced MMCs are being developed for use in energy components, such as fuel cells and solar cells. NRMMCs could

be used to make more efficient and durable energy components, such as turbine blades and heat exchangers. This could lead to lower energy costs and reduced emissions **[23, 36].**

- **Biomedical:** NRMMCs are used in medical applications to improve the strength and combination of biocompatibility and good wear resistance. For example, NRMMCs are used in dental implants and orthopedic implants such as artificial bones and joints **[2, 10, 18, 23, 25, 26, 27, 28]** .
- **Electronics:** Nano-reinforced MMCs are being developed for use in electronic components to improve heat dissipation and electrical conductivity. They can also offer good thermal conductivity and electrical insulation. For example, NRMMCs are used in heat sinks and circuit boards and electronic packaging materials **[23, 24]**.
- **Sporting goods:** NRMMCs are being developed for use in sporting goods such as golf clubs, tennis racquets, and bicycle frames. They offer the potential to improve performance and durability **[23]**.

FABRICATION of NRMMCs

Researchers fabricate NRMMCs using various methods, such as powder metallurgy, liquid metallurgy, solid-state processing, and some other novel techniques (Fig. 4) **[9].** Each method has its own advantages and disadvantages, depending on the type of metal matrix and nano-reinforcement, the desired properties, and the cost and complexity of the process. Here is a brief overview of some of the methods:

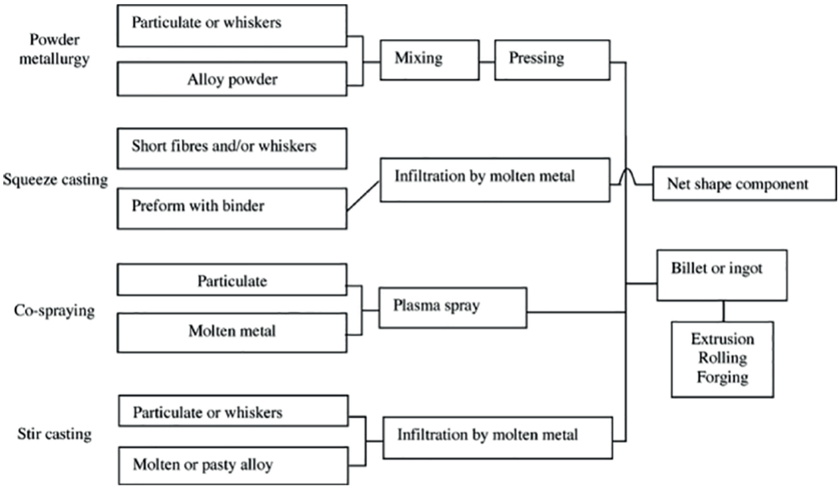

Fig. 4. Fabrication routes for NMMRCs [9]

Powder metallurgy: This method is the most employed technique to NRMMCs. The powder metallurgy method begins by an initial mixing of the raw material powders with a control agent through ball milling, ultrasonication, or both. Ball milling involves the use of small balls, usually steel or zirconia **[6].** The mixed powders are uniaxially compressed by using a wide range of forces for compacting. Afterwards, they need to be sintered at high temperature to form a solid composite (Fig. 5).

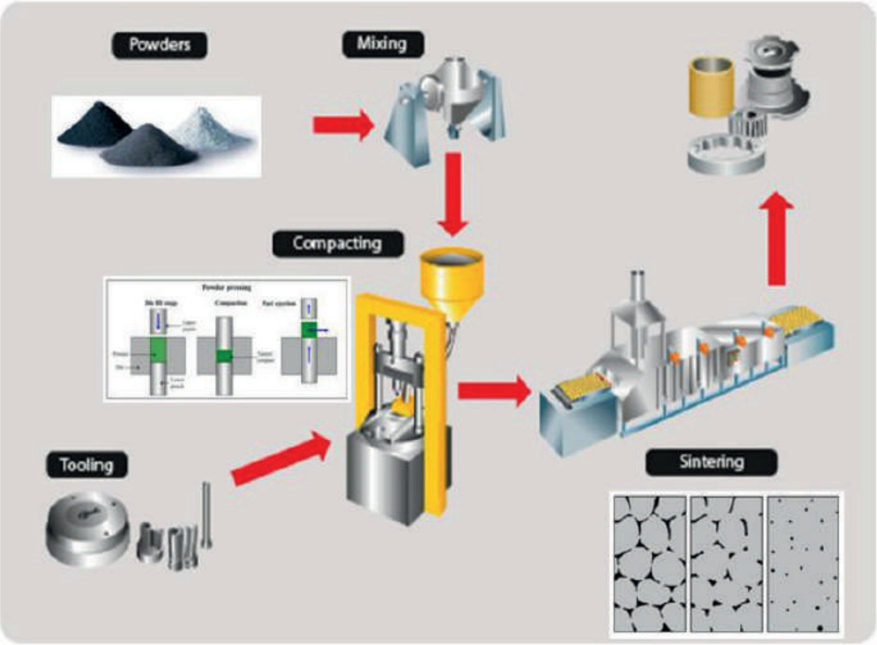

Fig. 5. Powder Metallurgy route for manufacturing NRMMCs [23, 27]

Compacting can be made at room and high temperatures. Room-temperature compression is followed by a sintering step up to 24 h **[29, 30].** Compacting at high temperatures includes hot pressing **[31]**, spark plasma sintering **[32]**, or deformation processing **[33].** Composites obtained by powder metallurgy are often subjected to post-treatment to improve their properties. Hot extrusion **[34]**, and hot rolling **[35]**, are some of the most common post-treatments for powder metallurgy-obtained NRMMCs **[36]**.

Powder metallurgy route can produce NRMMCs with uniform distribution of nano-reinforcements and good interfacial bonding. However, it also requires high temperature and pressure for sintering, which can cause oxidation and degradation of nano-reinforcements.

- **Liquid metallurgy:** This method involves melting metal matrix and adding nano-reinforcements into the melt and then casting or solidifying them to form a solid composite (Fig. 6).

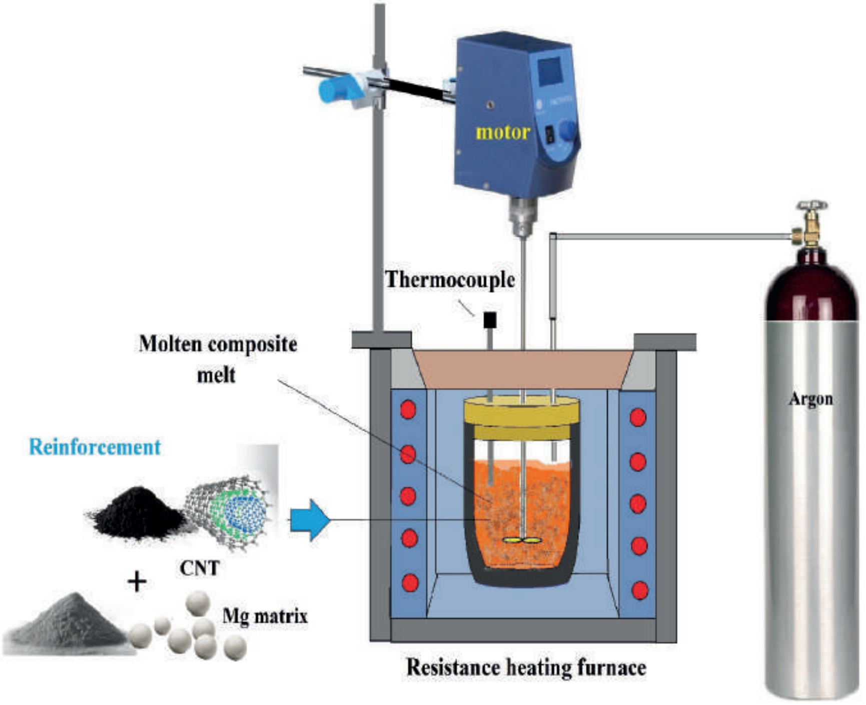

Fig. 6. Liquid Metallurgy route for manufacturing NRMMCs [1]

This method can produce NRMMCs with low cost and large scale. However, it also suffers from poor dispersion, the agglomeration and oxidation of nano-reinforcements during processing and low wettability of nano-reinforcements by molten metal, weak interfacial bonding of nano-reinforcements in metal matrix, and segregation of nano-reinforcements during solidification **[6].**

Several strategies have been implemented to increase the efficiency of this method, such as Centrifugal Casting **[17, 37]**, Squeeze Casting **[38, 39, 40]**, and Pressure Infiltration **[41, 42].** In centrifugal casting, the molten material is transferred to a rotating mold, which is maintained at high pressure. In the squeeze casting process, the composite is poured into a die in which the material is then hydraulically pressed. In pressure infiltration, the molten matrix is injected at high pressure into a mold that contains the reinforcement.

Some novel methods have been proposed for fabricating NRMMCs, to improve the wettability, dispersion, interfacial bonding, and stability of nano-reinforcements in metal matrix by using physical or chemical means. Some of the novel methods for fabricating NRMMCs are:

- ❖ **Electro-deposition:** This method involves depositing metal matrix and nano-reinforcements on a substrate using an electric current **[43].** This method can improve the wettability, dispersion, interfacial bonding, and stability of nano-reinforcements in metal matrix by using physical or chemical means.
- ❖ **Laser cladding:** This method involves melting metal matrix and nano-reinforcements on a substrate using a laser beam **[44].** NRMMCs can be produced with high quality and precision by controlling the laser parameters (Fig.7a).
- ❖ **Friction-stir processing:** This method involves stirring the metal matrix and nano-sized particles are mixed together in a molten state and then cast into a mold **[45]**. This method (Fig. 7b) can produce NRMMCs with fine microstructure and enhanced properties by generating high temperature and plastic deformation **[8, 9].**

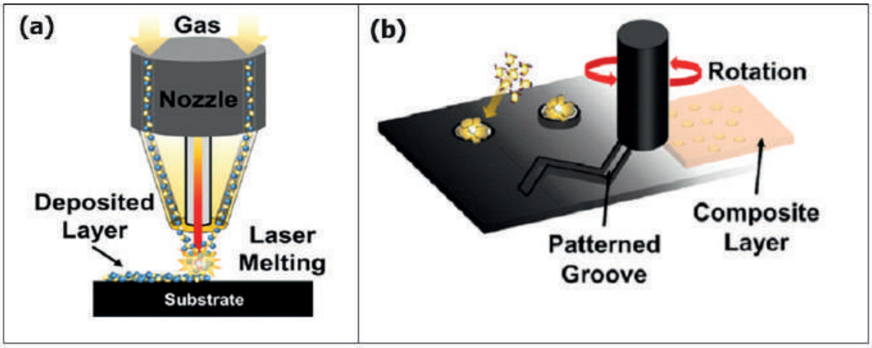

Fig. 7. Schematic illustration of Production Processes;

(a) Laser cladding, (b) Friction Stir Process [46]

Infiltration: A preform of the nanoscale reinforcement is infiltrated with a molten metal matrix. Pressure infiltration, pressureless infiltration and vacuum infiltration can be used to produce composites with high yield and approximate net shape **[47].** There are a variety of squeeze casting machines and systems that use an inert, pressurized gas to force the liquid metal into the preform **[28, 48].** Pressures of around 65–100 MPa are used for mechanical support, while lower pressures of 2–35 MPa are used for systems with inert pressurized gas. Pressureless infiltration, also known as capillary-controlled infiltration, is carried out by immersing the ceramic in a bath of molten aluminum alloy at atmospheric pressure **[49].** Vacuum infiltration, which is carried out just below atmospheric pressure, was investigated by Chung and Lin (1996). This study was conducted due to its simplicity, applicability and low pressure to minimize possible damage to the SiC foam **[50].**

In-situ processing is a process in which the reinforcement is created within the metal matrix during fabrication. In these techniques, the reinforcements are synthesized by exothermic reactions during the production of the composite itself **[51].**

In situ composites offer superior microstructural/mechanical characteristics as compared to their conventional counterparts where the reinforcement is made separately and introduced into the melt. In situ metal matrix composites have the advantage of the lower cost of fine-sized thermodynamically stable ceramic particles with clean and unoxidized ceramic-metal interfaces, since the reinforcement is formed within the melt.

Figure 8 illustrates the different in-situ processing methods for metal matrix composites, including reactive and non-reactive methods **[52].**

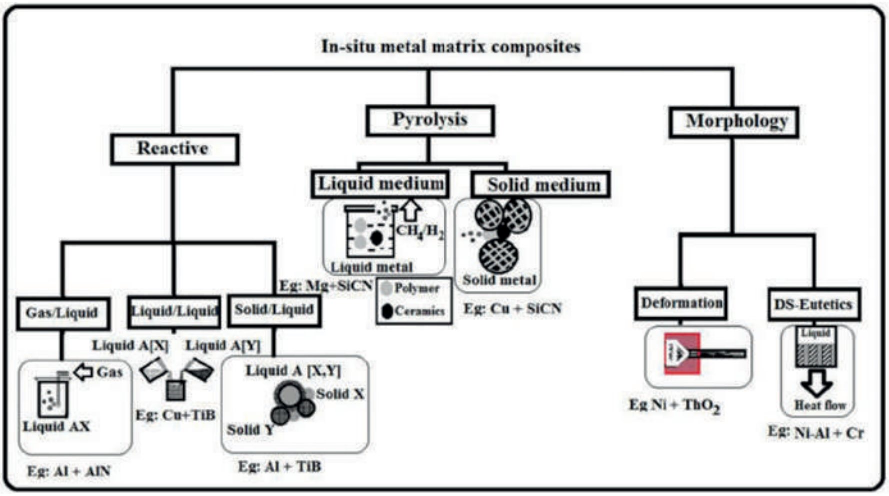

Fig. 8. Classification of in situ methods to fabricate NRMCs [52]

CHARACTERIZATIONS of NRMMCs

Researchers evaluate the quality of NRMMCs using various methods and criteria, depending on the type and purpose of the evaluation. Some of the common methods and criteria are:

- **Evaluating the quality of the fabrication process:** Researchers use different techniques to measure and analyze the physical and chemical properties of the NRMMCs, such as the Morphology, Distribution, Dispersion, Wettability, Interfacial Bonding, and Stability of the nano-reinforcements in the metal matrix. Some of the techniques include Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD), Energy Dispersive Spectroscopy (EDS), Atomic Force Microscopy (AFM), etc. **[21, 46, 53].**

These techniques can help researchers to identify and quantify the defects, impurities, and variations in the microstructure of NRMMCs that may affect their performance.

- **Evaluating the quality of the mechanical properties:** Researchers use different tests to measure and compare the mechanical properties of the NRMMCs, such as the Tensile Strength, Compressive Strength, Hardness, Modulus, Fracture Toughness, Fatigue Resistance, Creep Resistance, etc. **[54-56]**

These tests can help researchers to determine and optimize the optimal loading conditions and failure modes of the NRMMCs under different stress and strain scenarios.

- **Evaluating the quality of the functional properties:** Researchers use different experiments to measure and evaluate the functional properties of the NRMMCs, such as the Wear Resistance, Corrosion Resistance, Thermal Conductivity, Electrical Conductivity, Damping Capacity, etc. **[1, 2, 47, 51].**

These experiments can help researchers to assess and improve the performance and durability of the NRMMCs under different environmental and operational conditions.

FUTURE PROSPECTS of NRMMCs

NRMMCs are a promising new class of materials that have the potential to revolutionize a wide range of industries. While NRMMCs offer a number of advantages over traditional metal matrix composites, there are also some challenges associated with their fabrication and use **[56]**:

- *One of the biggest challenges is achieving a uniform distribution of the nano-sized reinforcement in the metal matrix.* This is important because it ensures that the composite has consistent properties throughout. This can be difficult due to the tendency of nanoparticles to agglomerate.
- *Another challenge is the cost of nano-sized reinforcements.* Nano-sized reinforcements are typically more expensive than traditional reinforcements, such as micro-sized reinforcements. NRMMCs are more expensive to manufacture than traditional metal alloys due to the cost of the nanoparticles and the complexity of the manufacturing process.
- *The developing fabrication methods that are scalable and cost-effective is another challenge.* There is significant research and development activity in the field of NRMMCs. For this reason, new fabrication methods are being developed, and new nanoparticle reinforcements are being discovered.
- *The lack of standardization for NRMMCs is another challenge.* There is currently no standard way to measure and test the properties of NRMMCs. This makes it difficult to compare different NRMMCs and to ensure that they meet the requirements of specific applications.

Consequently, further research is needed to optimize the processing parameters of NRMMCs, understand the reinforcement mechanisms, evaluate the performance under different conditions, and explore new types of nano reinforcements and metal matrices for NRMMCs. The specific research areas that are being pursued in the field of nano reinforced MMCs are given below **[36]:**

- Developing new fabrication methods that can produce nano reinforced MMCs with high reinforcement volume fractions and uniform particle distribution.
- Developing new nanoparticle reinforcements that have improved properties and are more compatible with metal matrices.
- Investigating the long-term performance of nano reinforced MMCs under various service conditions.
- Developing new applications for nano reinforced MMCs.

CONCLUSION

As a result, research and development investigations all over the world will contribute greatly to nano-reinforced MMCs becoming an important class of materials with a wide range of applications. As the manufacturing technology of NRMMCs continues to evolve and test and measurement standards are improved, the production cost of NRMMCs will decrease and the difficulties in their use will be overcome. Accordingly, NRMMCs are expected to play an increasingly important role in various applications such as aerospace and defense, automotive, biomedical, electronics and energy.

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Chapter 7

Finite Element Analysis of Glass/Carbon Hybrid Composite Pipes

Mehmet Çağrı Tüzemen[1]

Abstract

In recent years, due to the diversification of needs in industries, studies on hybrid composites in which different fibers are used together have begun to attract attention. In this study, Glass/Carbon interlayer hybrid composite pipes made of glass and carbon fibers with different stacking sequences were investigated by using the finite element analysis (FEA). Ansys was used for the FEA. In the models created from eight layers, the thickness of each layer is 0.25 mm and the wall thickness of the composite pipes is 2 mm. In hybrid composite samples, four layers of glass fiber and four layers of carbon fiber were used. In addition to eight hybrid composite samples with different stacking sequences, another two models consisting of pure glass fiber and pure carbon fiber was designed as a reference sample. Unidirectional (UD) glass fiber and UD carbon fibers were used when creating the models. While creating the mesh structure on the models, it was checked whether the skewness was within acceptable values. For this purpose, optimization was made in the mesh structure size. While fixed support was applied to the models from one end, tensile force was applied from the other end. Tsai-Wu criterion was used in the FEA. It was concluded that the use of carbon fiber in the inner layers of interlayer hybrid composites increased the strength. Among the interlayer hybrid composites, approximately 25% increases in maximum force were obtained with the change of the stacking sequence.

1. Introduction

Continuous fiber reinforced polymer matrix composites are frequently used in high technology products thanks to their low weight and high strength [1]. However, despite the high specific strength of carbon fiber, its usage area may be limited because it is a very expensive material [2].

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On the other hand, glass fiber has lower strength than carbon fiber, but it is a cheaper reinforcement element [3,4]. For this reason, studies on hybrid composite structures in which different fiber types are used together have gained momentum in recent years. Thus, while the cost will decrease compared to the final product consisting only of carbon fiber, the loss in specific strength will be lower compared to the final product consisting only of glass fiber.

There are various hybridization methods in composites such as intralayer, interlayer or woven [5–8]. In intralayer hybrid composites, different fibers are used in the same layer. The same applies to woven hybrids. In interlayer hybrid composites, different fiber structures are used in different layers. Hybrid composite pipes can also be produced in a wide variety of shapes using different production methods and different fiber reinforcements [9–11]. The mechanical properties of interlayer hybrid composites may also vary depending on the sequence. Since the mechanical properties of the fibers are different, each fiber adds a different feature to the hybrid structure. While glass fiber reinforcement has chemical resistance, heat and electrical insulation, carbon fiber has higher load-carrying capacity, higher hardness and fatigue resistance [12]. Telli et al. [13] examined the damage analysis of hybrid Carbon/Glass-Epoxy pipe elbows under bending and pressure loading. They noted that for a hybrid composite, the position of the plies has a large impact on the behavior, especially on the resistance of the tubular structure. Wang et al. [14] investigated the mechanical properties of fiber-reinforced hybrid composite pipes in their study. They observed that the innermost layer was exposed to the highest stress under axial tensile load. They concluded that increasing the proportion of fibers with high modulus of elasticity in the hybrid composite structure could improve the tensile properties of these structures. The reason for this is that the effect on the mechanical behavior of fiber-reinforced hybrid composite pipes is mainly attributed to the axial tension of the fibers.

The aim of this study is to investigate the effect of glass/carbon fiber stacking sequences under tensile load in hybrid composite pipes made of glass and carbon fiber fibers. The behavior of interlayer hybrid composite pipes with eight different stacking sequences under tensile load was examined by the finite element method. In the hybrid structure consisting of a total of eight layers, four layers of glass fiber and carbon fiber were used. In addition, composite pipes consisting of pure glass and pure carbon fiber were also analyzed for reference. Thus, hybrid structures were compared and interpreted both with pure fiber reinforced composites and among themselves.

2. Materials and Method

In this study, the behavior of interlayer hybrid composite pipes under tensile load was investigated by finite element analysis. Hybrid composite pipes are modeled as shell elements in SpaceClaim. Next, the model was transferred to the ACP (Pre) module in the Ansys. In the ACP (Pre) module, the materials are defined for the model. Unidirectional carbon fiber/epoxy and glass/epoxy were chosen as materials. Some properties of the selected materials are given in Table 1.

Table 1. Some properties of the materials used in the analysis

	Carbon Fiber	Glass Fiber
Tensile Strength (MPa)	1632	780
Tensile Strain	0,0143	0,0244
Modulus of Elasticity (GPa)	123	35
Poisson's Ratio	0,27	0,28
Shear Modulus (GPa)	5	4,7

After the selected materials were introduced to the model, the interlayer hybrid structure of the pipe was created. The models are designed to have eight layers in total. The designs and stacking sequence of the layers are shown in Figures 1. The part shown in green in Figure 1b is the layers of the section. The bottom layer in Figure 1c shows the innermost layer of the composite pipe, and the top layer shows the outermost layer. The blue-colored layers represent the glass fiber layers, and the dark gray-colored layers represent the carbon fiber layers. While samples 3–10 are composite pipes between layers formed in various ways, samples 1 and 2 are reference models consisting of only glass fiber and only carbon fiber, respectively.

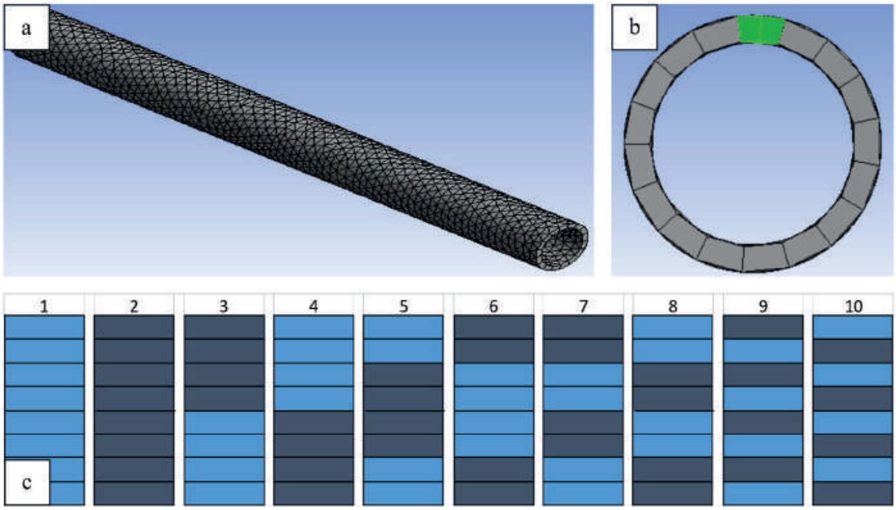


Figure 1. (a) design of interlayer hybrid composite pipes, (b) cross-sectional view and (c) layer sequences of the green area in the cross-section and numbering of the models (Blue color shows glass fiber layers, dark gray color shows carbon fiber layers)

The thickness of each layer is 0.25 mm, and the wall thickness of the composite pipes is 2 mm. The outer diameter of the model is 20 mm, and the length is 200 mm. The orientation of the unidirectional fibers is designed in the direction of the force. The triangle method was chosen as the mesh method. Improvements were made in the quality of the mesh structure, considering the solution times over the mesh size. The model is fixed supported at one end to prevent rotation and translation. From the other end, tensile force was applied and support was applied against translation (except in the direction of force) and rotation (see Figure 2). Models were analyzed according to the Tsai-Wu damage criteria.

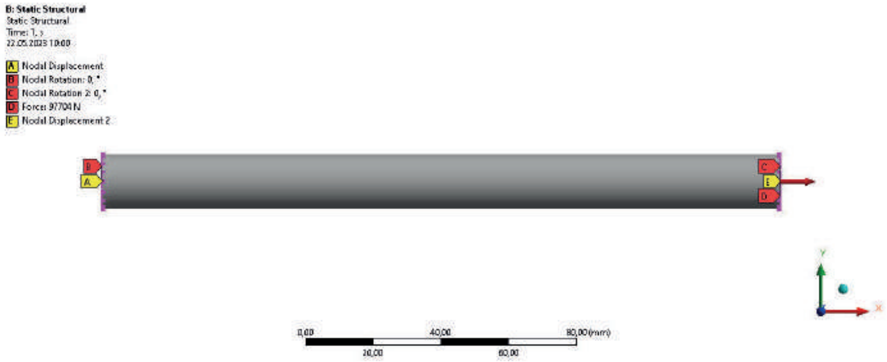
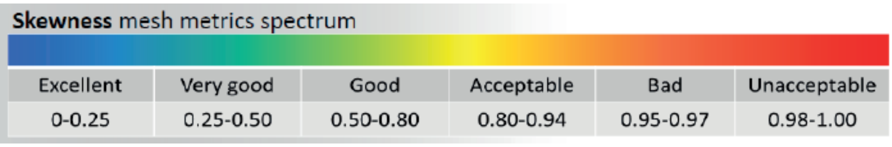


Figure 2. Loading and boundary conditions

3. Results and Discussion

Before determining the behavior of composite pipes under tensile forces, the quality of the mesh was checked, and improvements were made in the mesh size, taking into account the analysis solution times. The skewness values were examined to measure the quality of the mesh. Experimenting with different mesh sizes is aimed to optimize the skewness value in the skewness scale ranges of the Ansys program (see Figure 3). According to this scale, skewness values of 0.94 and below are acceptable.



Skewness mesh metrics spectrum

Excellent	Very good	Good	Acceptable	Bad	Unacceptable
0-0.25	0.25-0.50	0.50-0.80	0.80-0.94	0.95-0.97	0.98-1.00

Figure 3. Scaling of Ansys program showing network structure quality due to skewness [15]

The effect of the mesh structures formed in different sizes of the composite pipe model on the skewness is given in Figure 4. All the mesh structures of various sizes created on the model are in the "very good" range according to the scale in Figure 3. It has been observed that the mesh size gives the lowest skewness for 3 mm and the values greater than 8 mm. Larger mesh sizes were not preferred because they may cause convergence problems in the analysis. When the mesh size decreased below 1 mm, it caught a downtrend. However, the mesh structure created on the model with dimensions less than 0.5 mm extends the analysis time considerably. Therefore, taking into account the analysis times, it was decided that the most appropriate mesh size was 3 mm. The highest skewness value finding is 0.27 in this mesh size. According to the scale in Figure 3, this value is close to the lower limit of the "very good" range.

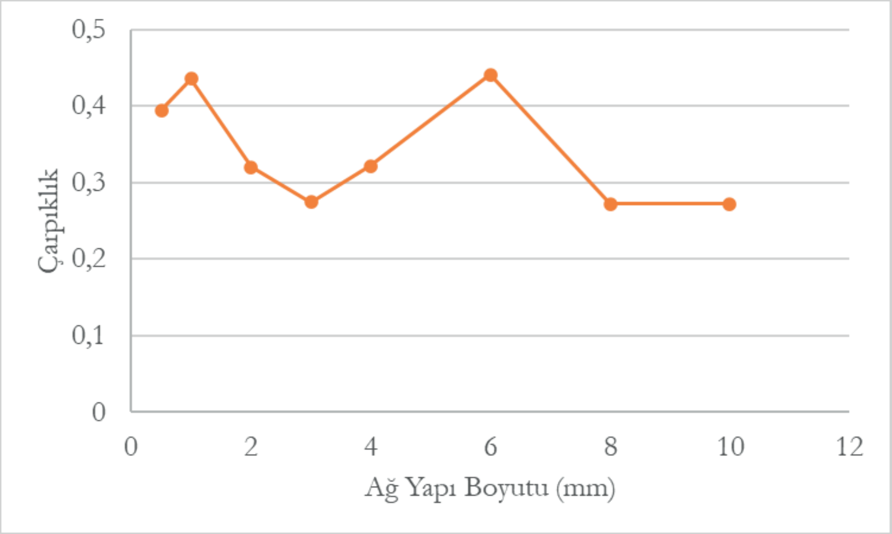


Figure 4. Change of maximum skewness depending on mesh structure size

Figure 5 shows the maximum forces that composite pipes can withstand according to the Tsai-Wu criterion. As expected, the reference samples consisting of only glass fiber and only carbon fiber were the samples with the lowest and highest strengths, withstanding 46 kN and 98 kN forces, respectively. The average of the maximum forces that the two reference samples can withstand is shown in the figure with a straight blue line (72 kN). The remaining samples are interlayer hybrid composite samples, and all of them use four layers of glass fiber and four layers of carbon fiber. In other words, the use of expensive carbon fiber has been halved. When the results were examined, it was seen that sample number 4 gave the highest value of 86 kN among the interlayer hybrid composites. Following this, samples 8, 5 and 10 withstood forces of 80 kN, 78 kN and 76 kN, respectively. When these samples are examined, it is seen that there is glass fiber in their outermost layers. Sample number 4, which has the four glass fiber layers at the outermost layers, had the highest strength among the mixed composites. As the use of carbon fiber in the innermost layer increased, the maximum force increased. In other words, as the use of glass fiber in the inner layers increased, the maximum force decreased. The highest load that sample number 3 could withstand was the lowest with 69 kN. Sample number 4 withstood 17 kN more load than sample number 3, just by changing the stacking sequences. This value, which means approximately 25% more load, shows how important the stacking sequences is, even though the usage of glass and carbon fibers are the same.

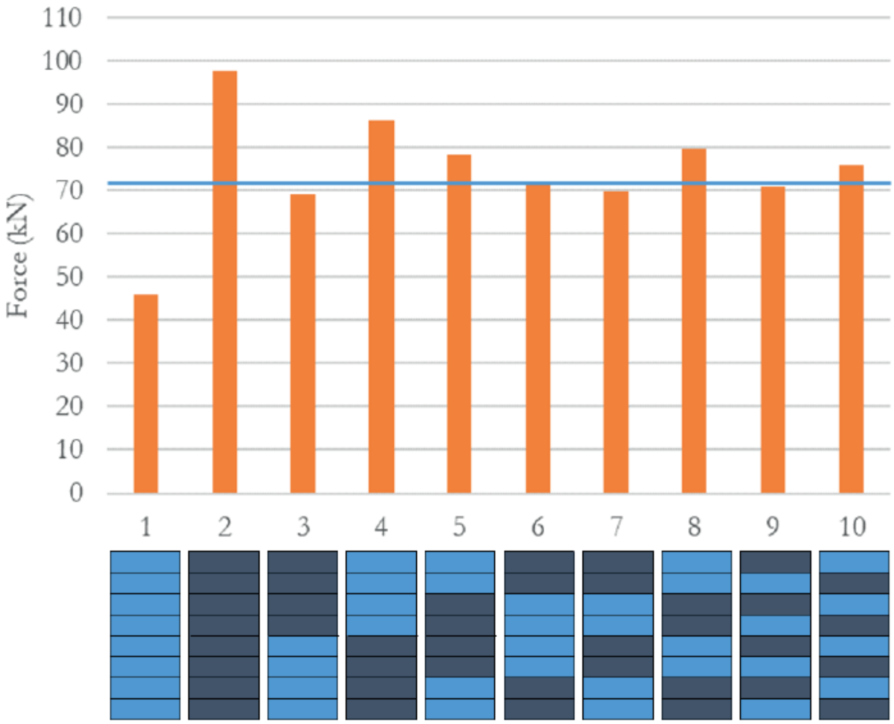


Figure 5. Maximum force that composite pipes can withstand (Blue layers show glass fiber, dark gray layers show carbon fiber)

Sample no. 4 withstood an 87% higher force than sample no. 1, just by converting 50% of the layers from glass fiber to carbon fiber. Although the use of carbon fiber was halved compared to sample no. 2, sample no. 4 only withstood a force approximately 12% lower than sample no. 2. Thus, while the use of carbon fiber, which is much more expensive, was reduced by half, there was only a 12% decrease in maximum force, but an 87% increase in maximum force was achieved compared to the glass fiber sample alone.

4. Conclusions

In this study, the behavior of interlayer hybrid composite pipes under tensile load was investigated. Fixed support was applied to the models from one end and tensile force was applied from the other end. According to the Tsai-Wu criterion, the highest forces it can withstand have been found. In hybrid composites, the samples that withstood the highest forces were the samples with glass fiber in the outermost layers. While the sample with glass fibers in the outermost layers and carbon fibers in the innermost layers withstood 87% higher force than the sample with all layers consisting of glass fibers, it could withstand only 12% lower force than the sample with all layers composed of carbon fibers. Therefore, with mixed composites, greater reductions in cost can be achieved with lower compromises in strength. Among the interlayer hybrid composites, 25% increases in maximum force were obtained with the effect of the stacking sequences. Thus, by simply changing the stacking sequences of the fibers, higher forces resistance can be achieved even using the same ratio of glass and carbon fiber.

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Chapter 8

Additive manufacturing in the automotive industry

Ali Avci[1]

Abstract

The market for materials derived from renewable resources has grown in recent years, driven by factors such as the need to decrease carbon emissions, lower fuel expenses in the automobile sector, address environmental contamination, and mitigate the risk of oil depletion. In the automotive sector, utilising components derived from sustainable sources not only mitigates emissions, but also decreases expenses, conserves fuel, and enhances vehicle weight efficiency. The automotive sector is a globally competitive industry. Continuously, fresh marketplaces and diverse designs are arising with the aim of enticing clients, necessitating the adoption of novel production methodologies to accommodate the automotive sector. Biocomposites are utilised in the automobile sector because of their biodegradability, lightweight nature, ease of manufacturing, and high specific strength. The utilisation of additive manufacturing in automobile parts production is advantageous due to its rapid production capabilities, minimal equipment requirements, and suitability for the fabrication of biocomposites. The paper provides examples derived from contemporary scientific findings and industrial applications. The additive manufacturing (AM) method facilitates both prototyping and the design and production of final products. AM enables the production of diverse profiles while minimising resource usage. Additive manufacturing offers a substantial competitive edge in this industrial sector by offering production flexibility and the ability to create customised vehicle components as needed.

1. Introduction

Recently, the additive manufacturing method (AM) has gained prominence as a promising technology capable of substituting both new and classic methods. The field of additive manufacturing has garnered

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significant attention as a study issue, and new advancements in this area are revolutionizing the technology, elevating it from a mere prototype method to a fully-fledged production process. AM printed components, subassemblies, and prototyping play a crucial role in every product development process. AM, or Additive Manufacturing, is a prime illustration of these technologies, as it completely transforms the process of creating new things and manufacturing final goods [1]. Contrary to conventional manufacturing techniques like CNC machining, the AM filament deposition method (FDM) allows for the production of a part with little material waste, eliminating the requirement for tools, cutters, milling machines, and similar equipment. Additionally, it eliminates the need for chemical post-treatment and curing, which are typically necessary for alternative selective laser melting (SLM) techniques. The filament deposition method, which is the most often used polymer additive manufacturing technique, has previously demonstrated successful application in producing carbon fiber polymer composites with a high degree of orientation in the printing direction. Research has demonstrated that this method can be employed to create composite systems with regulated anisotropic characteristics [2]. Although the approach is modern, its initial implementation may be traced back to the 1980s. Although the AM process was once limited to prototype production from the 1980s to the 2000s, it has now expanded its utility beyond just prototyping. The AM approach, now in use, has significantly reduced the time it takes to bring finished products to market by offering long-term strategic and economic benefits. In addition, although additive manufacturing (AM) has made tremendous advancements in recent decades, its use is primarily limited to fast prototyping due to constraints in material characteristics, production speed, and part size [3].

Fiber-reinforced composites provide a combination of low weight, cost-effectiveness, and high strength-to-weight ratio. Utilizing natural fiber in additive manufacturing can enhance material characteristics, hence decreasing the fabrication time for functional components in comparison to conventional subtractive technologies. Furthermore, it may be feasible to manufacture intricate biocomposites with complex shapes [3]. Extensive research has been conducted on the utilization of the Additive Manufacturing technique in the manufacturing of composite materials, particularly in the fabrication of composites reinforced with carbon fibers [4]–[12]. Nevertheless, research on composites reinforced with natural fibers is limited but has shown a recent upward trend. Through the integration of bio-based sustainable polymers with natural reinforcements, it is possible to create novel materials that are both renewable and serve as alternatives to petroleum-based polymers [13]. Many commercially available polylactides (PLA), for instance, exhibit brittleness and possess low thermal breakdown temperatures. The composite material concept offers a strategy for producing renewable materials that can achieve or surpass the performance of routinely utilized petroleum-based engineering polymers [14]. Composites derived from sustainable resources are being substituted for industrial composites due to significant factors such as global warming, environmental pollution, greenhouse gas damage, and the potential depletion of oil. Biocomposite materials are composite materials that contain at least one component derived from natural sources. Biocomposites refer to many types of materials, including natural fiber-reinforced petroleum-derived plastics, natural fiber-reinforced biopolymer matrix composites, and synthetic fiber-reinforced biopolymer matrix composites [14], [15]. Multiple publications exist on the incorporation of continuous fibers into a PLA matrix as a demonstration of producing biocomposites using the AM process. Matsuzaki et al. [16] created continuous fiber composites using PLA-based carbon and jute fiber, which are natural biodegradable materials, by a process including molten filament and in-nozzle impregnation. By employing this method, the authors successfully accomplished the production of new-generation composite materials without the need for molds. The production process involved impregnating continuous fibers and polymer filament through the heated nozzle of the printer. Automobile makers are increasingly utilizing biocomposites. They primarily contribute substantially to weight reduction. Biocomposites are currently being used in automobile parts such as the front door console (weighing between 1.2 and 1.9 kg), rear door console (weighing between 0.8 and 1.6 kg), and trunk console (weighing between 1.5 and 2.5 kg) of popular car companies like BMW, Ford, Renault, and Volvo. Starting in 2021, the European Union will implement a new standard for the average emissions of new cars, which will be set at 95 grams of CO_2 per km. This emission level is equivalent to approximately 4.1 liters of petrol or 3.6 liters of diesel fuel consumed every 100 km. Utilizing green composites will effectively decrease CO_2 emissions by diminishing the fuel consumption of cars [17]. In addition, the manufacturing process of natural fibers consumes less energy compared to synthetic fibers. Nova-Institute, located in Hürth, Germany, conducted an analysis revealing that the manufacturing of one metric tonne of glass fiber results in the emission of 1.7-2.2 metric tonnes of CO_2 equivalent. In contrast, the combined impact of four natural fibers (flax, hemp, jute, and kenaf) amounts to 0.5 metric tonnes. A study conducted in India found comparable results for jute, kenaf, hemp, and flax fibers, determining that the carbon footprint associated with the manufacturing of natural fibers was 20-50% lower than that of glass fibers.

The automotive industry will face some restrictions in the world, especially in the European Union (EU) countries, in the coming years. One of these limitations pertains to international accords aimed at decreasing greenhouse gas emissions. Following the climate summit held in Paris in 2015, world countries pledged to decrease their greenhouse gas emissions. During the second global climate summit in Glasgow in 2021, 197 countries reaffirmed their commitment to a cooperative framework aimed at mitigating carbon emissions. The second limitation is that the European Union, in collaboration with the Association of European Automobile Manufacturers, has established a target for the average emissions of new cars across the EU at 95 g CO_2 km^{-1}, effective from 2021 [18]. In order to achieve all goals in the automotive industry, lightening vehicles as well as using clean energy has an important place. With the use of biocomposites, lightweight vehicles that burn less fuel are produced and natural materials with a much lower carbon footprint are used. In addition, the fact that in the directive published by the EU (2000/53/EC), it was decided that 85% of the materials used in vehicles should be recyclable and this rate should be increased to 95% by 2015 [19], increases the importance of the use of biocomposites. Beyond these, the possibility of running out of oil can also be considered a constraint. Considering that the rate of depletion of petroleum resources is approximately 100,000 times faster than the rate of nature's renewal, the importance of using natural resources will be understood more clearly [20].

2. Biocomposites

Biocomposites are extensively utilized in several industries including automotive, plastic construction, and aircraft industry [21]. The reinforcement fibers utilized to enhance and fortify the strength of the composite structure predominantly consist of synthetic materials such as carbon boron, glass, kevlar, and aramid. These fibers offer exceptional performance while maintaining a low density. Over the past decade, numerous investigations have focused on producing composite materials using polymer matrix and reinforcement elements derived from natural and renewable resources. The primary objective of these investigations is to create novel composite materials that do not pose environmental concerns post-use. This will be achieved by employing reinforcements with high biodegradability instead of artificial reinforcements with low biodegradability while emphasizing the use of renewable resources. Biocomposites are formed by blending bio-based fibers and other bio-based materials with plastic resins, resulting in the production of novel and environmentally friendly products. Bio-based materials are derived from sustainable sources such as wheat straw, corn husks, and leftovers of soy and corn processing. These biocomposites are utilized in injection molding and additive manufacturing applications to efficiently produce intricate automobile components in an environmentally friendly manner with speed and precision [22].

Research indicates that the mechanical properties of the polymer (pure resin) are enhanced through fiber reinforcement, leading to a significant improvement in impact resistance. When comparing natural fiber composites to composite structures made of high-performance fibers, it is evident that the strength values of natural fiber composites are inferior. Therefore, it is advisable to use these items in simpler applications rather than in regions that demand high mechanical performance. Consequently, materials like aramid, carbon, and glass are recommended. Instead of being positioned as a substitute material for reinforced composites, it has been asserted that they can be utilized in indoor applications capable of bearing low and medium loads, as well as in outdoor applications such as roofs, automobile interior components, and drainage panels. Various types of natural fiber supplements include flax, hemp, cotton, jute, wood fiber, sisal fiber, ramie fiber, and coconut fiber. Table 1 provides the mechanical characteristics of various plant-based natural fibers and synthetic fibers.

Table 1. Mechanical properties of some fibers

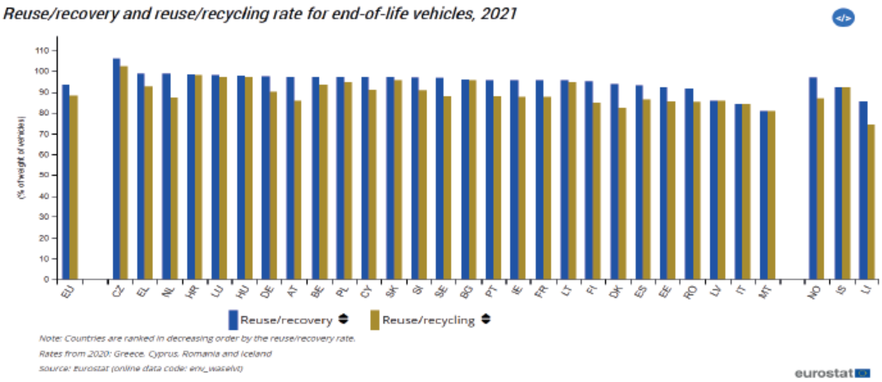
Fiber	Density (g cm^{-3})	Strain (%)	Tensile Strength (MPa)	Young's Modulus(GPa)
Cotton	1.5-1.6	7.0-8.0	287-597	5.5-12.6
Hemp	1.2-1.4	1.5-6.9	223-930	14.5-53
Jute	1.3	1.5-1.8	393-773	26.5
Flax	1.5	2.7-3.2	345-1035	27.6
Sisal	1.5	2.0-2.5	511-635	9.4-22.0
Wood	1.5	-	1000	40.0
E-glass	2.5	2.5	2000-3500	70.0
Aramide	1.4	3.3-3.7	3000-3150	37.0-63.0
Carbon	1.4	1.4-1.8	4000	230.0-240.0

2.1. The application of biocomposites in the automotive industry

Biocomposites offer several benefits when used in automotive applications. Composites are often lightweight substances, which leads to a decrease in vehicle fuel consumption and the release of greenhouse gas emissions. Biocomposites has superior acoustic and thermal qualities in comparison to synthetic composites, rendering them very appropriate as potential materials for vehicle interior components. Furthermore, biocomposites has numerous prospective uses within the automotive sector. Their inherent qualities make them very suitable for producing non-structural interior components, including timber flooring, seat cushions, seat backs, headliners, interior panels, dashboards, and thermo-acoustic insulation. Ongoing academic research is currently being undertaken on biocomposites, notwithstanding the absence of current implementation in structural part manufacture. Wood fibers are commonly used in the automobile sector for wood-plastic composites, whereas natural fibers including flax, hemp, jute, and sisal are utilized for natural fiber-reinforced composites [23], [24], [25]. These reinforcements can be applied with both thermoplastic and thermoset matrices. Various thermoplastic matrix choices are accessible, including biodegradable polyesters such as PLA, PHB, PBS, and natural polymers like bio-PC. The majority of these thermoplastic biopolymers are derived from the process of fermenting starch and glucose. Regarding thermosetting matrices, available choices encompass conventional resins containing bio-derived components sourced from natural oils and bioethanol (e.g. bio-epoxy, bio-polyester, bio-polyurethanes) [21]. Over the past decade, there has been a demonstration of the potential of lightweight, inexpensive natural fibers as alternatives to glass fiber and mineral fillers in automobile interior or exterior components. European automotive manufacturers have increased investments in the production of car door panels, seat backs, headliners, dashboards, and interior trim parts from natural fiber-reinforced thermoset or thermoplastic composite materials. The main reasons for the use of natural fibers such as kenaf, hemp, linen, jute, and sisal in the automotive industry are factors such as providing lightness, reducing costs, reducing CO_2 emissions, recyclability, and reducing dependence on foreign oil resources. With all these advantages, we can call natural fibers "sustainable" or "environmentally friendly" fiber sources. Although America has not yet made the necessary regulations considering the automotive scrap requirements, European and Asian countries have put forward strict principles on this issue [26]. In Europe, automotive manufacturers required 80% of car parts to be recyclable in 2006. In 2018, approximately 6.1 million vehicles became unusable within the borders of the European Union. As shown in Figure 1, more than 95%

of automotive parts or materials in the EU in 2018 were reused or salvaged. Figure 1 shows the graph of vehicles that have reached the end of their life, have finished their useful services, and have been treated as waste, broken down or disposed of in another way. During the dismantling phase, spare parts of the vehicle can be separated and reused for the repair of vehicles in service. The remainder of the dismantled vehicle will be recycled, used for energy production (energy recovery process), or ultimately disposed of.

Glass fiber-reinforced composites exhibit drawbacks including their elevated density (40% greater than natural fibers), challenging machinability, limited recyclability, and potential health hazards associated with glass fiber particles. In contrast, the environmental and economic benefits of natural fibers outweigh those of glass fibers. As an illustration, the total energy expenditure for producing flax fiber is 9.55 MJ/kg, but the energy requirement for producing glass fiber is 54.7 MJ/kg [28].



Note: Countries are ranked in decreasing order by the reuse/recovery rate.
Rates from 2020: Greece, Cyprus, Romania and Iceland
Source: Eurostat (online data code: env_waselvt)

Figure 1. Reuse/recovery rate and reuse/recycling rate of parts or materials in the automotive industry in European Union countries [27]

In general, natural fibers are used in the reinforcement of automobile parts;

- Reduction in cost
- Production processes are safer than those of glass fibers.
- It has good thermal and acoustic insulation properties
- Less reliance on foreign oil sources,
- They recycle and these fiber sources are "sustainable" or "environmentally friendly"

- High fiber volume fractions of low-density fibers in natural fiber-reinforced composites reduce the weight of the finished product as seen in Table 2

- Reduction in CO_2,

- Moreover, the interiors of automobiles with natural fiber reinforcement are physically safer than glass fiber parts because no sharp-edged surfaces are formed in the event of a collision [29].

In recent years, European companies such as Dieffenbacher (Germany), BASF (Germany), and Rieter Automotive (Switzerland) have led the way in the research of natural fiber-reinforced composites. In 2005, Rieter won first place in the "JEC Composite Showcase" competition with its success in the production of banana plant fiber reinforced composites, which saved more than 60% of energy [30]. In North America, to give a few examples, Delphi Interior Systems, Visteon Automotive, Kafus Biyo-Composites/ Flexform Technology and Cargill Ltd. companies have actively focused their research on such composites. In addition to all these developments, with the development of bio-based polymers, the use of 100% natural materials in the automotive industry will be inevitable.

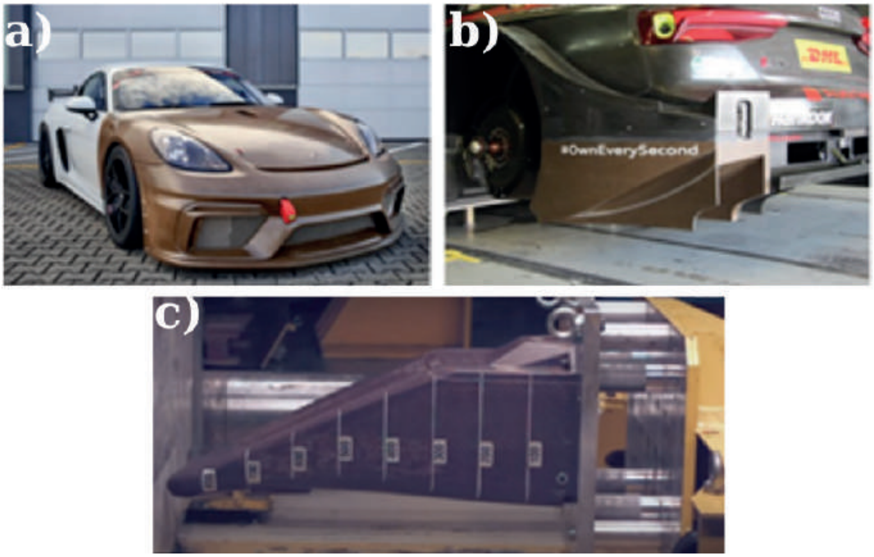


Figure 2. a) Porsche Cayman 718 GT4 CS MR with a natural fiber-reinforced composite body (September 2020) b) Natural fiber-reinforced composite "Shoebox" used by Audi motorsports (2020) c) Natural fiber-reinforced "crash box" crash test (October 2020)

In 2019 and 2020, significant developments have been made regarding the use of natural fiber-reinforced composites not only in automotive interior parts but also in body panels and areas exposed to impact during a collision. In 2019, Porsche manufactured the doors and rear wings made of carbon fiber-reinforced composite from natural fiber-reinforced composite for the first time in the Cayman 718 GT4 CS model used in motorsport, thus using natural fiber-reinforced composite parts in mass production for a vehicle used in motorsports. Another development is that in the Nürburgring race held on 24-27 September 2020, Porsche used a hood made entirely of natural fiber-reinforced composite on the Cayman 718 GT4 CS MR model (Figure 2a). Another important development is that a crash test of the natural fiber reinforced "Crash Box" part was conducted for the first time in October 2020 (Figure 2c). Another important development is that the part called "shoebox", which is made of glass fiber reinforced composite in the vehicles used in races by BMW sport and Audi Sport is manufactured using natural fiber reinforced composites (Figure 2b). [31]. All these new developments prove how important such composites are, especially in the automotive industry, and that natural fibers are gradually replacing synthetic fiber reinforcements today.

2.2. Additive Manufacturing in the automotive industry

3D printing or additive manufacturing AM is the creation of a three-dimensional object from a CAD model or digital 3D model. It can be done by processes in which material is deposited, combined, or solidified under computer control, where the material is added together (such as fusing plastics, liquids, or powder grains), typically layer by layer. AM technology has made a significant contribution to the automotive industry, from rapid prototyping to increasingly widespread production of final car parts and structural production of almost the entire car. It is known that natural fiber-reinforced biocomposites produced by AM and used in automotive parts will function as well as the currently used petroleum-derived plastics. However, there are some challenges in meeting the quality and safety standards expected from auto parts produced with the AM technique. Sustainable, relatively fast, and accurate production of complex automotive parts is possible with the AM printing method, as with the plastic injection method. Although it is not yet possible to buy a fully AM-printed car from a dealer today, AM printing has been prominent in the prototyping of auto parts and part development processes for many years. The initial technology for manufacturing parts was selective laser sintering or binder sputtering. These methods have helped designers and manufacturers create more aesthetic parts [32]. Additionally, AM printing has enabled a wide range of manufacturing applications, adding tremendous value to supply chains. New, flexible materials have made it possible to produce high-precision, functional parts that can replace final parts and offer high performance [33].

The AM approach provided a platform for creative designers and engineers to actualize daring concepts through the utilization of technology. Car components manufactured using the filament deposition technique exhibit reduced weight, leading to enhanced vehicle performance, improved fuel efficiency, and decreased energy use. Large companies such as Mitsubishi Chemical or BASF, which care about using filament deposition technology in the automotive industry, produce many automotive parts with the AM method. Long gone are the days when rapid prototyping was the primary use of AM technology in the automotive industry. By 2029, the AM market is predicted to generate as much as $9 billion in revenue. Volkswagen, BMW, and Ford respectively stand out in using AM printing technology to produce final automobile parts [34]. The parts and accessories market in the automotive industry is predicted to reach approximately 17 Billion USD by the end of 2025. According to Machine Design, the automotive industry's consumption of AM materials is expected to reach approximately $530 million by 2021 [32]. One of the most commonly used AM technologies currently in the automotive industry is FFF (Fused Filament Fabrication). Its advantage is the possibility of using many different materials whose properties are similar to plastic. With the use of AM, the required parts and details can be created, which allows companies to become independent from external suppliers and facilitate their production processes, as well as ensure production continuity, which is very important today. Bocar, a company engaged in the manufacture of fire trucks, uses the AM technique to create plastic subassembly prototypes. In collaboration with 3DGence, it has prepared a 1:1 scale extruded collector model. Figure 3. Thanks to the professional 3DGence INDUSTRY F340 printer, the element creation process was shortened by several months. Precast casting eliminates the need for manual welding of elbows, pipes, and flanges. In this way, hydraulic systems are more sensitive and the failure rate is reduced.

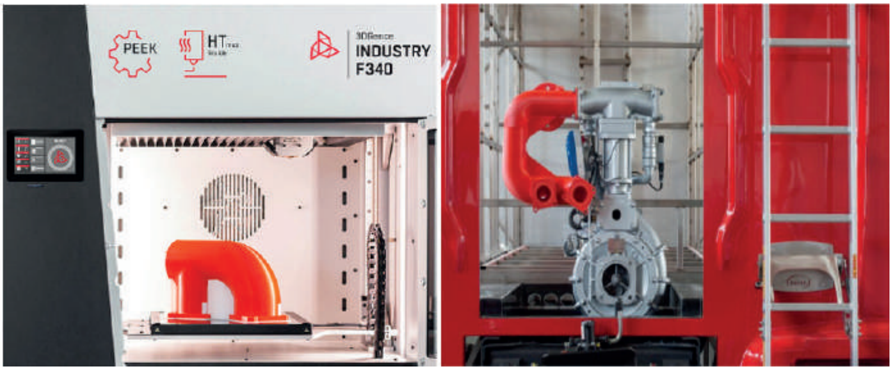


Figure 3. Extruded collector model [35]

The latest engineering solutions available on the market, including AM printing, were applied in the construction of the race car (Figure 4). Among other things, the casing of the battery pack was printed from a flammable material on a 3DGence INDUSTRY F340. In addition, this use of the AM technique enabled the creation of other parts and models, including molds of aerodynamic elements, from which we were able to independently prepare the necessary components for the racing car [36].

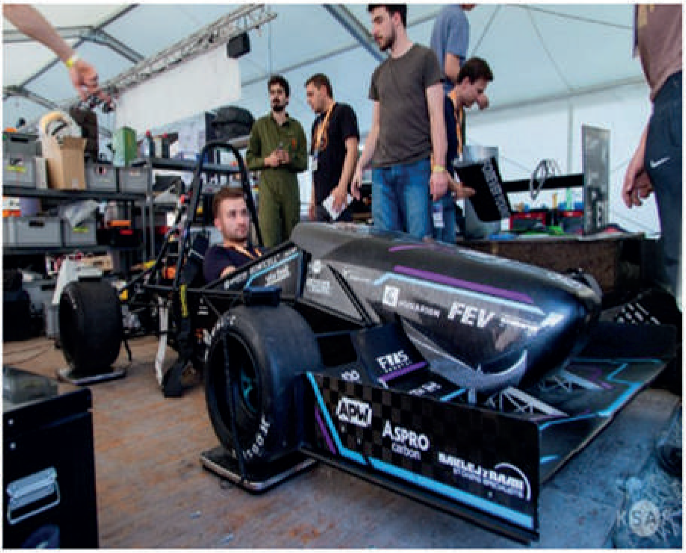


Figure 4. Example of a racing car produced with the AM technique

Formula Student is an annual engineering design competition in which student teams from all around the world compete to develop and race formula-style automobiles. Teams are judged based on their business plan, design concept, cost report, and race performance, particularly power, efficiency, and durability. This year, the team added a Form 3 SLA 3D printer to their toolbox in order to save time and money and build parts that would not be possible otherwise:

1. Prototypes: They print prototypes for various parts, such as anti-roll bar assemblies or HV Battery stakeholders.

2. Carbon fibre part moulds: The team printed a dozen moulds to make carbon fibre parts that couldn't be created any other way.

3. End-use parts: Approximately 30 final parts for cars have been printed directly with the AM technique, from button holders and steering wheel shifters to sensor connectors of hoses and cooling systems (Figure 5).

Figure 5. Carbon Fiber Molding and End-Use 3D Printed Parts for Formula Student Race Cars

One proof that AM is at a stage of dynamic development is the growing interest in it from large and well-established companies that were previously dealing with completely different topics. Companies have started to cooperate with printer and filament manufacturers and are developing solutions for both operating materials and software. They mainly focus on introducing AM printing in the aerospace and automotive industries. Only the best ones remain on the market, those that can deliver devices at affordable prices, and thus new projects can actually be realized. It is beneficial to evaluate the changes in the AM market today and get ahead of your competitors with the opportunities offered by technology.

Jorge et al. [37] showed that, according to the experimental results of their study, samples obtained with 20% wood flour showed lower mechanical properties, while those obtained from 30% of test samples became very brittle. They reported that mechanical properties such as torsional strength were higher in the test samples obtained by injection molding compared to AM FDM. TGA results of samples to understand the thermal behavior of composites showed that optimum temperatures were suitable for processing composites via AM. They claimed that composites could potentially be applied in the design of auto parts due to their biodegradability and mechanical strength.

2.3. Prototyping

In the automotive industry, the AM method is a widely used method for prototyping. Due to its ability to perform rapid prototyping, the 3D printing method and the prototype have become almost synonymous. With the AM method, prototypes of many parts, from very simple parts to dashboards and even scale models of the vehicle, can be produced quickly. Rapid prototype production with high precision and features close to the real product before mass production is important for the efficient operation of the factory. Using additive manufacturing (AM), it is possible to produce prototypes that are extremely persuasive, representative, and functional in just one day. Moreover, the cost of creating these prototypes is significantly reduced compared to traditional manufacturing techniques [33].

3. Manufacturing Methods in Additive Manufacturing

AM, like any other manufacturing process, necessitates good materials (including high-quality 3D printers with good resolution and high-quality software) that adhere to strict specifications and consistently produce major elements [38]. Traditional manufacturing techniques necessitate seriously elegant supply chain management, a significant business advantage to be robotized, the AM printing process necessitates robotization, and are reliant on CAD programming to print items using a variety of materials, radically reducing the measure of supply chain management. When everything is said and done, AM printing does not require any expensive dies, tools for machining, structures, or punches, and is cost effective. Depending on the source, AM print production procedures vary. Depending on the applications of the components, any of the strategies can be used. The classifications of AM print production techniques are shown in Figure 6 [39]. Figure 6 depicts the classification of several AM approaches.

Powder-Based Systems

Powder-based additive manufacturing (AM) is a technique where a powdered substance is fused together to create solid, functional components.

Bonding can be achieved through the use of heat, which causes the powder material to undergo partial or complete melting and fusion. Alternatively, bonding can be facilitated by introducing a coupling agent to the powder. The powder-based system is a method used in 3D printing for production. The manufacturing process utilises standard and traditional inkjet printheads to produce components. The powder bed exhibits porosity and undergoes condensation during the solidification process, leading to dimensional alterations or potential failure [40], [41].

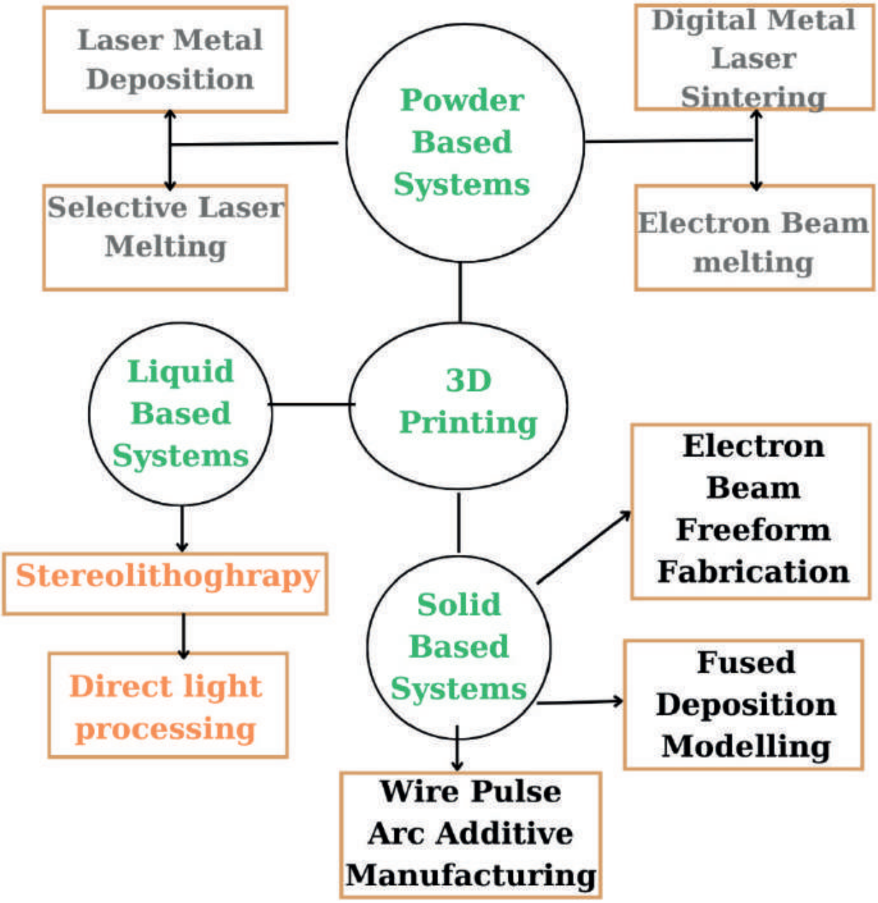


Figure 6. Classification of additive manufacturing

Laser Metal Deposition (LMD)

LMD, short for Laser Metal Deposition, is an additive manufacturing method that use a laser beam to convert a metallic base material into a molten pool of dissolved metal. This procedure entails injecting metal powder into the substrate by use of a gas flow.

Direct laser metal sintering (DLMS)

Direct laser metal sintering (DLMS), also known as direct laser metal forming (DLMF) and selective laser melting (SLM), is a process where a powerful laser beam is focused onto a bed of metal powder, causing the metal particles to fuse together in a predetermined shape [42].

Selective Laser Melting

Selective laser melting (SLM) is a technique that involves using a laser beam to heat metallic powder materials to their melting temperature, causing the powder layer to fully melt. Notably, SLM does not require the use of binders or fluxing agents in the metallic powder materials [43].

Electron Beam Melting (EBM)

Electron beam melting (EBM) is a recently developed additive manufacturing (AM) method that use a computer-controlled electron gun to create solid 3D objects directly from metal powder [42]. Electron beam melting (EBM) is an advantageous method of additive manufacturing that offers distinct benefits in the production of intricate metal components of superior quality. It is particularly helpful in industries that prioritise precision, performance, and the use of lightweight materials [38].

Laser Metal Deposition (LMD)

The pieces are fabricated utilising the material in its solid state, regardless of its prior liquid state, save for powdered material. Diverse configurations of solid materials, including rolls, laminates, wires, pellets, and more. It has the capacity to exist in that particular form. The initial solid-based additive technology comprises wire-pulsed arc additive manufacturing, fused deposition modelling, electron beam manufacturing, and laminated object manufacturing [44].

Liquid-Based Systems

Stereolithography is the technical term for liquid-based rapid prototyping. The primary methodology employed in liquid-based systems entails the production of components utilising a photocurable semi-liquid resin, which is subjected to irradiation by a laser beam to induce photopolymerization. Consequently, the process of polymerization induces the transformation of a substance into a solid state following a specific duration of laser exposure. Typically, in liquid-based additive manufacturing (AM) systems, parts are created by immersing them in a container filled with a light-sensitive liquid resin. This resin, which is capable of hardening or solidifying when exposed to light, particularly in the ultraviolet (UV) spectrum, is used. The light causes the resin to solidify close to the surface, resulting in the formation of a thin, solid layer [45], [46].

Wire Pulse Arc Additive Manufacturing (WPAAM)

Wire arc additive manufacturing (WAAM) is a method of additive manufacturing that utilises metal wire as the raw material. This wire is melted using an electric arc to create a complicated 3D item by depositing layers one at a time. When compared to laser or electron beam-based additive manufacturing (AM) technologies, the WAAM process requires a significant amount of heat input. This is because the electric arc used in WAAM has a comparatively low energy density, resulting in low melting efficiency [47].

Stereolithography (SL)

Stereolithography (SL) is the method of solidifying layers of polymers that are responsive to UV light. Stereolithography is an additive manufacturing technique that enables the production of items from a CAD file, similar to other creative manufacturing methods. In order to produce three Objects using stereolithography, it is necessary to carefully control liquid tar so that it undergoes photopolymerization and solidifies [48].

Fused Deposition Modeling (FDM)

Fused Deposition Modelling (FDM) is a widely utilised technology in additive manufacturing (AM) that involves the extrusion of thermoplastic materials from a nozzle tip. These materials are heated to a semi-molten state and then deposited onto a substrate, resulting in a three-dimensional structure [49].

Electron Beam Freeform Fabrication (EBFF)

Presently, there is ongoing development of a cross-cutting process known as EBFF, which generates conceptual metal pieces. This technique can be employed to fabricate intricate, consolidated components using a layer-by-layer material method. However, it is more efficient in terms of speed when utilised to add intricate features to pre-existing castings, forgings, or plated goods. EBFF employs a powerful electron beam that operates within a confined region [38].

Direct Light Processing (DLP)

DLP, an acronym for Digital Light Processing, is an advanced 3D printing method used to quickly manufacture photopolymer components. SLA and DLP devices share similarities, although they diverge in their curing techniques. SLA machines utilise a laser to track and cure one layer at a time, while DLP machines use a reflected light source to cure the entire layer all at once. The use of DLP technology allows for the simultaneous solidification of the entire layer [50].

4. Conclusion

Consequently, the automobile industry is experiencing a steady rise in the manufacturing of biocomposites. The use of additive manufacturing techniques in the creation of composite materials for the automobile industry is increasingly prevalent due to its ability to guarantee precision, cost-effectiveness, and efficiency. The manufacturing business has had a substantial metamorphosis in recent years, primarily attributable to the advent of 3D printing technology, sometimes referred to as additive manufacturing. This groundbreaking manufacturing approach has provided opportunities for inventive applications that offer potential cost reductions, more design flexibility, and increased effectiveness. Over the years, 3D printing has transitioned from being a specialized industrial process to becoming a widely used technology with diverse applications. The automotive sector also reaped the advantages of this manufacturing technique and actively promoted the production of diverse components, particularly composite parts.

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