

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

**SYNTHESIS OF POLY(METHYL METHACRYLATE) REINFORCED BY
GRAPHENE NANOPATES**



M.Sc. THESIS

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Department of Nano Science & Nano Engineering

Nano Science & Nano Engineering Program

JUNE 2021

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**GRAFEN NANO PLAKALAR İLE GÜÇLENDİRİLMİŞ POLİ(METİL
METAKRİLAT) SENTEZİ**

YÜKSEK LİSANS TEZİ

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To my family,



FOREWORD

Behind these pages that you will turn, there are not only hours of research, but there is also the support I got from my advisor, family, colleague.

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ABBREVIATIONS

T_m	: The crystalline melting temperature
T_g	: The glass transition temperature
T_d	: Thermal degradation temperature
ATRP	: Atom transfer radical polymerization
CRP	: Controlled radical polymerization
RAFT	: Reversible addition-fragmentation chain transfer
SFRP	: Stable free radical polymerization
NMP	: Nitroxide mediated polymerization
MMA	: Methyl methacrylate
DP	: The degree of polymerization
RX	: Alkyl halides
PMMA	: Poly(methyl methacrylate)
PS	: Polystyrene
QDs	: Quantum dots
SCs	: Stereo complexes
PNMs	: Polymeric nanostructured materials
UV	: Ultraviolet
NP	: Nanoparticle
PQ	: Phenanthrenequinone)
RGO	: Reduced graphene oxide
CNTs	: Carbon nanotubes
f-CNTs	: Functionalized carbon nanotubes
SERS	: Surface-Enhanced Raman Scattering
AuNRs	: Gold nanorods
GFs	: Glass fibers
GO	: Graphene oxide
DMC	: Dual modified organoclay
nm	: Nanometer
0D	: Zero-dimensional nanomaterials
1D	: One-dimensional nanomaterials
2D	: Two-dimensional nanomaterials

3D	: Three-dimensional nanomaterials
NMs	: Nano materials
NPs	: Nanoparticles
GNPs	: Graphene nanoplatelets
CVD	: Chemical Vapor Deposition
PPF	: Poly(propylene2,5-furandicarboxylate)
PP	: Polypropylene
PA6	: Polyamide 6
HDPE	: High density polyethylene
PPy	: Polypyrrole
Bu₄NBr	: Tetrabutylammonium bromide
EBIB	: Ethyl 2 -bromoisobutyrate
PMDETA	: Pentamethyldiethylenetriamine
wt.	: Weight
SEM	: Scanning Electron Microscope
MEM-TEK	: National Research Center on Membrane Technologies
XRD	: X-Ray Diffraction
ATUM	: Prof. Dr. Adnan Tekin Applied Research Center of Materials Science and Production Technologies
FTIR	: Fourier Transform Infrared Spectroscopy
TGA	: Thermogravimetric Analysis
DSC	: Differential scanning calorimetry
XPS	: X-ray Photoelectron Spectroscopy
KUYTAM	: Koç University Surface Science and Technology Center
CA	: Contact Angle
PLA	: Polylactic acid
PVDF	: Polyvinylidene fluoride

SYMBOLS

Cu	: Copper
CuBr	: Copper Bromide
k_{act}	: The activation rate constant
k_{deact}	: The deactivation rate constant
K_{ATRP}	: The equilibrium constant of ATRP process
g	: Gram
Pa	: Pascal
J	: Joule
m	: Meter
Å	: Angstrom
V	: Volt
Hz	: Hertz
Ar	: Argon
C	: Carbon
O	: Oxygen
C_L	: The velocity of longitudinal waves
C_T	: The velocity of transverse waves
ρ	: density
ν	: Poisson's ratio
G	: Shear modulus
E	: Young's modulus
H	: Hardness



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SYNTHESIS OF POLY(METHYL METHACRYLATE) REINFORCED BY GRAPHENE NANOPlates

SUMMARY

Poly(methyl methacrylate) (PMMA) is the transparent and clear thermoplastic and it has a lot of applicable usages in different industrial areas. Nevertheless, electrical conductivity, mechanical performance, and thermal stability are a disadvantage for PMMA. In the aim of enhancing its structural characteristics, several nanomaterials are utilized as fillers. Graphene nanoplatelets (GNPs) was used as a nanofiller in Poly(methyl methacrylate) (PMMA) synthesized by the Atom Transfer Radical Polymerization (ATRP) method. The first step in the synthesis of the PMMA/GNPs was the dispersion of GNPs in the PMMA liquid monomers by combining the solutions so that GNPs had superior thermal stability, mechanical properties and electrical conductivity also lower density of mass. Then the crosslinked PMMA/GNPs nanocomposite samples were produced by using the in-situ polymerization method. However, there was a challenging technical problem in the application of GNPs (at a large amount) in the polymer. For the purpose of benefiting from the advantageous properties of GNPs (especially in bulk quantities) at PMMA, the major problem at the synthesis of PMMA/GNPs nanocomposite was the GNPs dispersion in the polymer matrix. This research has focused on solving the dispersion problem. The aims of the enhancement of the mechanical properties of the nanocomposite were performed by utilizing the ATRP method as the effective production technique. The structural characterization of PMMA/GNPs nanocomposite was performed for the examination of the integration of GNPs in PMMA. In the aim of determining the interactions of materials, several methods were used to characterize the materials' structural and chemical properties: SEM, XRD, FTIR, TGA, Raman Spectroscopy and XPS analysis, Static Contact Angle measurement, and Ultrasonic test.

The surface morphology of the PMMA/GNPs nanocomposite was analyzed using SEM analysis images. In the analysis of scanning electron microscopy, micron-scale lack of huge agglomerates shows outstanding dispersion of GNPs in the PMMA matrix. X-Ray Diffraction (XRD) as a non-destructive test method was used to examine the changes in the crystalline features of the nanocomposites' structure with the rise of the nanofiller amount in PMMA. The nanocomposite XRD diffraction patterns had a $\sim 26.5^\circ$ peak, which corresponded to the 0.34 nm distance graphene layers stacking. With the rise of the nanofillers concentration, the peak intensity has increased. Improving crystallinity with the addition of GNPs results in enhancement in the mechanical properties of polymer nanocomposites as well. FTIR was utilized to investigate the chemical structure of polymer nanocomposites and PMMA. Pure PMMA spectra were similar to the spectra of the nanocomposites, indicating that the polymer and nanofiller interaction was successful. TGA analysis was utilized to measure the change of mass associated with temperature increase. There was a $\sim 47^\circ\text{C}$

heat increase and weight loss of 5% at GNPs 3% compared to pure PMMA. Raman spectroscopy was used to evaluate the GNPs bonding interaction and exfoliation extent with PMMA. Raman spectra of PMMA/ GNPs nanocomposite samples and Pure PMMA have shown similar changes of the main three peaks which depend on the concentration of GNP (~ 1350 , ~ 2700 and $\sim 1580\text{ cm}^{-1}$). All of the Raman peaks slight decrease of intensity was caused by the increase of graphene layer amount.

XPS analysis method was used to examine the PMMA/GNPs nanocomposites' surface chemistry and change of chemical composition. The XPS spectrum displayed higher intensity of C1s and O1s peaks with GNPs amount increase. The locations of these peaks in this study were almost identical with the locations of the peaks (with the other Polymer/GNPs structures) in the literature. Static Contact Angle Measurement was taken place to analyze the strength of contact, wettability, and hydrophobicity in the interaction between solid and liquid. By measuring the contact angle of a distilled water drop that was deposited on the polymer's surfaces, the determination of the nanocomposite wettability was carried out. PMMA is a polymer that is hydrophilic with an approximately 68° water contact angle. At GNPs 0.2% a 73.6° contact angle was measured and at GNPs 3% was 82.4° . In this study, the nanocomposite contact angle has increased with the nanofillers' addition. By utilizing ultrasonic tests, the examination of the nanocomposite structure discontinuous or volumetric changes and the nanofillers dispersion quality was carried out. The polymer matrix nanofillers excellent homogenous dispersion was proved by the results of this study. The nanocomposite mechanical properties detailed information about the enhancements were gained by utilizing the ultrasonic nondestructive test. At GNPs 3% the optimum values of Microhardness, Young's modulus and Shear modulus were achieved. In comparison to the pure PMMA an 18.22%, 17.54% and 17.63% respectfully enhancement rate was gained. With the concentration increase of GNPs, the elastic properties got slightly improved. In spite of using very low amounts of graphene the nanocomposites' mechanical and thermal properties were improved dramatically.

GRAFEN NANO PLAKALAR İLE GÜÇLENDİRİLMİŞ POLİ(METİL METAKRİLAT) SENTEZİ

ÖZET

Polimerler günümüz toplumunda oldukça büyük bir öneme sahiptir. Sentetik bir polimer türü olan plastikler hayatımızın vazgeçilmez bir parçası haline gelmiştir. Bir termoplastik türü olan Poli(metil metakrilat) (PMMA) bunlardan biridir ve farklı endüstriyel alanlarda pek çok uygulanabilirliğe sahiptir. PMMA; olağanüstü optik özellikler, saydamlık ve parlaklık, mor ötesi ışınlarla ve hava koşullarına karşı gösterdiği direnç, sertlik ve çizilmeye karşı dayanıklılık, rijitlik ve boyutsal sağlamlık ve sınırsız renk seçenekleri gibi üstün özelliklere sahiptir. PMMA'nın bir diğer yararı ise %100 geri dönüştürülebilir olması ve bu sayede doğal kaynak israfına neden olmamasıdır. PMMA, bu avantajlı özellikleri sayesinde diğer plastikler arasında öne çıkmaktadır ve birçok mühendislik uygulaması için yaygın olarak kullanılmaktadır. Bununla birlikte, PMMA, uygun mekanik performans ve termal kararlılık gibi bazı özelliklerden yoksundur. Bu noktada, bilim insanları tarafından, polimerlerin özelliklerini iyileştirmek için bazı dolgu malzemeleri kullanılmaktadır. Son yıllarda etkisini her alanda gösteren nanoteknolojinin önemi bu alanda da göze çarpar. PMMA'nın yapısal özelliklerini iyileştirmek için farklı nanomateryaller dolgu maddesi olarak kullanılabilir. Bu çalışmanın konusu; endüstrinin çeşitli alanlarında, özellikle uzay sanayi ile uydu ve havacılık alanlarında kullanılmak üzere, birçok avantajlı özellik barındıran PMMA'nın üstün özelliklere sahip nano malzemeler ile bir araya getirilerek avantajlı özelliklerinin artırılması ve geliştirilmesidir. Bu bağlamda, PMMA'nın mekanik ve termal özelliklerini geliştirmek için, son yıllarda nano dolgu malzemeleri arasında üstün özellikleri ile göze çarpan Graphene Nanoplatelets (GNPs) dolgu malzemesi olarak seçildi. Bu nedenle, bu tez çalışmasında GNPs katkısı ile PMMA yapıda meydana gelen değişimler incelenmiştir.

Grafen, 21. yüzyılın mucize malzemesi olarak görülür. GNPs, katmanlar arası mesafe 0.34 nm olan birkaç katman grafenden meydana gelir ve bu katmanlar birbirlerine zayıf Van der Waals kuvveti ile tutunur. Plastikler ile yaygın kullanımı olan Graphene Nanoplatelets (GNPs); mükemmel elektriksel ve termal iletkenlik ve yüksek elastik modül ve mekanik dayanım gibi üstün özelliklere sahiptir. Aynı zamanda, yüksek en boy oranı özellikleri ile nanokompozitler için umut vadeden bir nano dolgu malzemesidir. Bu bağlamda, GNPs'nin sahip olduğu üstün özellikler dikkate alınarak bu tez çalışmasında PMMA/GNPs nanokompozitleri geliştirilmiştir.

Bu çalışmada, Poli(metil metakrilat) (PMMA) sentezi için Atom Transfer Radikal Polimerizasyon (ATRP) yöntemi seçildi. ATRP yöntemi ile polimer sentezi birçok avantaja sahiptir. ATRP işlemi, zahmetsiz reaksiyon koşulları altında ticari olarak erişilebilir reaktifler kullanılarak gerçekleşir. ATRP ayrıca dikkat çekici derecede makro moleküler yapının kontrol edilmesini sağlar. ATRP ile çeşitli uygulamalarla çok sayıda yeni malzemenin oluşturulması mümkündür. Bu avantajlarının yanında, ATRP'nin zorlayıcı ve dikkat gerektiren bazı özellikleri de mevcuttur. ATRP, çok

bileşenli yapısı nedeniyle karmaşık bir süreçtir, bu nedenle optimum koşulları bulmak yorucudur. Yüksek performanslı kompozitler üretebilmek için üretim aşamasında oldukça dikkatli ve titiz çalışmak gerekir. ATRP yönteminin bir diğer dikkat gerektiren yönü oksijen duyarlılığıdır. Oksijen sürekli olarak radikallerin üretilmesine neden olur. Reaksiyon karışımında az miktarda oksijen olsa bile, reaksiyonun tüm seyri etkilenebilir. Bu durumda istenen üstün özelliklerde nanokompozit üretmek imkânsız hale gelir. Bu yüzden, nanokompozit üretim süreci argon gazı bulunan ortamda gerçekleştirilir ve bu konuda gerekli tüm önlemler alınır. Polimer, katılaşmaya başlayıp kalıba döküleceği ana kadar oksijen ile temas ettirilmez. Bu sayede istenilen termal ve mekanik özelliklere sahip nanokompozit üretimi mümkün hale gelir. Çapraz bağlı PMMA/GNPs nanokompozit numuneleri yerinde polimerizasyon yöntemi kullanılarak sentezlendi. GNPs dolgu malzemesinin polimer matrisi içinde homojen dağılımını sağlayan en etkili yöntemi yerinde polimerizasyon yöntemidir. Ancak, polimerde GNPs dolgu malzemesinin (özellikle büyük miktarlarda) uygulanmasında zorlayıcı bir nokta vardır. GNPs dolgu malzemesinin (özellikle toplu miktarlarda) avantajlı özelliklerinden yararlanmak amacıyla, PMMA/GNPs nanokompozit sentezindeki en büyük problem, polimer matrisinde GNPs'lerin homojen dağılımıdır. Bu çalışma, etkin bir üretim tekniği olarak ATRP yöntemini kullanarak nanokompozitlerin mekanik özelliklerini geliştirmek amacıyla bu dispersiyon problemini çözmeye odaklanmıştır.

PMMA/GNPs nanokompozit örneklerinin karakteristik özelliklerini çeşitli yönlerden analiz etmek; nano dolgu malzemesinin polimer üzerindeki etkisini gözlemleyebilmek ve PMMA'ya entegrasyonunu inceleyebilmek amacıyla birçok karakterizasyon yöntemi uygulanmıştır: SEM (Taramalı Elektron Mikroskop) karakterizasyonu, XRD (X-Işını Kırınımı) analizi, FTIR (Fourier Dönüşüm Kızılötesi Spektroskopisi) analizi, TGA (Termogravimetrik) analizi, Raman Spektroskopi Analizi, XPS (X-Işını Fotoelektron Spektrometresi) analizi, Statik Temas Açısı ölçümü ve Ultrasonik test.

PMMA/GNPs nanokompozitlerinin yüzey morfolojisi SEM görüntüleri kullanılarak analiz edildi. Nanokompozitlerin yüzeyinde büyük aglomeraların görülmemesi, GNPs'lerin PMMA matrisinde homojen dağıldığını gösterir. Bu homojen dağılım, GNPs nano malzemenin PMMA'nın yüzeyine iyi bir şekilde yapıştığı anlamına gelir. Homojen dağılım aynı zamanda gelişmiş mekanik özelliklere işaret eder. Bu yüzden oldukça büyük bir öneme sahiptir.

XRD analizi, PMMA'daki GNPs miktarının artmasıyla nanokompozit yapının kristal özelliklerindeki değişiklikleri incelemek için yapıldı. Nanokompozit XRD kırınım desenleri, 0.34 nm mesafeli grafen katmanlarının istiflenmesine karşılık gelen ~ 26,5°'lik bir tepe noktasına sahipti. GNPs konsantrasyonunun artmasıyla pik yoğunluğu artmıştır. Bununla birlikte, kütlece düşük konsantrasyonlu numunelerde (%0,2 ve %0,5) zar zor farkedilir bir GNPs zirvesi vardır. Bu durum GNPs nanomalzemenin PMMA içerisinde tamamen dağıldığını gösterir. GNPs'lerin eklenmesiyle kristallliği iyileştirmek, polimer nanokompozitlerin mekanik özelliklerinde de iyileşme ile sonuçlanır.

PMMA'nın kimyasal yapısının, GNPs eklenmesiyle birlikte nasıl bir değişiklik gösterdiği FTIR analizi yapılarak araştırılmıştır. Saf PMMA spektrumları, PMMA/GNPs nanokompozitleri ile eşdeğer spektrumlar gösterdi; bu da PMMA polimer matrisi ile GNPs arasında güçlü bir etkileşimin var olduğunu gösterir.

TGA analizi, üretilen nano kompozitlerin termal kararlılığını incelemek amacıyla uygulandı. Analiz sonuçlarından elde edilen verilere göre, GNPs nano dolgu malzemesinin katkısı ile PMMA'nın termal kararlılığı önemli derecede artmıştır. GNPs nano katkı malzemesinin nanokompozitler içerisindeki kütlece yüzdesi arttıkça, nanokompozitlerin termal kararlılığı da artmıştır. En iyi termal kararlılık kütlece %3 GNPs ile görülmüştür. Saf PMMA'ya kıyasla, kütlece %3 GNPs eklendiğinde PMMA/GNPs nanokompozitin %5'lik kütle kaybı $\sim 47^{\circ}\text{C}$ 'lik bir sıcaklık artışı ile gerçekleşmiştir.

GNPs nano dolgu malzemesinin PMMA ile bağlanma etkileşimini ve pul pul dökülme derecesini değerlendirmek için Raman spektroskopi analizi uygulandı. Raman analiz sonuçları, GNPs konsantrasyonuna bağlı olarak üç ana pik değişimi (~ 1350 , ~ 2700 ve $\sim 1580\text{ cm}^{-1}$) göstermiştir. PMMA/GNPs nanokompozitlerinin içerisindeki grafen katmanlarının sayısındaki artış nedeniyle, Raman zirve noktalarının şiddeti azalmıştır.

PMMA/GNPs nanokompozitlerinin kimyasal bileşimindeki değişikliği ve yüzey kimyasını karakterize etmek için XPS analizi uygulandı. XPS spektrumu, GNPs miktarının artmasıyla daha yüksek yoğunlukta C1s ve O1s zirveleri sergiledi. XPS analiz sonuçları, PMMA/GNPs nanokompozitlerin nanometre mertebesinde homojen bir yapı oluşturduğunu gösteriyor. Bu çalışmadaki piklerin pozisyonları, literatürdeki piklerin pozisyonları (polimer yapısında GNPs'lerin varlığı) ile benzerdi.

Statik Temas Açısı ölçümü, katı ve sıvı arasındaki etkileşimde temasın mukavemeti, ıslanabilirlik ve hidrofobikliği incelemek için yapılmıştır. Nanokompozitlerin temas açısı, nano dolgu ilavesiyle artmıştır. PMMA, yaklaşık 68° temas açısına sahip hidrofilik bir polimerdir. GNPs nano dolgu malzemesi, PMMA'nın temas açısı değerini arttırmada etkili oldu. En yüksek temas açısı değeri ağırlıkça %3'te $82,4^{\circ}$ olarak ölçülmüştür. Bu temas açısı değerinin literatürdeki diğer Polymer/GNPs nanokompozitlerinin temas açısı değerleri ile karşılaştırıldığında yüksek bir değer olduğu görülür.

PMMA/GNPs nanokompozitlerin mekanik özelliklerini tespit etmek için Ultrasonik test uygulandı. Mekanik özelliklerin tespiti, nanokompozitlerin yoğunluk değerleri ve malzeme içerisinde ilerleyen boyuna ve enine dalga hızları kullanılarak hesaplanmıştır. PMMA/GNPs nanokompozitlerinin yoğunluk ölçümü Gaz Psikometrisi tekniği kullanılarak yapılmıştır. Ultrasonik test yöntemi kullanılarak PMMA/GNPs nanokompozitlerinin Mikrosertliği, Kesme modülü ve Young modülü değerleri hesaplanmıştır. GNPs, PMMA'nın mekanik özelliklerini arttırmak için faydalı ve etkili bir nano dolgu malzemesidir. GNPs nano dolgu malzemesinin polimer matrisi içerisindeki kütlece yüzde artışı ile elastik özellikler geliştirildi. Kütlece %3 GNPs'den oluşan nanokompozitte; Mikrosertlik, Young modülü ve Shear modülü için optimum değerlere ulaşılmıştır. Sonuçlar saf PMMA ile karşılaştırıldığında: Mikrosertlik, Young modülü ve Shear modülü için sırasıyla %18,22, %17,54 ve %17,63 oranında iyileşme oranı elde edildi. Polimer matris içindeki nano dolgu malzemelerin mükemmel homojen dağılımı bu çalışmanın sonuçları ile kanıtlanmıştır. Bu çalışmada, düşük miktarlarda grafen kullanılmasına rağmen nanokompozitlerin mekanik ve termal özellikleri önemli ölçüde iyileştirildi.



1 INTRODUCTION

1.1 Polymer

Polymers are used in daily life in almost every material, which means they are advanced widely used materials. Thanks to polymers' wide applications in different sectors such as science and industry, polymers' importance has been much more highlighted. Before the manufactured polymers natural polymers such as natural rubber, starch, and cellulose have been there since the beginning. The study of manufactured polymers has started in the middle of the nineteenth century. Recently, the industry of polymer has developed rapidly and it is larger than the aluminum, steel, copper industries combined[1].

"Poly" and "mono" are Greek prefixes, and mean "many" and "single" respectively. The expression of "Polymer" implies that the molecules have been created by monomers connecting via covalent bonds. Monomers are the building materials of polymers. Polymers consist of several monomers which connect jointly in an identical manner repeatedly (Figure 1.1). Many parameters affect the polymers' properties such as polymerization degree, monomers type, chemical bonds among with repeated blocks, chain structure, monomers order in copolymerization, some particular interactions (e.g., dipole-dipole interaction), additives, and material process[2].

Polymers (or conventional macromolecules) which is formed from at least some hundred atoms that are linked covalently and their molar masses obviously over 10³ g/mol. Almost all the properties in bulk and solution depend on the molecular weight and the polymerization degree which makes them the most important macromolecular substances characteristics. The number of monomer units that are linked to form the chain of polymer is indicated by the polymerization degree[3].

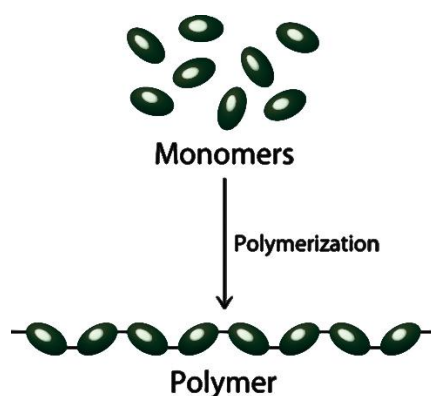


Figure 1.1 Forming of Polymer [2].

Properties of polymers are connected intimately to their shape and size. The polymers' shape is connected intimately to the several secondary and primary bonding forces that are present between and in chains and several sizes of units that comprise the macromolecule. Macromolecules or polymers got lengths of chains that are longer than the entanglement critical length, also are compounds that have a high molecular weight. When the length of the chain is greater than the critical length high molecular weight polymers' physical properties and melt viscosity will have an abrupt change [4].

The size of polymers gains them importance. The manufacture of polymers uses widely available and cheap materials which make major production cost-effective, however, they are just a cheap substitute to non-polymers compounds. Their chemical and physical properties are usually desirable. On a basis of weight, some polymers got greater mechanical strength than steel[4].

The integration of numerous efficient features of polymers makes them successful in all sectors. The primary motives to utilize polymers are: Polymers are easily processable, and moldable materials. They also possess some superior properties such as good environmental stability, corrosion resistance. They are capable of modifying by in-organic components or other polymers. Other significant arguments are low cost on production and lightweight. Besides, they are capable of recycling[5].

The crystalline melting temperature T_m and the glass transition temperature T_g are two main types of transition temperatures characterizing polymeric materials. The melting temperature of the crystalline domains of a polymer sample is the crystalline melting temperature. At glass transition temperature, polymer transforms from rubber to glass[6].

1.1.1 Classification of polymers

The classification of polymers is depending on different considerations.

1.1.1.1 Classification based on origin of source

Natural polymers: Nature-sourced polymers are referred to as a class of polymers named natural polymers. They can be found in animals and plants and they mainly contain proteins and carbohydrates which mainly provide structural support [7].

Natural polymers are separated into two groups basically on the method of formation as condensation and addition polymers. There are mainly six classifications for natural polymers according to the source: Lignin, polyisoprenes, polynucleotides, polysaccharides, polyesters, and proteins[7].

Semi-synthetic polymers: Modifying natural polymers can give semisynthetic polymers which are created by chemical derivatization of macromolecules that are natural and organic, based generally on polysaccharides[8].

Synthetic polymers: Thanks to non-toxic, high available, and economical natural there are wide applications especially in the sector of pharmaceutical for natural polymers and synthetic. Also, they have the capability to chemical modifications, biocompatible (with some exceptions), and possibly biodegradable[9].

1.1.1.2 Classification based on (molecular forces) the behavior of polymers with rising temperature.

Since it is mainly based on polymers underlying molecular structure this classification method has superiority over other methods. Figure 1.2 shows the most used polymer classification method. They separate into three groups, thermosets, elastomers, and thermoplastics. Thermoplastics separate into amorphous and crystalline[10].

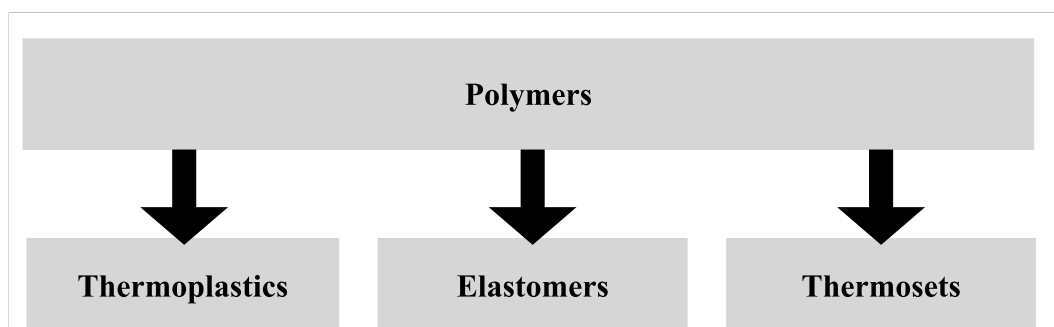


Figure 1.2 Schematic scheme of classification of polymers based on molecular forces [10].

Thermoplastic polymers: Thermoplastic polymers are polymers that possess the fibers and elastomers' intermediate intermolecular forces. They are linear polymers without a cross-link chain in the chemical structure [11].

Thermosetting polymers: Thermosetting polymers are manufactured from semi-fluid polymers with low molecular mass. Chain molecules that branch extensively with broad cross-links when heated are known as Thermosetting. The polymer will be unrecyclable and cannot be fused[11].

Elastomers: Polymers like rubber with temperatures under room temperatures and glass transition are known as Elastomeric materials. Polymers that are substantially stretchable beyond their default dimensions and retractable forcibly and rapidly to their default dimensions[12].

Thermoset polymers are made of cross-linked systems; however, thermoplastic polymers are composed essentially of branched and linear molecules, this is the main structural difference between them. The consideration of modulus change with temperature for thermosets and thermoplastics polymers illustrates thermal behavior differences of both polymers in the best way (Figure 1.3) [13].

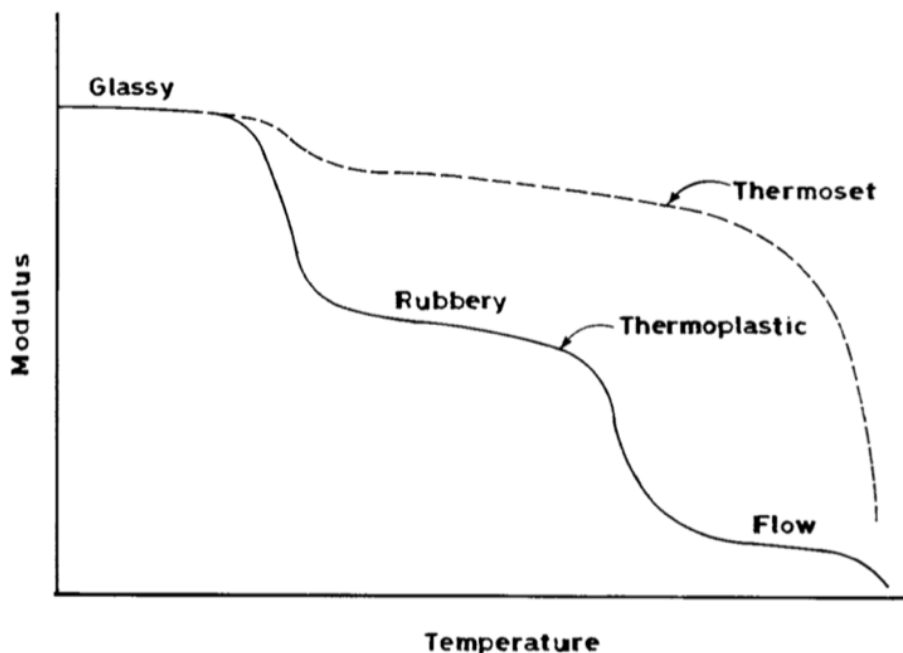


Figure 1.3 The thermal behavior differences of polymers[13].

1.1.1.3 Classification based on crystallinity

Unordered and ordered polymers are indicated by the terms amorphous and crystalline respectively. Crystalline behavior degree differs between polymers. Partially crystalline polymers are referred to using the semicrystalline term. It is rare to encounter a polymer that is completely crystalline. Only a T_g is shown by polymers that are completely amorphous. Only a T_m is shown by polymers that are completely crystalline. Both glass transition and crystalline melting temperatures are exhibited by semicrystalline polymers[6].

1.1.1.4 Classification based on the structure of polymer

Linear polymers: Linear polymers have repeat units that are connected to each other consecutively in a sole chain. Between the chains, hydrogen and Van der Waals bonding could exist. These long chains are supple, as illustrated in (Figure 1.4a). Poly(methyl methacrylate), poly(vinyl chloride), polyethylene, and nylon are some of the conventional polymers that are formed by linear structures[14].

Branched polymers: Structural units that are resulted from the polyfunctional molecule's reaction could be linked in a way to form structures that are nonlinear. Sometimes before the ability of chains to linked with each other each polymer side growth can be terminated (Figure 1.4b) [14].

Cross-linked polymers: At various positions, adjoining linear chains that are connected one to another form crosslinked polymers (Figure 1.4c) [14].

Network polymers: In network polymers, three or more active covalent bonds are formed by multifunctional monomers (Figure 1.4d). In fact, highly crosslinked polymers can be described as network polymers [14].

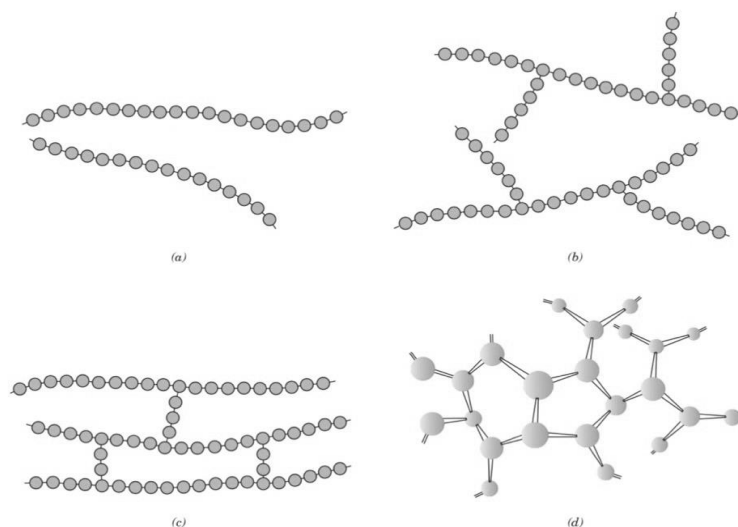


Figure 1.4 (a) Linear, (b) Branched, (c) Cross-linked, and (d) Network (three-dimensional) molecular structures are schematized. The circles represent distinct repeating units [14].

One of the first types of polymers that have been commercialized is Network polymers called resins[15].

1.1.1.5 Classification based on homogeneity of polymers

Homo Polymers: Homo Polymers polymer molecules have a single repeating unit.

Copolymers: Copolymers' polymer molecule has dual repeating units[13].

Copolymers have various groups; along the polymer chain a repeat unit particular arrangement characterizes each one of them [10].

Statistical copolymers: When the repeat units' sequential distribution follows a particular statistical law, these copolymers are known as statistical copolymers [10].

Random copolymers: When the repeat units' sequential distribution follows a random pattern truly these copolymers are statistical copolymers special type known as random copolymer (Figure 1.5) [10].

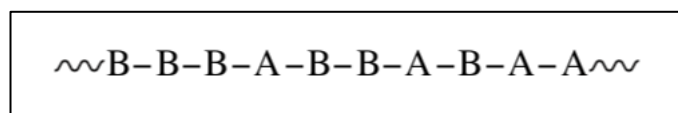


Figure 1.5 Random copolymer chain [10].

Alternating copolymers: Copolymers that have just two different arranged alternately repeat unit types along the polymer chain are known as Alternating copolymers (Figure 1.6).

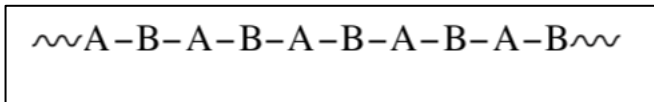


Figure 1.6 Alternating copolymers chain [10].

Block copolymers: Linear copolymers that their repeat units are only in blocks or long sequences of the same kind are known as the term block copolymers. Figure 1.7 show two of the most common structures for block copolymers also mostly the copolymers are termed AB di-block and ABA tri-block.

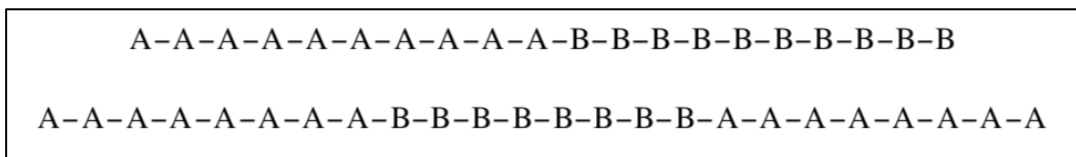


Figure 1.7 Block copolymers chain [10].

Graft copolymers: When the branches of a polymer chemical structure are different from that of the main chain these polymers are called graft copolymers. The simplest form of graft copolymers consist of the main chain of a homopolymer by different homopolymer branches (Figure 1.8) [10].

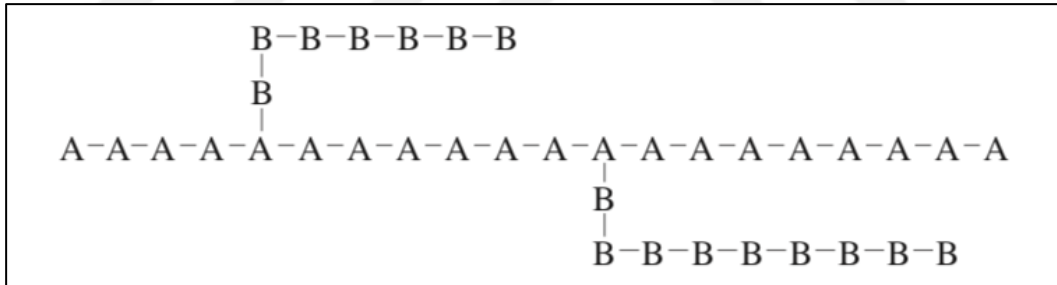


Figure 1.8 Graft copolymer chain [10].

Each constituent homopolymers characteristic property is usually shown by graft and block copolymers, in the copolymers types that were mentioned earlier[10].

Polymer Blends: Blending two or more types of polymers will give a polymer blend. The phase behavior is a two or more polymers polymer blend most essential characteristic. Mixing various levels and phase separation or miscibility in between the extremes can be exhibited by polymer blends[16].

1.1.1.6 Based on tacticity

Polymer tacticity which determines the physical properties of polymers is the neighboring chiral centers' relative stereochemistry inside of polymers. Hydrolysis, crystallinity, solubility and glass transition temperature (T_g) are an example for a polymer physical property that depend on the types of the monomers consist of it depends on the tertiary and the secondary structures, which is the linkage stereochemistry. PMMA can be isotactic, syndiotactic, or atactic depending on the stereochemistry (Figure 1.9)[17].

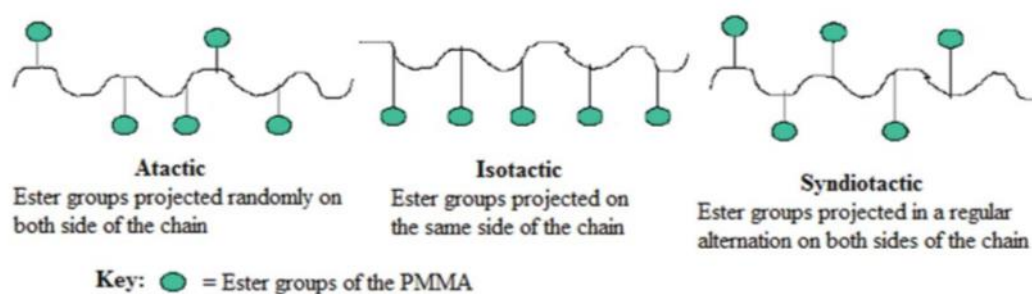


Figure 1.9 Schematic diagram of the different tacticity's of PMMA [17].

1.1.2 Polymerization

1.1.2.1 Classification of polymerization based on the old classification

In the early years of polymer science, comparing the molecular formula of a polymer with that of the monomer(s) from which it was composed has determined the classification of polymerization reactions [10].

a. Condensation polymerization: Condensation polymerization: When the polymerization yield polymers having repeat units with atoms fewer than the present form in the monomers that polymerization is termed Condensation polymerizations. Small molecule elimination chemical reactions are the origin of this [10].

b. Addition polymerization: When polymerizations yield polymers that have repeat units with identical formulate of molecular to the formed monomers these polymerizations are called Addition polymerizations[10].

1.1.2.2 Classification based on the mechanism of chain growth

Synthetic polymers formation is a process that happens by many hundreds or thousands of monomer molecules' chemical connections. In consequence, the formation of macromolecular chains happens. The chains, generally, are linear, yet can

be crosslinked, or branched also. On the other hand, based on the different monomers number and how the monomers are connected, the result will be homo- or a type from the various copolymers types. The classification of the chain formation chemical process can be roughly two classes, based on it proceeds as a step-growth or chain-growth reaction[3].

a. Step growth polymerization: The polymer chain molecular weight increase in a slow way and there is just one polymer formation reaction mechanism in a step-growth polymerization. Functional groups' reactions to the monomers proceed with the reaction of polymerization. The process carries on, each functional group's reaction essentially proceeding with the same rate of reaction for a relatively substantial period, obtaining a polymer with high molecular weight[18].

b. Chain growth polymerization: monomers repeated additions to the reactive sites growing chains initiate the chain growth. Throughout the polymerization process, monomer's slow consumption is present[15].

Chain growth polymerization involves three discrete steps initiation, propagation, and termination. A reaction among the monomer unit and a species of initiator (or catalyst) forms a propagation capable active center during the stage of initiation. Monomer sequential addition polymer chain linear growth to the active growing chain molecule is involved in the propagation. There are two possible distinct ways for the end or termination of propagation. Two propagating chains' active ends linkage together in the aim of forming a molecule is the first possibility. The reaction of two growing molecules with the aim of forming two “dead chains” as then ending each chain growth is the second possibility of termination[14].

The difference between chain growth and step growth polymerization: A greatly reactive initiator is used in chain-growth polymerization, whereas an initiation does not occur in the manner of chain-growth polymerization in step-growth polymerization. The other distinctive features between these two polymerization processes are could be summarized in the following paragraph [2].

In chain growth polymerization: A big part of the molecules are not reactive, so that they can be merely reacted by radicals. The remaining small part can involve earnestly in the polymerization process. The chain increases rapidly to a higher molar mass usually in a time of seconds [2].

In Step-growth polymerization: All molecules are included equitably, that is, possess equal reactivity. The high molar mass products are generated exclusively at an extremely high conversion[2].

1.1.3 Free-radical chain polymerization

Adding monomer units continuously to a growing radical chain is involved in this polymerization method. Figure 1.10 shows vinyl monomer polymerization process typical mechanism[19].

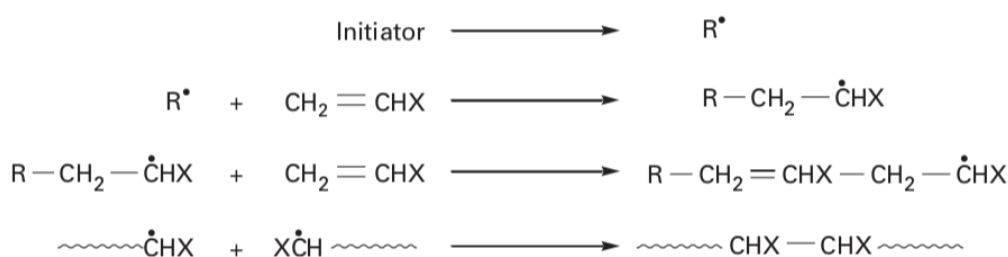


Figure 1.10 Mechanism of free-radical polymerization [19].

The most commonly utilized technique of radical polymerization is Free-radical polymerization. The reaction consists of three individual steps alike other types of chain polymerization: initiation, propagation and termination. Another complementary process, called chain transfer, contributes to the process significantly and can take place all in all chain polymerizations.

Initiation often occurs in two stages and includes formation of the free-radical active center. In the first step, free radicals form from an initiator. In the second step, one of these free radicals are added to a molecule of monomer.

In the propagation stage, the polymer chain grows by addition monomer is connected to the active center sequentially and rapidly.

Termination stage involves terminating propagation after destroying of the active center irrecoverably. Bimolecular reaction of propagating chains takes place in the two most widely termination mechanism in radical polymerizations. Two growing chains couple together in the aim of forming an individual polymer molecule in this combination.

Chain transfer reactions involve transferring the active center from the active chain end to other species in the polymerization process. This process takes place in most chain polymerization[10].

One of the most famous and generally utilized polymer production techniques free-radical. Thanks to its various applications with monomers and its inertness to impurities like water, make these techniques robust. On the other hand, its polymer properties control inability like chain topology and tacticity is a huge drawback. In the aim of combining free-radical polymerization flexibility and robustness with keeping polymer properties control ability, several techniques have been developed. One of the most favorable is atom transfer radical polymerization (ATRP)[20].

1.1.4 Living polymerization

In 1956 Szwarc termed this type of polymerization as a ‘living’ polymerization[21].

Living polymerization concept is the current chemistry of synthetic polymer central. Over the past five decades, synthetically inclined polymer engineers and scientists’ central unifying concept is arguably living polymerization. Also, a development influential role for living polymerization is played by macromolecules[22].

The propagation rate must be exceeded by the initiation rate to consider a polymerization ‘living’. As a consequence, all the chains of propagation polymer grow at the same rate and are formed simultaneously. As well, over the reaction lifetime, any propagating polymer chain termination must not be exhibited by an ‘immortal’ or ‘living’ polymerization to consider the polymerization ideal. As a result, distributions of molecular weight that are extremely narrow characterize the ‘living’ polymerizations [19].

One of the ‘living’ polymerizations key features is the propagating species ability to undergo polymerization until full monomer conversion after that continuing the polymerization upon another monomer addition. The ability of synthetic polymer chemists to construct is a result of the ‘living’ polymerization methodologies development, accurately, various polymer architectures (Figure 1.11)[19].

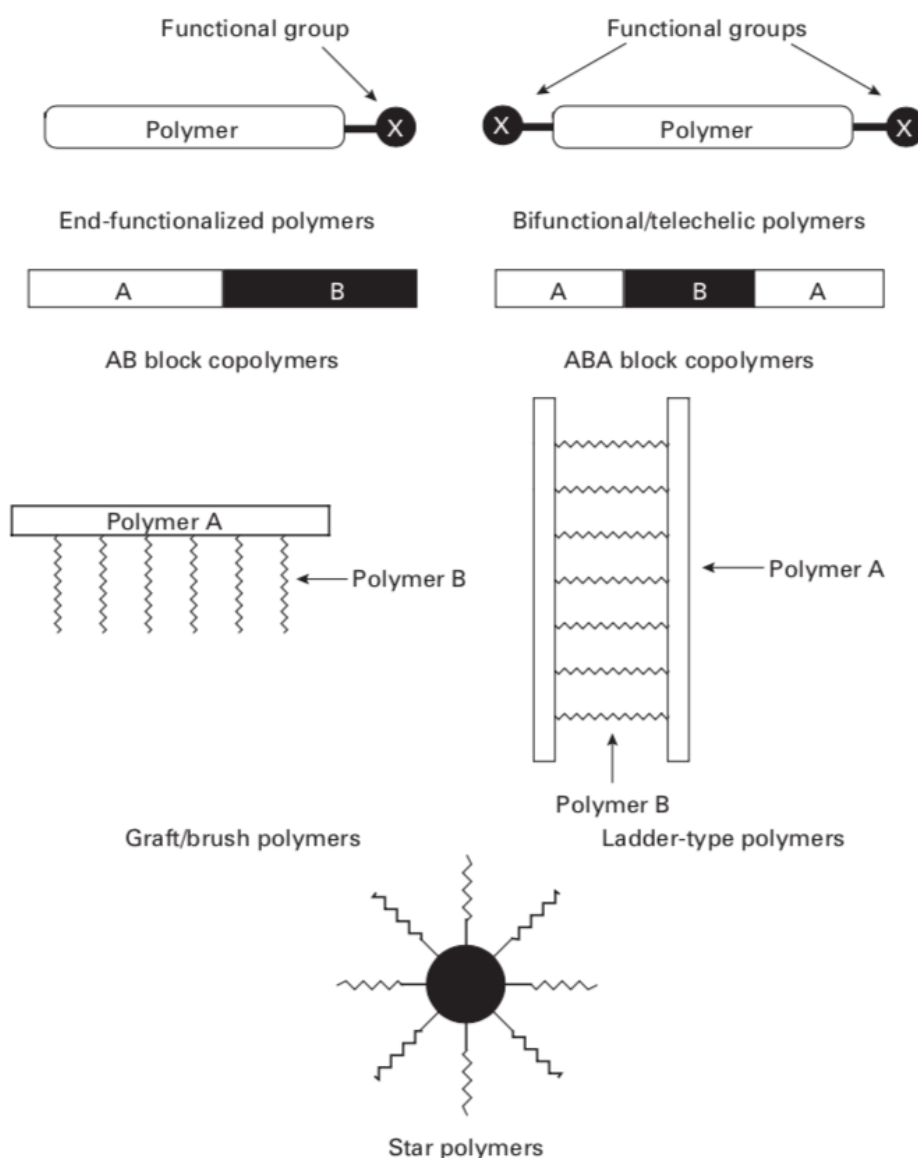


Figure 1.11 The variety of architectures of copolymer and polymer that are synthesizable by techniques of ‘living’ polymerization [19].

Types of Living Polymerization are:

- Anionic Living Polymerization
- Cationic Living Polymerization
- Covalent Living Polymerization
- Free Radical Living Polymerization[23].

1.1.4.1 Controlled/living radical polymerization

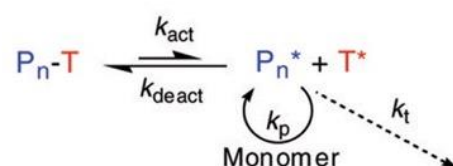
Techniques of controlled radical polymerization are radicals’ concentration quantitative regulation and initiation based during the reaction of polymerization[20].

Precisely controlled architectures, low polydispersity, and predetermined molecular weights well-defined polymers can be synthesized using controlled radical polymerization. Controlled radical polymerization got few disadvantages compared with different controlled/living systems for example termination is not completely eliminable. On the other hand, (co)polymerizable monomers' huge range is an example of the many techniques' advantages of controlled radical polymerization[24].

CRP has three general requirements which are, quantitative and fast initiation, chain-breaking reactions in small proportion, and fast exchange between growing radicals and dormant species (Figure 1.12)[20].

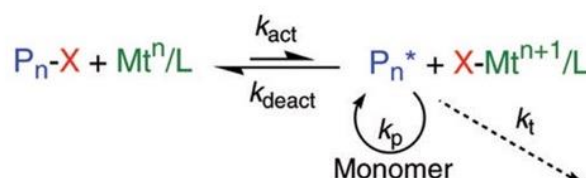
1) SFRP or NMP

Thermal dissociation of dormant species (k_{act}) provides a low concentration of radicals



2) ATRP

Transition metal activation (k_{act}) of a dormant species with a radically transferable atom



3) Degenerative Transfer or RAFT

Majority of chains are dormant species that participate in transfer reactions (k_{exch}) with a low concentration of active radicals

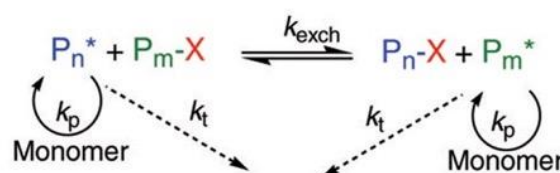


Figure 1.12 Three major methods of CPR [25].

Reversible addition-fragmentation chain transfer (RAFT), metal-catalyzed atom transfer radical polymerization (ATRP), and stable free radical polymerization (SFRP) are three techniques for CRP which can be applied for a lot of monomers and appear to be the most efficient and successful[25].

The concept of all CRP methods is identical. In this concept, a dynamic equilibrium forms between a low concentration of active propagating chains and a large number of dormant chains. These two chains are not able to self-terminate or propagate[25].

1.1.4.2 Atom Transfer Free-Radical Polymerization (ATRP)

In 1995 two research groups independently described the first concept of Atom transfer free-radical polymerization[26, 27].

An equilibrium between propagating radicals and dormant species, mainly appearing as initiating alkyl halides/macromolecular species (P_n-X), controls ATRP.

The periodical reaction of dormant species with the activation rate (k_{act}) constant with activators acting lower oxidation state transition metal complex Mt^m/L (L is a ligand and Mt^m is oxidation state m transition metal species; counterions and ionic species charges are omitted) in the aim of intermittent formation of growing radicals (P_n^*), also high oxidation state metal complexes of transition-deactivators, halide ligands $X-Mt^{m+1}/L$ coordination (Figure 1.13)[28].

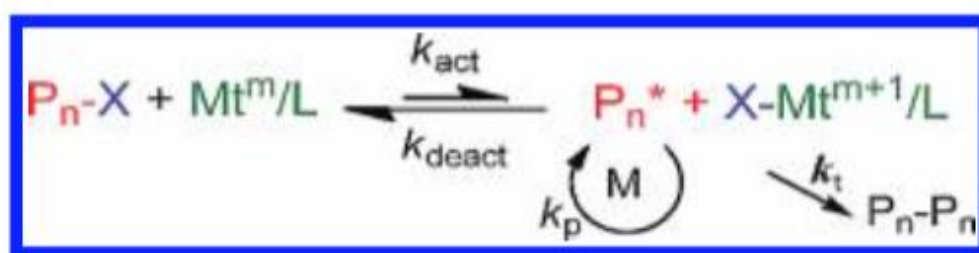


Figure 1.13 ATRP MECHANISM (X: Halogen, Mt: Metal, L: Ligand, M: Monomer) [28].

Using a transition metal catalyst, a reversible deactivation and activation of an alkyl halide initiator are involved in Atom transfer radical polymerization (ATRP). Well-defined polymers of dienes, acrylamides, acrylonitrile, (meth)acrylates, and styrene are preparable, which has been shown by catalyst right selection[20].

The main factor which affects the success of ATRP is mainly the convenient equilibrium between the activation process (formation of radicals, k_{act}) and the deactivation process (creation of alkyl halides, k_{deact}). The rates of polymerization and termination, and the radicals' concentration are depending on the equilibrium constants between the two rate constants (K_{ATRP}) k_{act} / k_{deact}). A narrow distribution of molecular weight and linear correlation between the monomer conversion and the molecular weight can be enabled by an excellent polymerization control. A reasonable polymerization rate maintenance and an excellent polymerization control can be provided by an ideal large k_{deact} and k_{act} (though $k_{deact} \gg k_{act}$)[29].

ATRP takes place in solution, bulk, aqueous emulsion, and suspension at 60–120 °C; exceptionally some reactions can proceed at lower temperatures. The process is endothermic so that by increasing temperature, the rate of polymerization increases.

The range of polymerizable monomers can be expanded by the novel catalysts and initiators in conjunction with modifying reaction conditions from this point forward[6].

ATRP process occurs by utilizing commercially accessible reagents under effortless reaction conditions. ATRP also provides checking remarkably macromolecular structure. ATRP can control numerous properties such as composition, chain topology, functionality, tacticity. ATRP has broken through as a highly robust synthetic method before less than two decades. The creation of plenty of novel materials with various implementations is possible by ATRP. The detailed studies of mechanistic opened the path for the rule's creation of reaction conditions rational selection in the aim of well-defined functional macromolecules synthesis achievement, is the attribution of the method[30].

The kinetics and the mechanism of ATRP process have provided the synthesis of numerous polymers with new compositions, functionalities, and architectures that are shown in Figure 1.14. ATRP is a complicated process because of its multi-component structure so that finding optimum conditions is strenuous. All of its components need to be understood and considered to utilize this methodology and determine the optimum polymerization conditions[31].

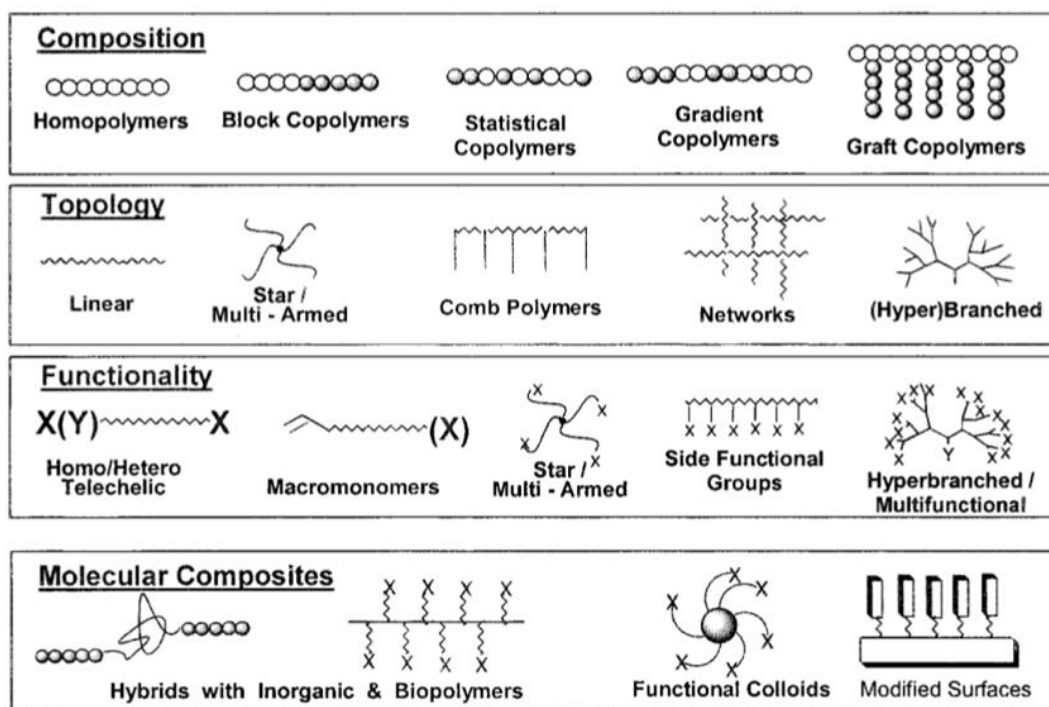


Figure 1.14 Functionalities, compositions and controlled topologies schematic representation and ATRP prepared molecular composites [31].

In numerous biological and medical implementations, Atom Transfer Radical Polymerization (ATRP) has been utilized effectively with the aim of designing and preparation multifunctional, nanostructured materials. ATRP method is capable of synthesis a variety of different materials. For instance; cross-linked microgels/nanogels, block copolymer-based drug delivery systems, tissue engineering hydrogels, diagnostic and imaging platforms, and degradable polymers. Using ATRP, macromolecular structure, functionality, and order can be controlled precisely[32].

ATRP method's handicap is its sensitivity to oxygen. Oxygen cause producing of radicals constantly. Even if a small amount of oxygen in the reaction intermixture, the whole course of the reaction can be affected[20].

Other disadvantages of ATRP method contain:

- (1) High amount of metal ions (e. g. copper) exist in polymer relatively.
- (2) To produce colorless polymers, the amount of copper and ligands are needed to be reduced. Obtaining colorless polymers is laborious.
- (3) Supplement of solid materials is required.
- (4) Tuning reaction rates or polydispersity up in the "catalytic system" is rough[33].

1.1.4.2.1 Components

Figure 1.15 shows the main components of a typical ATRP polymerization [34].

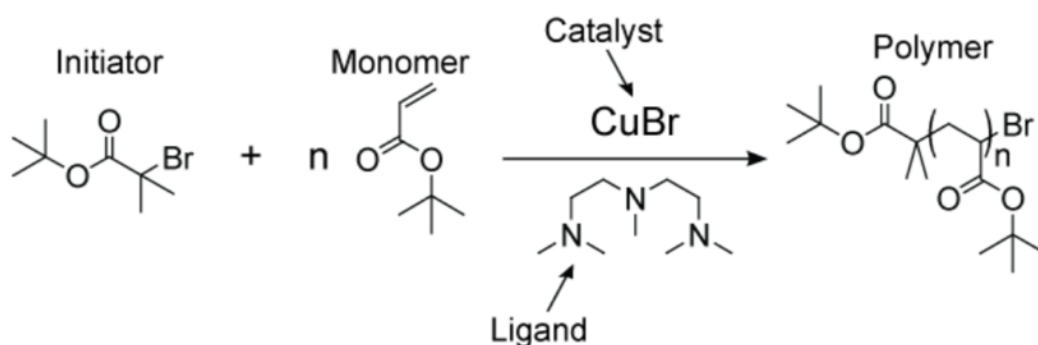


Figure 1.15 The main components of a typical ATRP polymerization[34].

1.1.4.2.2 Ligand

Fig 1.16 shows Mediated by copper ATRP used ligands.

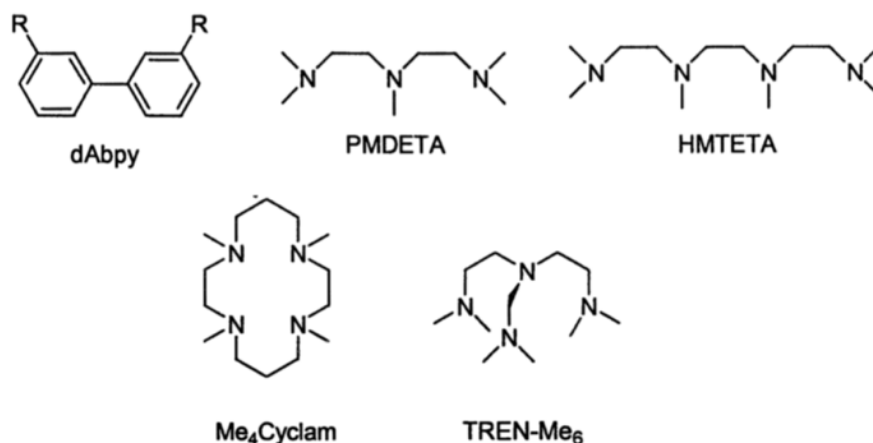


Figure 1.16 Mediated by copper ATRP used ligands[20].

Convenient ligands are necessary for the accurate operation of a metal catalyst. Ligands have essential functions. They are in charge of fine-tuning the redox potential of the metal center for appropriate activity and solubilizing the transition metal salt in organic media[6].

1.1.4.2.3 Monomer

Numerous monomers which possess their own intrinsic radical propagation rates can be efficiently polymerized utilizing ATRP. The monomers polymerized in ATRP can stabilize the propagating radicals. Commonly used monomers are (meth)acrylates, styrenes, (meth)acrylamides, and acrylonitrile[31].

MMA (Methyl methacrylate): Figure 1.17 shows MMA structure.

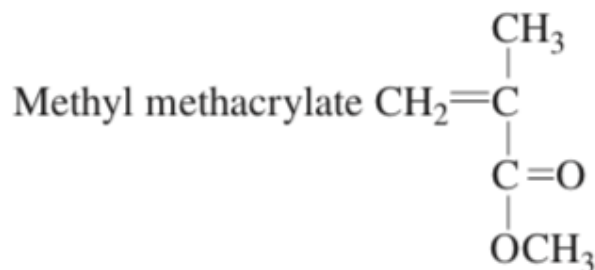


Figure 1.17 MMA Structure[10].

ATRP reaction available catalysts large range and MMA facile polymerize ability is because of the equilibrium constants of ATRP high values and dormant species activation relative ease. Controlled process of ATRP obtaining occasionally requires a too high equilibrium constant [31].

70-90 °C is the range of the temperatures of the solution which the MMA most polymerization took place in. $100 < T_g$ °C is the glass transition temperature of the necessary PMMA formation solubilization by solvents. Also, the keeping of low growing radicals' concentrations is helped by the solution polymerization [31].

If MMA and styrene is compared with equilibrium constant of MMA mediated by copper ATRP, the equilibrium constant is displayed really high. Consequently, for polymerization of MMA lower catalyst and higher dilution must be utilized[31].

1.1.4.2.4 Initiators

Figure 1.18 shows ATRP initiators used commonly.

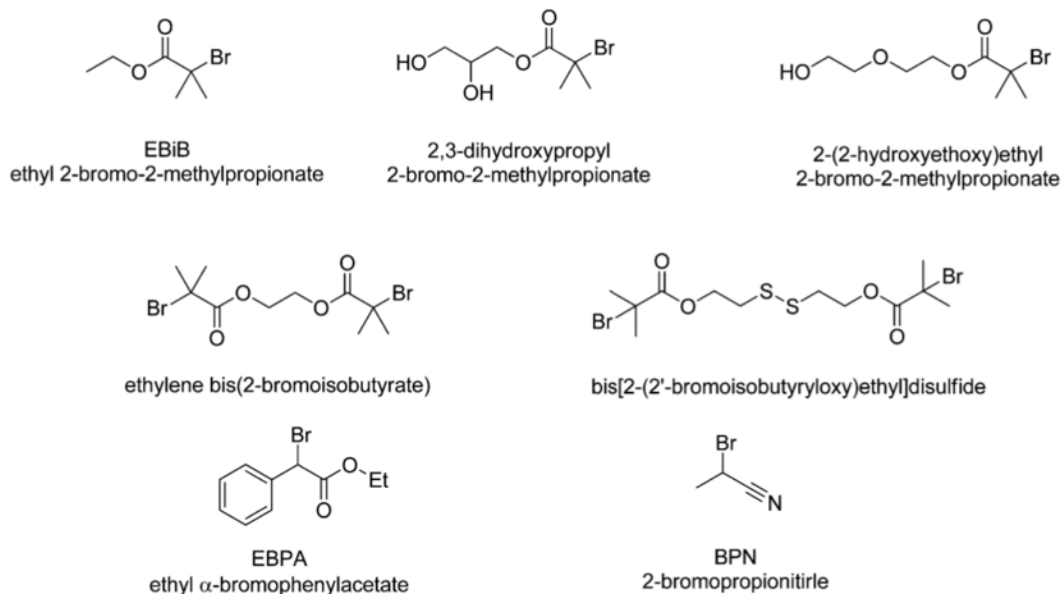


Figure 1.18 ATRP initiators[35].

The number of growing polymer chains controls by the initiator. When the transfer and termination are insignificant, and initiation is rapid, the amount of growing chain does not change and, the initial initiator concentration equals the number of growing chains. In a living polymerization, the initial concentration of the initiator raises with the degree of polymerization (DP) or the theoretical molecular weight mutually. Alkyl halides (RX) are typical initiators used in ATRP[31].

1.1.4.2.5 Catalyst

The catalyst is one of the most significant components of the polymerization process in ATRP. Catalyst controls the rate of exchange between the dormant and active species and the atom transfer equilibrium[31].

The metal catalyst must possess an affinity for halogen, two accessible oxidation states readily for a one-electron transfer, a powerful complexation with the ligand, and a growable coordination sphere to domicile the halogen[6].

1.1.4.2.6 Solvents

ATRP process takes place in solution, bulk, or a heterogeneous system. If synthesized polymers are not able to soluble in their monomer, a solvent is required. Select of solvent is depending on few parameters. The interplay between solvent and the catalytic system must be taken into account. Besides, chain transfer to solvent must be held minimum[31].

1.1.4.2.7 Temperature and reaction time

When the temperature increases, the rate of ATRP increases too because of the rise in both the radical propagation rate constant and the atom transfer equilibrium constant. At high temperatures, chain transfer and other side reactions turn into marked, the catalyst' solubility increases generally. On the other hand, catalyst decomposition might take place by rising temperature. The main parameters which affect the optimal temperature are monomer and catalyst [31].

In a considerable matter the propagation rate slows down at monomer conversions that are high. On the other hand, A significant change in any side reaction rate does not occur, because they are monomer concentration independent mostly. End groups loss is induced by almost complete monomer conversion lead by prolonged reaction times yet it possibly will not lead to the final polymer polydispersity increase. Consequently, in the aim of subsequently synthesize block copolymers or to gain high end-group functionality polymers, to avoid loss of end-group 95% conversion should not be exceeded[31].

1.1.5 Poly(methyl methacrylate) (PMMA)

Table 1.1 PMMA structure, class, acronym and name[36].

Common name	Acronym, alternate name	Class	Structure of repeat unit
Poly(methyl methacrylate)	PMMA	Vinylidene polymer, acrylic polymer	$\begin{array}{c} \text{CH}_3 \\ \\ \left[\text{C} - \text{CH}_2 \right]_n \\ \\ \text{C} - \text{O} - \text{CH}_3 \\ \\ \text{O} \end{array}$

Fiber or acrylic glass are common names for PMMA. Hass and Rohm developed it in 1928 and in 1933 it became commercially available. Methyl methacrylate polymerization utilizing bulk free radical, solution and emulsion polymerization produce fiber, transparent plastic or thermoplastic known as PMMA. Usually, PMMA is utilized as a glass alternative. Regarding, PMMA is a material that is positive for the environment because the products when it is burned completely are water and carbon dioxide[4].

Compered to glass, PMMA is has a better strength of impact and is weight less than glass or PS. Glass is harder to get scratched but, yet PMMA has low reflection and

98% light transition which is similar optical properties to glass. In solvent resistance and environmental stability respect glass is better, yet better than most other plastics[4].

PMMA resistance of scratching could be enhanced by modifying it and it has a very good weathering resistance. It has the ability to bond, weld, thermo-form, injection mold, extrude. Generally, it is utilized for spectacles, optical fibers, aircraft glazing extra. Prostheses, and tooth filling are another use for it[2].

Parameter of solubility of PMMA is around $18.8 \text{ MPa}^{1/2}$ and it can be solute in similar solubility parameters solvents which include toluene, chloroform, trichloro-ethylene, ethylene dichloride and ethyl acetate. PMMA has resistance to most inorganic salt solution, water and alkalis yet mineral acids can damage it[37].

Table 1.2 shows the physical properties of PMMA.

Table 1.2 Physical properties of PMMA[17].

Property	Value
Color	Colorless
Density (g/m^3)	1.18
Melting Point($^{\circ}\text{C}$)	220-240
Glass Transition Temp. (T_g)	110-120
Linear Thermal Expansion ($\times 10^{-5} \text{ mm/mm.k}$)	6.3
Mold Shrinkage (%)	0.3-0.6
Thermal Expansion Coefficient 20°C ($\times 10^{-4} \text{ K}^{-1}$)	1.8
Thermal conductivity at 20°C (k(W/mK))	0.12, 0.17

Table 1.3 shows the mechanical properties of PMMA.

Table 1.3 Mechanical Properties of PMMA[12].

Property	Value
Tensile modulus (GPa)	3.10
Tensile strength (MPa)	72
Elongation at break (%)	5
Hardness (Rockwell)	M90-M100
Notched Izod (kJ/m)	0.4

1.1.5.1 Applications of PMMA in nanotechnology

1.1.5.1.1 Biomedical applications

PMMA can be used in many biomedical applications. For instance, PMMA is used in nanocomposites combining with a nanoparticles' superparamagnetic behavior in the aim of treatment with a tumor. Iron oxide nanoparticles have many advantages such as biocompatibility are suitable for this purpose. In this process, PMMA is used to encapsulate nanoparticles in the purpose of preventing agglomeration, providing stability, low cytotoxicity, good dispersibility and functionality. The core-shell nanocomposites are synthesized by mini emulsion polymerization method using with PMMA and iron oxide nanoparticles. The experimental method of PMMA/Fe₃O₄/poly(vinyl pivalate) nanoparticles is summarized in Figure 1.19. This novel polymeric structure exhibits promising properties such as good colloidal, mechanical, and chemical stability [38].

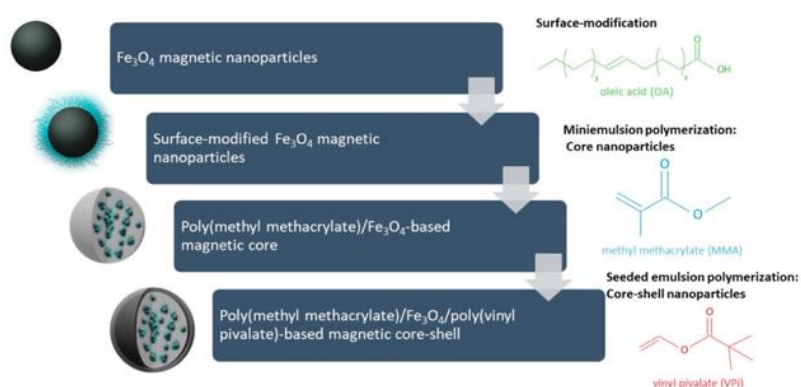


Figure 1.19 The synthesis method of poly(methyl methacrylate)/Fe₃O₄/poly(vinyl pivalate) nanoparticles[38].

In another work, A simple electrospinning method fabricated (PMMA)-CdSe/ZnS quantum dots (QDs) nanocomposites. Especially for high concentrations of polymer the pristine fibers of PMMA shows lower thermal stability than the nanocomposite

fibers. While serving as scaffold for tissues the enhanced thermal stability favors retaining the materials structural integrity. The cells of Chinese hamster ovary have an excellent biocompatible ability with PMMA-QDs nanocomposite from the adhesion, the cell proliferation and viability characteristics, it has an advantage in the bio-applications future thanks to the fiber sharp fluorescence signal[39].

In the diseases' treatment and diagnosis, polymeric nanostructured materials (PNMs) are getting alluring day by day. Poly(methyl methacrylate) (PMMA) makes a contribution to numerous biomedical implementations thanks to its inert and biocompatible properties. Stereo complexes (SCs), possess crystallinity in their structure that is denser than every single component, can be formed by PMMA. PMMA stereo-complexed nanofibers have a great future in the application of tissue engineering[40].

1.1.5.1.2 Optical applications

ZnO nanoparticles have a good impact on enhancing PMMA optical properties. PMMA/ZnO nanocomposites are produced by dispersion polymerization of monomer (MMA) and nanoparticles. Reinforcement of PMMA by ZnO nanoparticles mainly affects PMMA's optical properties efficiently and provides them superior properties in refractive index, UV absorption, and visible light transmittance. The large-scale manufacturing of PMMA is amicable with the synthesis route[41].

1.1.5.1.3 Photonic applications

PMMA can be utilized as a Photopolymer Material for Holographic Storage. In a study, SiO₂ NPs-PQ/PMMA Photopolymer Material is utilized for Holographic Storage. SiO₂ nanoparticles are used to increase the saturated diffraction efficiency of PQ/PMMA nanocomposite under a polarized hologram. Holographic photopolymer storage material performance enhancement can be gained from photosensitizer concentration and nanoparticles' doping control[42].

1.1.5.1.4 Applications in polymer conductivity

Graphene Oxide Composites. In a study, the surfactant-free emulsion polymerization method is used in the synthesis of the PMMA latex. Also, a cationic free radical is used as an initiator. This initiator creates positive charges on the PMMA particle's surface. The PMMA latex and graphene oxide dispersion are mixed. Thanks to electrostatic interaction, negatively charged graphene oxide sheets are readily

assembled with positively charged PMMA particles. The produced PMMA-RGO displayed good electrical properties. The generation of a segregated network of RGO sheets in the PMMA matrix provided the good electrical properties of PMMA-RGO. Besides, PMMA-RGO thermomechanical properties were reinforced notably. The important improvement in Tg of PMMA-RGO and storage modulus was attributed to powerful interfacial interactions between the PMMA matrix and RGO sheets[43].

1.1.5.1.5 Sensor applications

In the gas sensing implementations, PMMA can be utilized in the synthesis of Carbon Nanotube/PMMA composites thin films. Polymethylmethacrylate (PMMA) composite thin films were produced with surface-modified multiwalled carbon nanotubes (f-CNTs) and multiwalled carbon nanotubes (CNTs) in a study. These nanocomposites are tested with distinct organic vapors. These nanocomposites were tested with distinct organic gases. Some changes were observed in the resistance of composite thin films because of exposure to vapors. According to the results, the f-CNT/PMMA nanocomposite had higher responses than the other type of PMMA nanocomposite. The mechanism of sensing is based on the expansion of volume and polar interactions of numerous vapors on the CNT surface[44].

Elastic SERS (Surface-enhanced Raman Scattering) substrate can be produced by some superior properties such as transparency, lightweight and great sensitivity via merging polymers with the noble metals. According to a study, AuNRs/PMMA films are good candidates for elastic SERS substrates. Besides, AuNRs/PMMA film has great SERS activity, good optical transparency and excellent flexibility. The AuNRs/PMMA film detects trace thiram on the surface of cucumber directly and readily (Figure 1.20). Consequently, the AuNRs/PMMA substrate will display excellent capacity in detection implementations according to expectation[45].

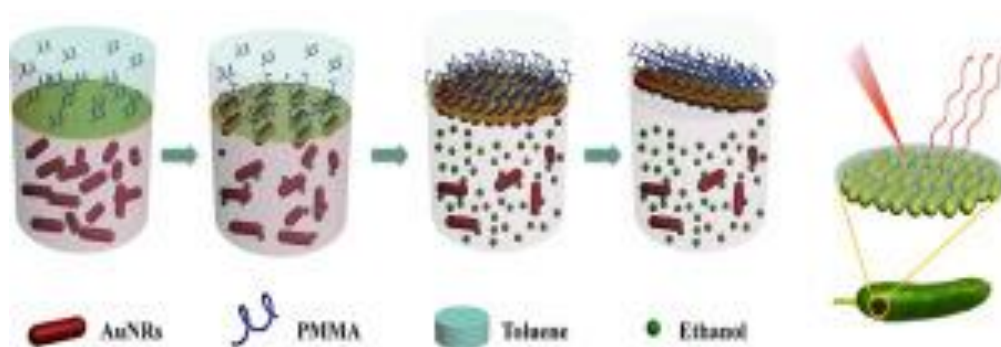


Figure 1.20 Simplified schema of the production of AuNRs/PMMA SERS substrate [45].

1.1.5.2 Reinforcement nanomaterials in PMMA

Table 1.4 shows the PMMA reinforcement aim and effect in literature.

Table 1.4 PMMA reinforcement aim and effect.

Materials of Reinforcement	Technique	PMMA Structural Characteristics Reinforcement Effect	Reinforcement Aim
Surface-modified silica nanoparticles [46]	Solution polymerization	Increasing the glass transition temperature (T_g) Increasing UV absorptivity Improving the hardness, impact energy and flexural property Increasing the tensile strength and tensile modulus	Obtaining polymeric materials with the improved properties

Table 1.4 (continued) PMMA reinforcement aim and effect.

Materials of Reinforcement	Technique	PMMA Structural Characteristics Reinforcement Effect	Reinforcement Aim
Multi-walled carbon nanotubes [47]	Solvent casting	Affecting the fracture behavior of the PMMA causing brittle fracture	
		Improving stiffness and modulus of the films.	Obtaining polymeric materials with the desirable electrical and mechanical features
		Increasing the mechanical strength of the composites	
		Increasing the thermal resistivity of the composites	
PA-6 (Nylon-6) nanofibers [48]	Coaxial electrospinning method	Improving the strength of the composite	
		Improving thermal stability and mechanical properties	Obtaining a transparent PMMA composite with desirable properties
zirconium oxide nanoparticles (nano-ZrO ₂) and glass fibers (GFs) [49]	Water bath technique	Improving the flexural and impact strengths	Evaluating the hybrid reinforcement impacts.

Table 1.4 (continued) PMMA reinforcement aim and effect.

Materials of Reinforcement	Technique	PMMA Structural Characteristics Reinforcement Effect	Reinforcement Aim
ZrO ₂ nanotubes [50]	Stirring by a mechanical blender	ZrO ₂ nanotubes showed a better reinforcement effect than ZrO ₂ nanoparticles	Maximizing the flexural strength of the composite
Cellulose nanofibrils [51]	Solution casting method	Maintaining thermal stability Decreasing the transmittance of PMMA/cellulose	Obtaining a transparent PMMA Composite with improved properties Obtaining material for use in several implementations such as: light-weight transparent material, flexible screen Obtaining polymer composites with outstanding mechanical properties and good energy storage characteristics
BaTiO ₃ nanoparticles and fiberglass [52]	Solvent evaporation, compression molding	Providing high stiffness Increasing the dielectric constant	

Table 1.4 (continued) PMMA reinforcement aim and effect.

Materials of Reinforcement	Technique	PMMA Structural Characteristics Reinforcement Effect	Reinforcement Aim
Graphene oxide (GO) and functionalized carbon nanotubes (f-CNTs) [53]	Ultrasonication	Improving mechanical properties	Improving a novel PMMA-based nano- composite bone cements
Dual modified organoclay (DMC) [54]	Solution cast method	Increasing thermal stability, glass transition temperature and the tensile mechanical feature enhancing the flame retardancy remaining the PMMA's transparency	Obtain DMC organoclay good-dispersed and highly exfoliated in the PMMA structure Obtaining a transparent PMMA composite with desirable properties Obtain polymer composite with homogeneous distribution and good interface
Al ₂ O ₃ /ZrO ₂ [55]	Solution polymerization	Increasing fracture toughness and flexural properties	Obtaining a denture base material with improved mechanical properties

1.2 Nanotechnology and Nanomaterials

Nanotechnology comes into existence from two words: nano and technology. The word “nano” which means tiny or dwarf had used in ancient Greek. Nanoscale materials large surface area exhibit excellent characteristics; this advantage is gained by the tiny scale materials manipulation or in other word “nanotechnology”[56].

In almost all technology and science fields nanotechnology has a contribution, which is a fundamental multidisciplinary science. Nanometer level structure or objects production and design is dealt by nanotechnology. In 1959 nanotechnology were found by the physics noble laureate Richard P. Feynman which inspired many researchers[57, 58].

1.2.1 Properties of nanomaterials

Change of size from nanoscale from microscale from macroscale significantly changes matter properties that is a known fact. The quantum phenomena are in the range of 1-100 nm also nanomaterials which they show unique properties dependent on size. Study field of nano technology involves 100 nm smaller and 1 nm larger materials and excellent properties are shown by these materials[59].

In compression to large form produced materials that has the same mass or volume nanomaterials has surface area that is larger in a relative way. Ratio of surface area to volume becomes really high when bulk materials are crashed to smaller size particles. The Electrical properties and strength of materials that has been crashed are affected because they become more reactive chemically[60].

Nanomaterials and bulk materials relationship are shown in Figure 1.21[61].

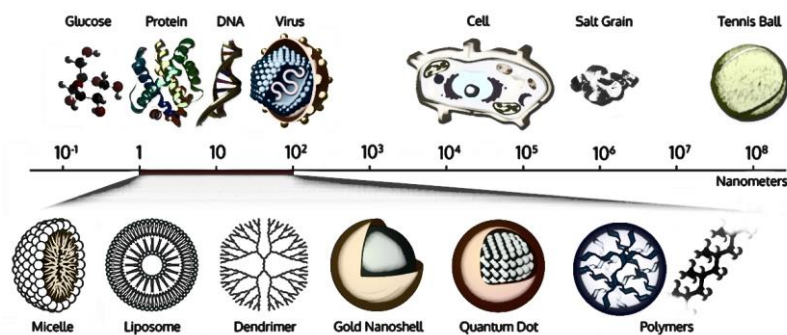


Figure 1.21 Nanoparticle size comparison (nanotechnology chart ruler).

1.2.2 Classification of nanomaterials

Various criteria can classify nanomaterials to several groups. In general, chemical composition, state, morphology and dimensionality of nanomaterials categorize them. They are also classified according to their size (1-100 nm)[62].

Four classes of nanomaterials, dimension based:

- Zero Dimensional: Sub 100 nm sized (nanoscale dimension). Quantum dots, core shell, metal, hollow sphere, polygon, nanorod and cube nanomaterials.
- One Dimensional: one of its dimensions are not in nanoscale. nanofibers, nanowires, fiber or filament nanorod, nanotube, ceramic, polymeric and metallic nanomaterials.
- Two Dimensional: two of its dimensions are not in nanoscale. nanocoating, nanoplates, thin films, amorphous, crystalline nanomaterials.
- Three Dimensional: several dimensions are not in nanoscale[62].

All of that is shown in the scheme in Figure 1.22 [60].

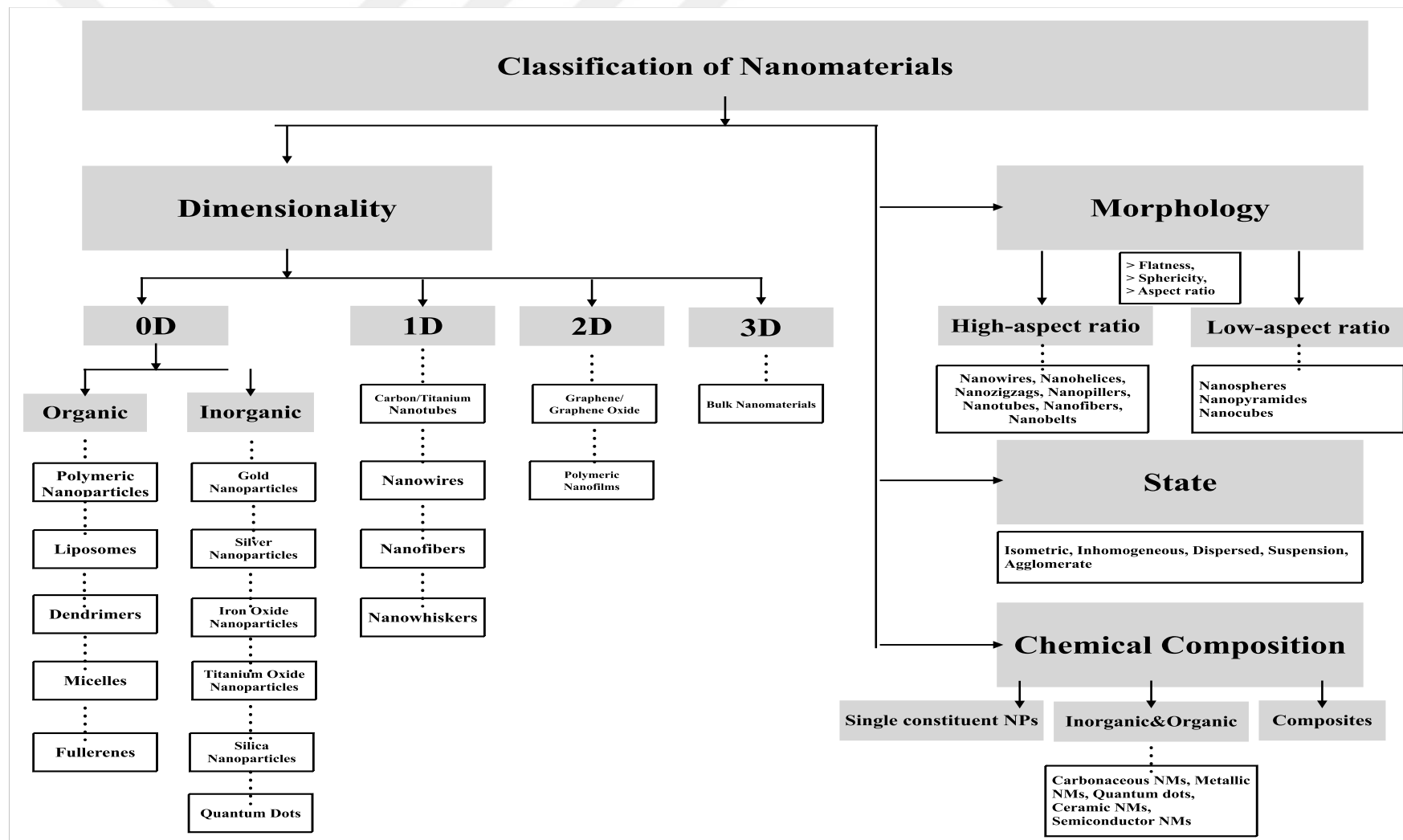


Figure 1.22 Various criteria-based nanomaterials classification.

1.2.3 Nanomaterials synthesis

Nanoparticles produce in countless ways. There are two main methods applied in nanofabrication: Top-Down and Bottom-Up Approaches. Top-Down Approach is related to physics which means more lithography, more machines, energy beams. Otherwise, Bottom-Up Approach is more related to material science and pure chemistry (Figure 1.23)[63].

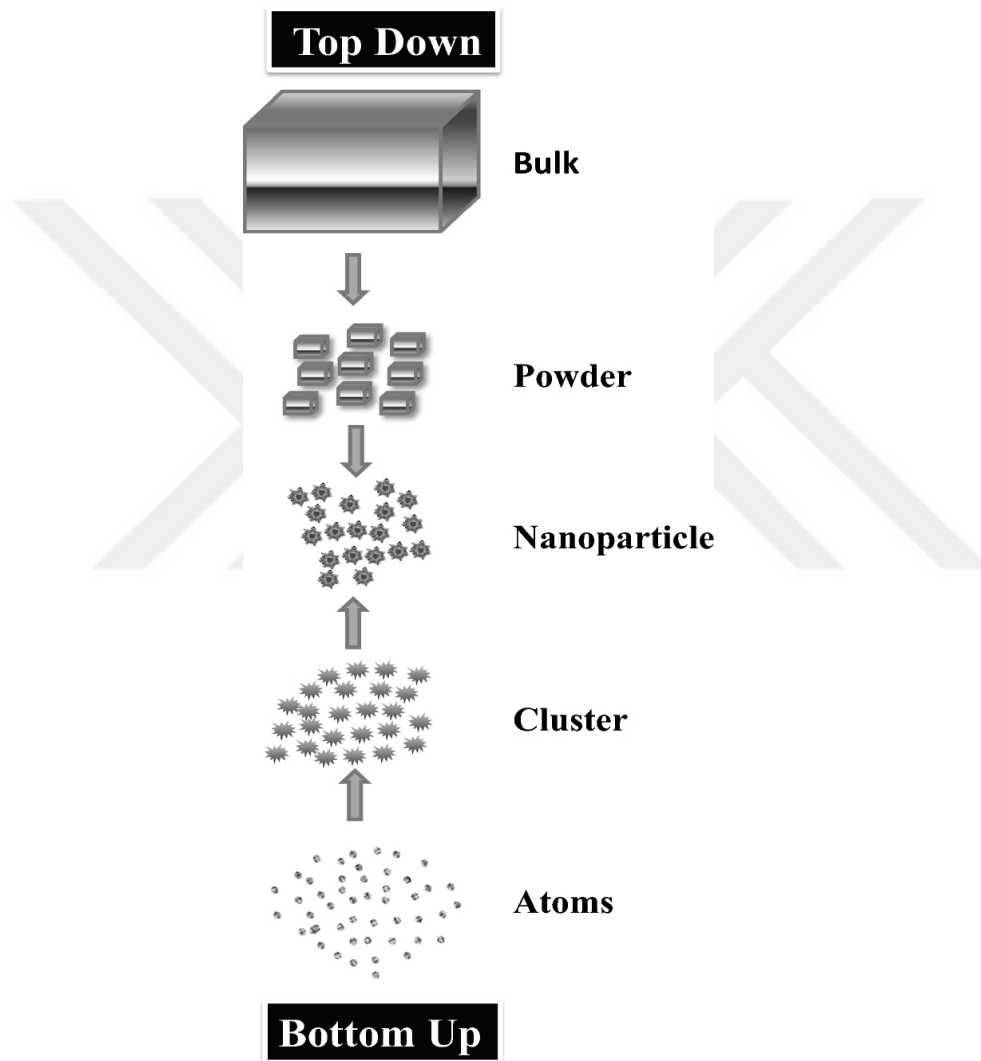


Figure 1.23 Synthesis of nanoparticles bottom up and top-down approaches.

1.2.3.1 Top-Down approach

The Top-Down Approach includes a process that is reducing the particle size into nano-size. This approach is utilized only for fragile and rigid materials. The top-down method is intrinsically more straightforward than the bottom-up method. The top-down technique implies shredding or consecutive slicing of bulk matter to form

nanomaterials. Contamination comes from the environment. In the industrial area, it is preferable.

Examples: Ball milling, Attrition, Manufacturing computer chips, lithography, Laser-beam processing[64].

Advantages: The Top-Down Approach can be applied in large-scale production. And also, this approach does not require any purification process[64].

Disadvantages: The Top-Down Approach has a big problem that is the defect of surface construction and crystallographic detriment. These defects cause additional challenges in nanofabrication. This approach is not inexpensive and requires putting quite an effort to force to smash. All of the precursors cannot break to the desired particle size. Controlling deposition parameters is hard in this method. The produced particles may have varied shapes and geometries. Some impurities eventuate such as stress, defects and, imperfections[64].

1.2.3.2 Bottom-Up approach

Bottom-Up Approach includes the expansion of nanoparticles from the atomic dimension. This approach applied on gas, liquid and solid is the building-up of matter from the bottom: atom by atom, molecule by molecule. Creating homogeneously distributed size nanomaterials is the main point of this nanofabrication technique. Conditions have a huge impact on contamination. Manipulating size, composition, structure, geometry is possible via this technique, so preferable in scientific research.

Bottom-up synthesis has two approaches: Physical Processing and Chemical Processing. Examples: Sol-gel method, Gas condensation process, Colloidal dispersion, Plasma etching, Laser ablation, Precipitation[64].

Advantages: Ultra-fine nanoparticles can be produced and deposition parameters (such as temperature, pressure, medium) can be controlled readily and perfectly via this technique. Narrow size distribution is possible. It is cheaper compared to top-down approach. It enables to control particle size well. Other main advantages are the fewer possibility of contamination and lower temperature comparing with industrial techniques. Doping of foreign atoms is possible during synthesis. Large quantities of material can be obtained (Microfluidic systems or Microwave systems). Self-assembly or patterning is possible which means it is possible to manipulate everything[64].

Disadvantages: Large-scale production is hard to apply compared to the Top-Down approach. Chemical purification of nanoparticles is required to get rid of byproducts, some chemicals[64, 65].

1.2.4 Applications of nanotechnology

Nanomaterials 'production requires high-tech implementations and specific procedures. Fabrication conditions and raw materials' properties provide to increase the yield of the fabrication of the nanomaterials. There is a huge demand for nanoparticles (NPs) in the global market. This demand is estimated to reach 98 billion dollars in the future (Figure 1.24)[66].

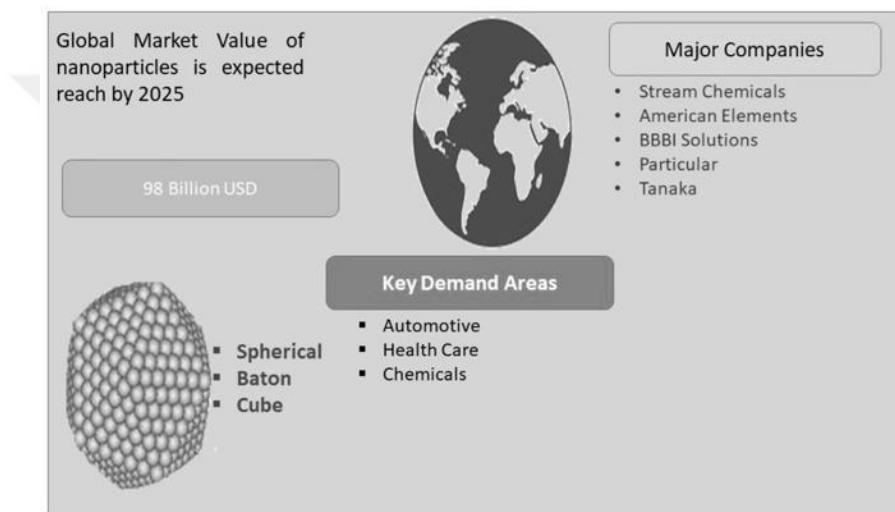


Figure 1.24 Nanoparticles' value in the global market (in 2025) [66].

Application fields of nanotechnology is summarized in Figure 5[56].

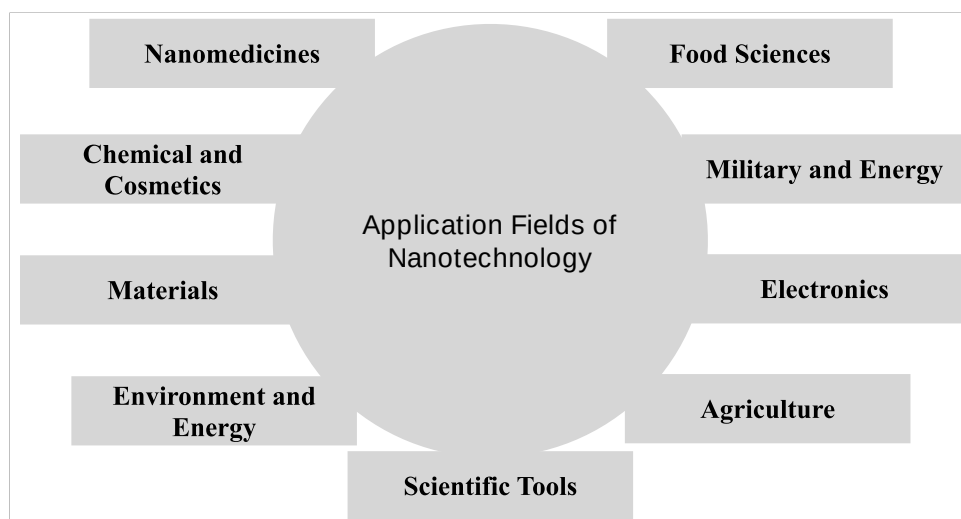


Figure 1.25 Applications of nanotechnology [56].

1.2.5 Graphene and graphene nanoplatelets

In 2004 Graphene is defined as a bi-dimensional allotropic separating it from graphite for the first time[67].

Graphene is a carbon single atomic layer attached via hybridized bonds of sp^2 . Graphene can also be described as purely atomic crystals that are free-standing, and seen as atomic planes that are singular and withdrawn from bulk crystals or as single-wall nanotubes that are unfolded[68].

Graphene is alluring for composite materials implementation, thanks to its high aspect ratio beside its chemical, barrier, mechanical and electronic properties. Graphene gives to the neighboring polymer matrix gas and moisture hindrance properties, strain monitoring capability, thermal conductivity, electromagnetic shielding, and electrical conductivity[67].

Graphene has unmatched physical features (Figure 1.26). Thanks to its unique properties, it is an excellent candidate in different implementations such as protective coatings, photonics, gas barrier films, advanced nanocomposites, and optoelectronics[69].

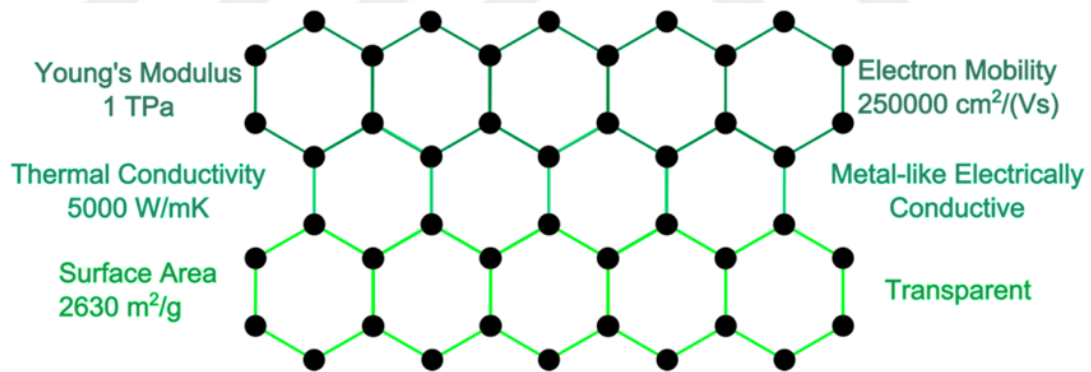


Figure1.26 Graphene Chemical Structure and Physical Properties [69].

Graphene fabrication is complicated. That is why the mass production of graphene is still a challenging issue. At this point, graphene nanoplatelets (GNPs) are becoming more attractive due to their advantageous properties. GNPs have a future for a cost-effective large-scale fabrication[70].

GNPs have a structure in between graphite and graphene. GNPs consist of a single and few layers of graphene. Thickness, lateral size, and carbon to oxygen atomic ratio used to categorize the graphene-based materials in the literature. Graphene can be categorized in single-layer graphene, few layers graphene (2–10 layers), and graphite

nano- and micro-platelets regarding morphological features. Commercially available GNPs are a mixture of a single layer, few layers, and nanostructured graphite. The thickness of GNPs is between 0.34-100 nm[69].

1.2.5.1 Graphene and graphene nanoplatelets production

Graphene can be made in several ways, counting top-down and bottom-up methods. The top-down methods for production of graphene and modified graphene starting from graphite or via graphite oxide (GO). Otherwise, the bottom-up method starts from atoms of carbon to manufacture graphene. Figure 1.27 illustrates a block diagram which summarizes the Top-Down and Bottom-Up Methods for Graphene Production[71].

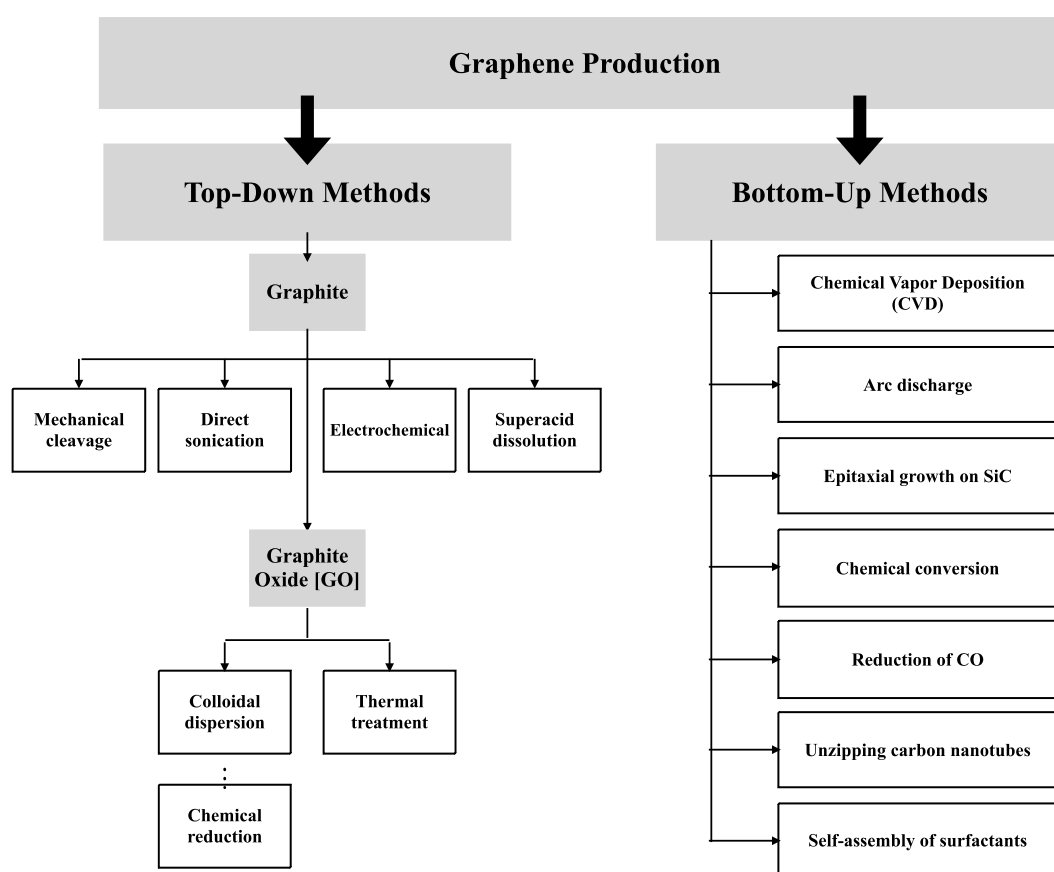


Figure 1.27 Top-Down and bottom-up methods for graphene production [71].

Production of graphene nanoflakes powder takes place via liquid-phase exfoliation method (no need for centrifugation steps) (Figure 1.28). Further common production methods are shear-exfoliation, the exposure of acid-intercalated graphite to microwave radiation, wet-jet milling, and ball-milling[69].

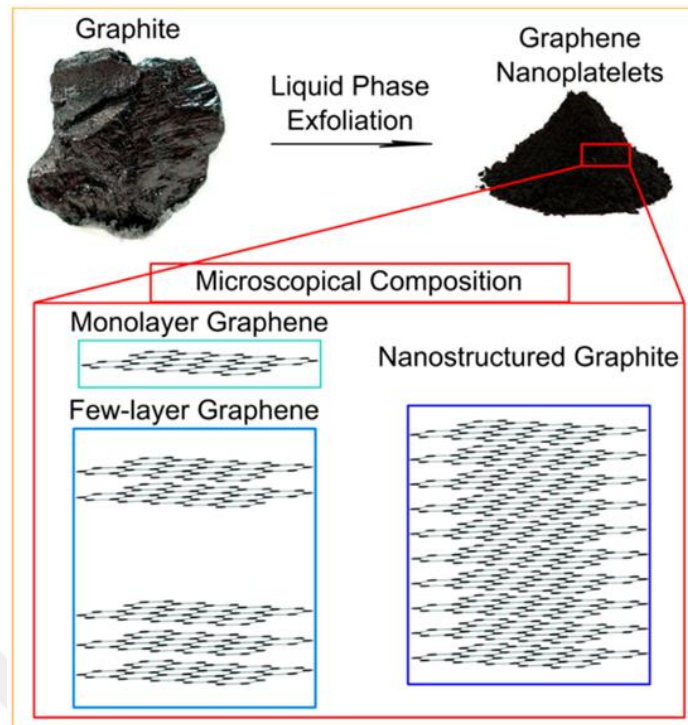


Figure 1.28 The fabrication of GNPs starting from graphite [69].

1.2.6 Nanocomposites

Nanocomposites have nano dimensional phase(s) or structures within a bulk matrix. Figure 1.29 shows the fabrication methods for ceramic, metal, and polymer nanocomposites[72].

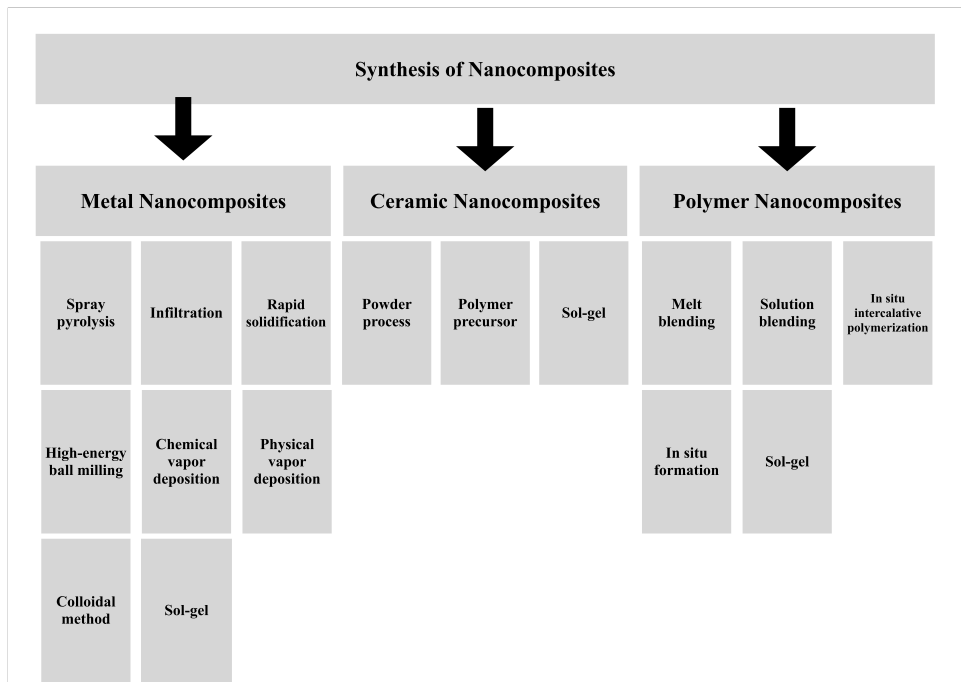


Figure 1.29 Nanocomposite fabrication techniques [72].

1.2.6.1 Polymer nanocomposites

Polymers possess lower strength and stiffness than metals, so usage of polymers is restricted. Therefore, there is a demand for reinforcement of polymers via nanomaterials that have superior mechanical properties. For aerospace structures, there is a need for stiff, strong, and light materials. At this point, polymers are becoming more attractive day by day[10].

The amount of the used nanomaterials determines the features of polymers. Compared to conventional polymer composites, using nanofillers for reinforcing provide a totally novel road. Producing ultra-large interfacial areas in nanocomposite polymers is possible with uniform dispersion. The big difference between polymer nanocomposite and conventional polymer composite is to have immense interfacial areas[73].

1.2.6.2 Polymer/GNPs nanocomposites

The graphene content, dispersion, and functionalization dictate the electrical conductivity, flexural strength, modulus, tensile strength, and thermal stability of polymer/ graphene nanocomposite. The processing technique used is another parameter that determines the enhancement in the mechanical properties of polymer/graphene nanocomposite[74].

Aggregation (owing to the platelet–polymer interactions) and interfacial adhesion (owing to the platelet–polymer interactions) are two significant factors that restrict GNPs' applications[75].

1.2.6.2.1 Preparation methods of polymer/GNPs nanocomposites

To obtain a fine dispersion in the polymer matrix is the difficult part of utilizing graphene nanosheets in the polymer. The condition and selection preparation approach are very important because nanocomposites last properties change with the GNP dispersion status in the polymer structure. The production of GNP nanocomposites got three main approaches which are melt blending, solution blending, and in situ polymerization[76].

In the method of in-situ polymerization, the polymerization reaction starts by radiation or heat after dispersing GNP in the monomer solution. The macromolecules that are created during the reaction of polymerization can disperse in the nanosheets and smooth the exfoliation structure establishment[76].

In the solution blending technique, a solvent that dissolves polymer by ultrasonication or mechanical stirring is used. Firstly, graphene is exfoliated in this solvent. Afterward, the graphene nanosheets are adsorbed by the polymer. Lastly, the solvent is removed. The scalability in available industrial apparatuses like extrusion is possible in the melt mixing method. For this reason, melt mixing is the most popular of these three methods. Nevertheless, the processing temperature is a drawback. The functionalized groups are not stable at this temperature. Oxygen-containing structures exposure thermal degradation at high mixing temperatures[76].

In situ polymerization and solution methods provide better matrix/nanofiller interaction and dispersion than the melt blending method[77].

1.2.6.2.2 polymer/GNPs nanocomposites applications

There are various industrial applications where high-performance nanocomposites are used (Figure 1.30).

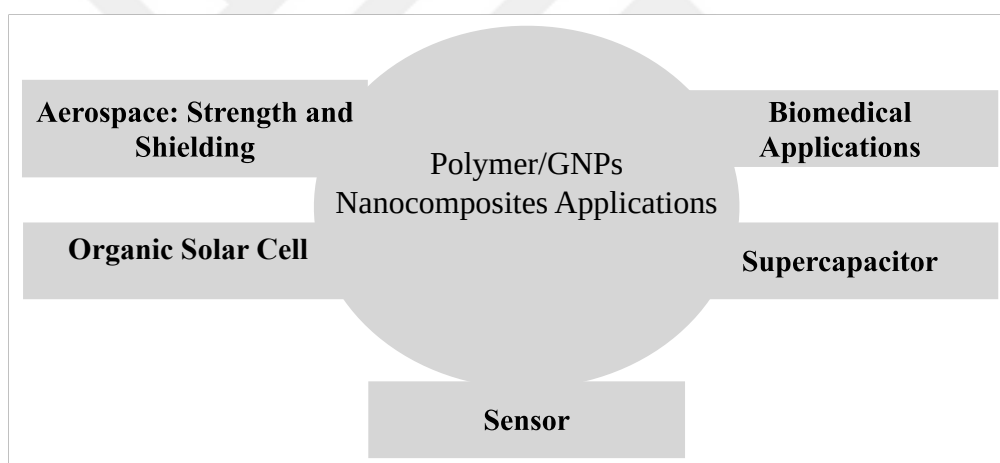


Figure1.30 Polymer/GNPs nanocomposites applications[56].

Various Polymer /GNPs have been reported in Table 2.1.

Table 1.5 Example studies for Polymer/GNPs

Polymer	GNPs content	Fabrication of nanocomposites	GNPs Influence on Nanocomposite Properties
Silicone rubber [78]	0–8 wt%	Solution blending	Improving the thermal, electrical, and mechanical properties of silicone rubber.
Poly lactide[79]	0-15 wt%	Melt mixing	Increasing the conductivity and permittivity, Enhancing the shielding effectiveness.
Poly(propylene2, 5-furandicarboxylate) (PPF) [80]	0.5, 1, 2.5 wt. %	In-situ melt polycondensation	Improving the thermal stability, Increasing the activation energy value. Causing occurrence of homolytic degradation reactions
Polypropylene (PP) [81]	0.1-0.5 wt. %	Melt mixing	Increasing the values of the Young's modulus, the tensile yield strength and the tensile fracture of the composites, Decreasing the values of the tensile elongation at break.
Polyamide 6 (PA6) [82]	10-20 wt%	Melt mixing	Increasing crystallinity, Enhancing Young's modulus, Increasing conductivity.

Table 1.5 (continued) Example studies for Polymer/GNPs

Polymer	GNPs content	Fabrication of nanocomposites	GNPs Influence on Nanocomposite Properties
High density polyethylene (HDPE) [83]	1, 2 and 3 wt%	Solution blending	plastic deformation under tensile loading and flexural strength increased in the case of 1% wt GNPs, is being dramatically decreased for greater GNPs contents
Polypyrrole (PPy)[84]	10-50 wt%	In situ chemical oxidative polymerization	Increasing the photocatalytic degradation of bromophenol blue (BPB) Obtaining a multifunctional material for bacterial growth inhibition and cleaning contaminated water
Poly(lactic acid) [85]	0.25 wt. %	Melt-blending	Improving thermo-mechanical properties



2 EXPERIMENTAL

2.1 Materials

Nanocomposite of PMMA/GNPs production was made using in situ ATRP polymerization. The process is optimized by carrying out Copper (I) bromide (CuBr). High-efficiency, simple and inexpensive synthesis aim is gained by using the catalyst. Materials which are needed to start are widely available. The materials which are used in this study and their properties showed in Table 2.1.

Table 2.1 The materials which are used in this study and their properties.

Name	Methyl methacrylate (MMA)	Ethyl 2 - bromoisobutyrate (EBIB)	Tetrabutyl - ammonium bromide	Copper bromide	Pentamethyldiethylenetriamine (PMDETA)	Argon
Chemical Formula	C ₅ H ₈ O ₂	C ₆ H ₁₁ BrO ₂	Bu ₄ NBr	CuBr	C ₉ H ₂₃ N ₃	Ar
Molecular Weight(g/mole)	100.121	195.05	322.37	143.45	173.3	39.94
Purity	≥99.0%	≥98.0%	≥99.0%	≥99.99%	≥99.0%	≥99.99%
Manufacturer	Sigma Aldrich	Sigma Aldrich	Sigma Aldrich	Sigma Aldrich	Sigma Aldrich	Özvarış Firm
Task in ATRP	Monomer	Initiator	Solvent	Catalytic	Ligand	Noble Gas

Different amounts of Graphene Nanoplatelets (GNPs) were used to reinforce PMMA. Table 2.2 shows the study used GNPs properties.

Table 2.2 Graphene Nanoplatelets (GNPs) which is used in this study and its properties.

Name	Graphene Nanoplatelets (GNPs)
Purity	$\geq 99.5\%$
Thickness (nm)	6
Diameter (μm)	5
Specific surface area (m^2/g)	150
Manufacturer	Nanografi Nanotechnology AS
Task in atrp	Nanofiller/Nano Additive

2.1.1 PMMA/GNPs Nanocomposite and base PMMA synthesis equipment and devices

The main equipment and devices used in the synthesis of PMMA/GNPs Nanocomposites and base PMMA are shown in Figure 2.1.

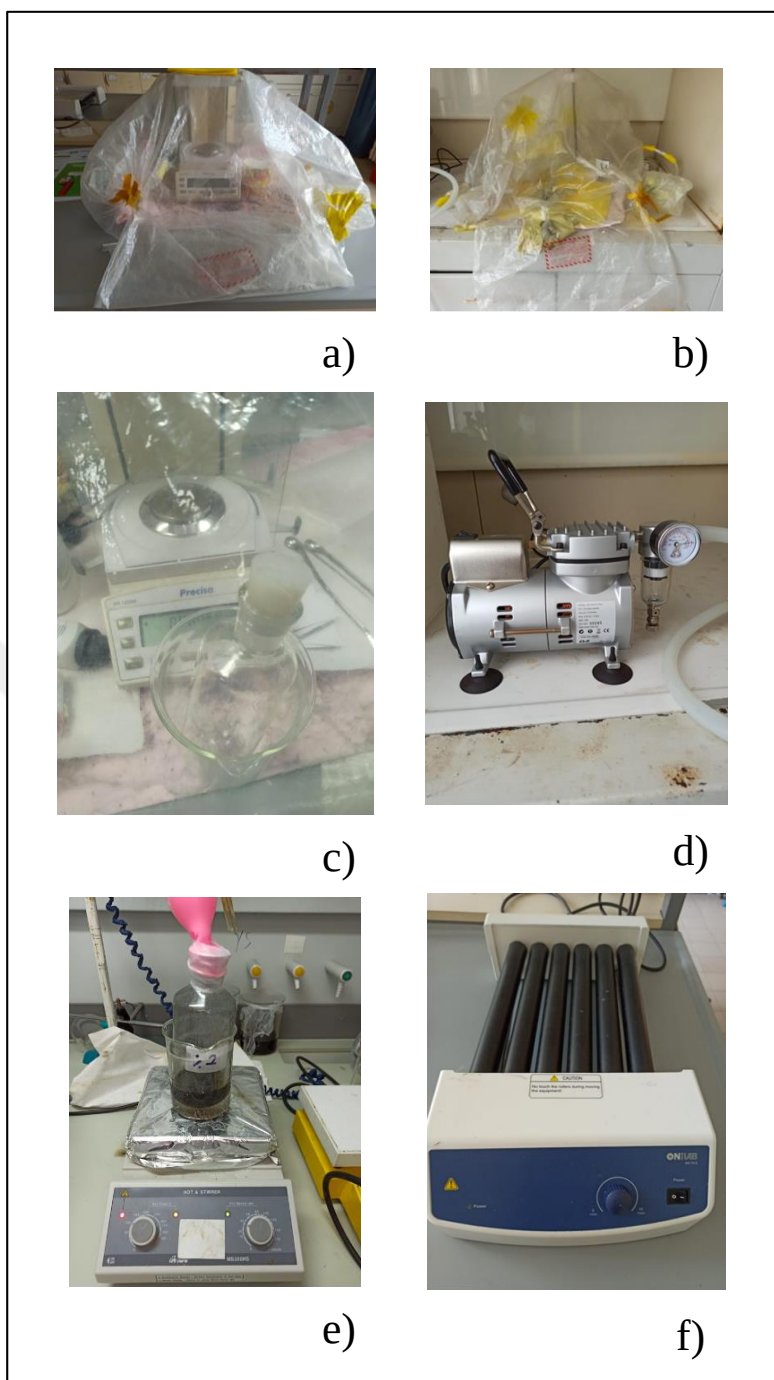


Figure 2.1 a) Atmos-Bag 1, b) Atmos-Bag 2, c) Weighing Instrument, d) Vacuum Pump, e) Magnetic Stirrer, f) Rotary Stirrer.

2.2 Synthesis of PMMA/GNPs Nanocomposites and Base PMMA

The schematic diagram for the stages of the Manufacturing Process to produce the PMMA/GNPs nanocomposite is illustrated in (Figure 2.2)[86].

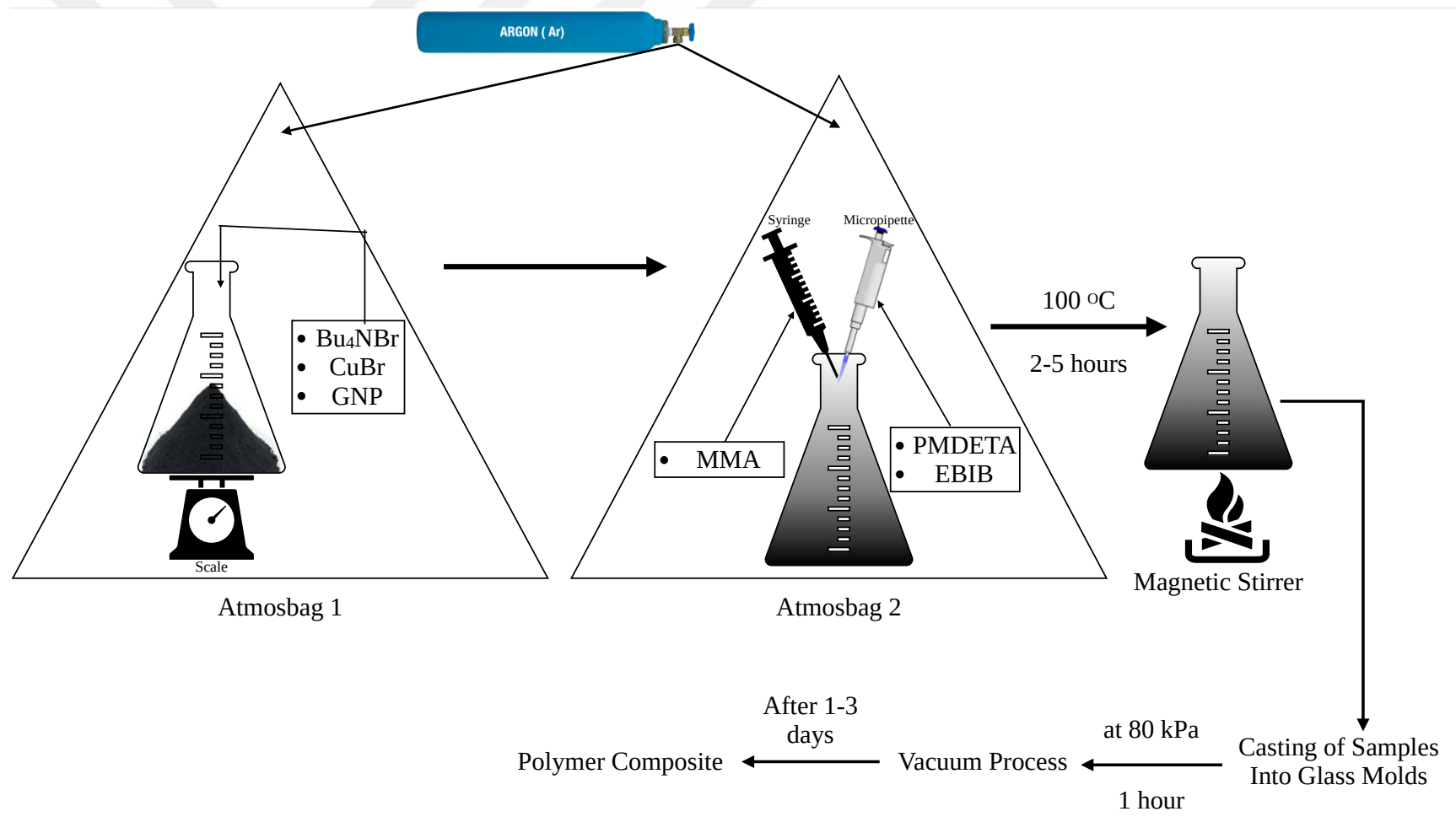


Figure 2.2 PMMA/GNPs Nanocomposite Manufacturing Process [86].

To intercept being oxidized of copper, two two-handed Atmos-Bags were used. Besides, A two-handed Atmos-Bag enables a polymer nanocomposite manufacturing process practical and cost-effective. Before placing into a two-handed Atmos-Bag, all chemicals were made prepared.

All the air was discharged via a vacuum pump after the chemicals in solid form were accommodated into two-handed Atmos-Bag. In the aim of avoiding undesirable reactions which take place during the polymerization, argon gas is used in filling two-handed Atmos-Bag. Subsequently, the solvent Bu₄NBr (3.76 mmol, 1.211 g), the catalyst CuBr (0.47 mmol, 0.067 g), and GNPs with dissimilar quantities (such as 0.2, 0.5, 1, 1.5, 2, 3 and 5 weights %) were weighed with a high degree of accuracy in the weighing instrument. After that, the components in solid form were placed into the glass. The weighed solid chemicals were mixed in the glass and sealed with paraffin just at the moment that. The solid mixture was taken away out of the first two-handed Atmos-Bag. After removing the mixture in solid form from the two-handed Atmos-Bag, it was placed into another two-handed Atmos-Bag. All the air was expelled via a vacuum pump after the chemicals in liquid form were placed into two-handed Atmos-Bag. Instantly after, this two-handed Atmos-Bag also was charged with argon gas. After getting rid of the paraffin, the monomer (MMA) (28.2 g, 0.282 mol), and ligand PMDETA (0.47 mmol, 0.081 g) were added into the mixture which is in solid form. After both the ligand and the initiator were inserted into the mixture, the gas-tight syringe was utilized to perform the degas process for 10 minutes. Following up, the initiator EBIB (0.47 mmol, 0.092 g) was put in the solution, and then the glass was sealed with stopper and paraffin. In some experiments, a balloon was used instead of a stopper to observe the amount of produced gas during the polymerization.

After adding EBIB, the polymerization process started. To locate the mixture glass on the magnetic stirrer operating at 100°C and 300 rpm/min, it was taken out of Atmos-Bag. The magnetic stirrer enables to keep temperature characteristics under control and set manually. The solution was taken away from the magnetic stirrer for 5 minutes per half an hour and located on a rotary stirrer to prevent copper- ligand complex compound from settling at the bottom of the mixture. The magnetic stirrer and the rotary stirrer dictate the mixture to mix homogeneously and more swiftly. As polymerization continues carrying out in the solution within the glass, the solution initiates to solidify. At the end of the pourable stage of the solution, the solution was

cast into glass molds. In the aim of oxidation prevention, the mixture pourable stage end was chosen. 2-5 hours is the section time (from magnetic stirrer until pouring). 80 kilo Pascal vacuum is applied to the samples for an hour (paraffin prevent air entry). Thanks to that, the polymer is more mechanically stable than to minimizing the air bubbles in the structure. The samples are kept in vacuum for 1 to 3 days. Figure 2.3 shows the whole polymer composite synthesis process.

In the synthesis of base PMMA, the manufacturing process and their steps are similar to PMMA/GNPs, however, GNPs is not added while solid form chemicals were mixed. And also, the duration of polymerization is changeable.

Figure 2.3 shows the steps of synthesis PMMA/GNPs 0.5% Nanocomposite. After solid components were weighed by the weighing instrument in Atmos-Bag 1 (Fig 2.3a), the liquid components were added into this mixture in Atmos-Bag 2. The mixture was taken out of Atmos-Bag 2 and located on the magnetic stirrer (Figure 2.3b). After the sample was kept in the glass for 2 days, the nanocomposite was gained (Figure 2.3c).

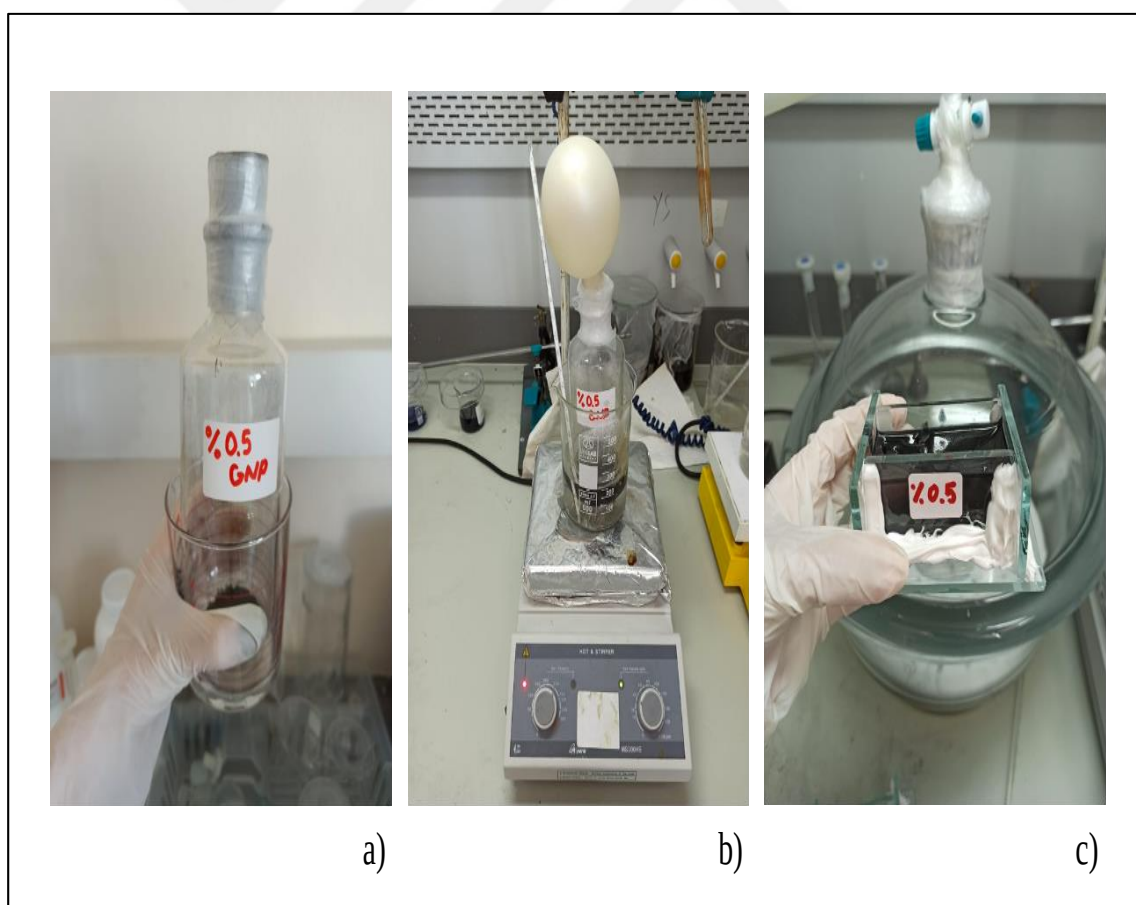


Figure 2.3 The Synthesis PMMA/GNPs 0.5% Nanocomposite.

Figure 2.4 displays the stages of synthesis PMMA/GNPs 3% Nanocomposite. After solid components were weighed in Atmos-Bag 1(Figure 2.4a), the liquid components were added into this mixture in Atmos-Bag 2. The mixture was located on the magnetic stirrer (Figure 2.4b), after it was taken out of Atmos-Bag 2. Figure 2.4c shows the final state of the PMMA/GNPs 3% Nanocomposite at the end of the manufacturing process.

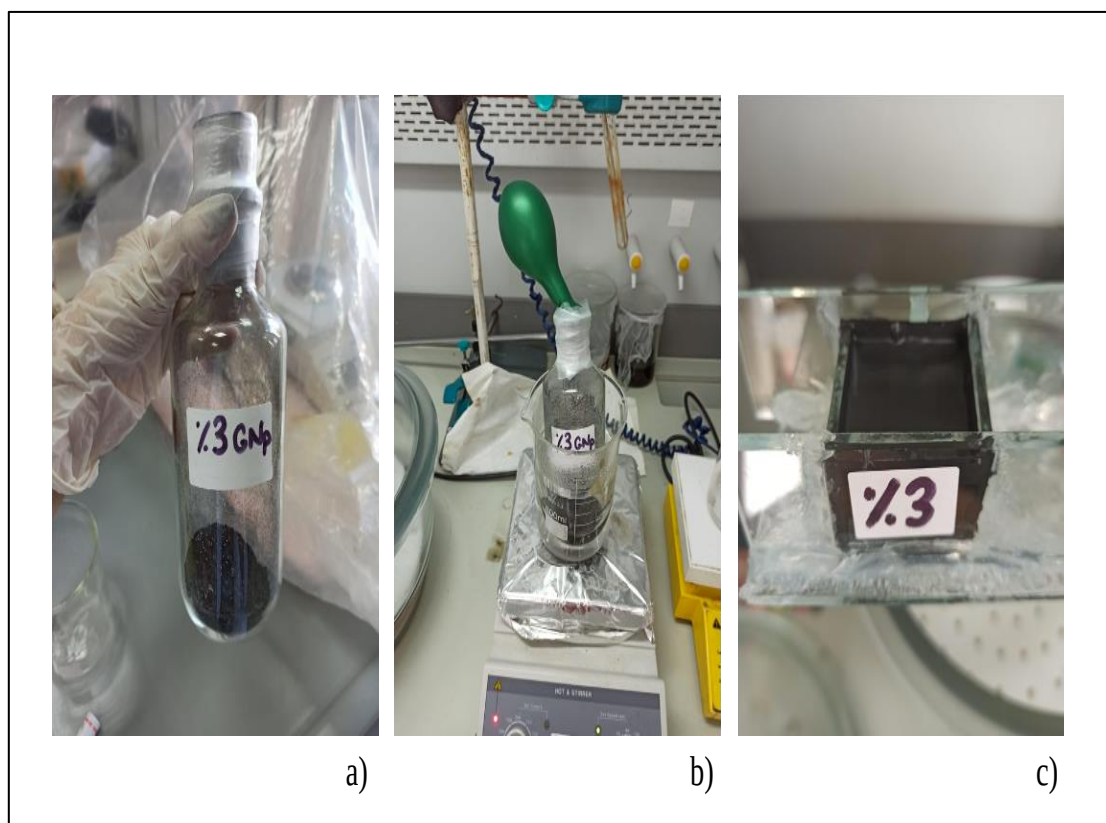


Figure 2.4 The Synthesis PMMA/GNPs 3% Nanocomposite.

Fig. 2.5 exhibits some stages of synthesis PMMA/GNPs 5% and PMMA/GNPs 2% Nanocomposites jointly. After the weighing process of components, the mixtures were heated on the magnetic stirrers separately (Figure 2.5 a). At the end of their pourable stages of the solutions, they were poured into the glass molds (Figure 2.5 b).

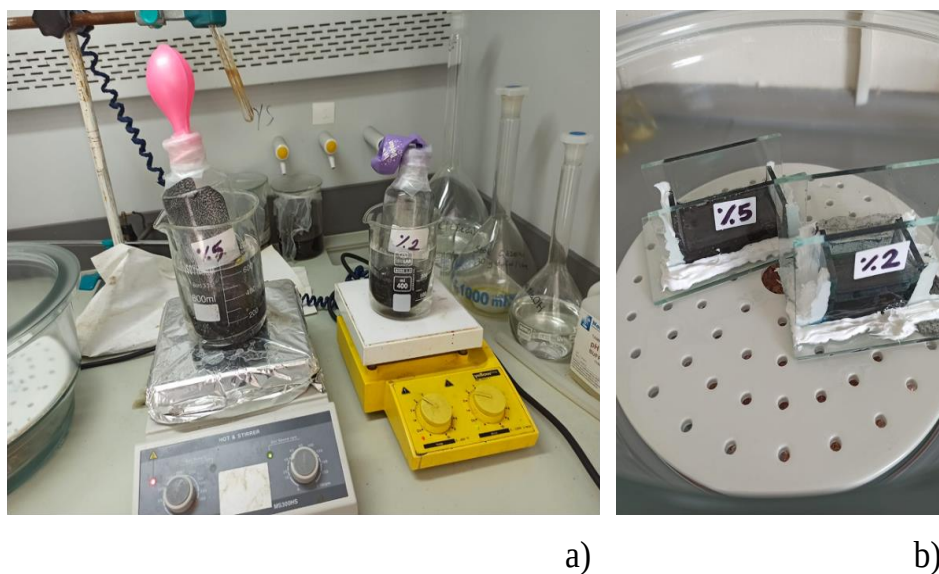


Figure 2.5 The Synthesis of PMMA/GNPs 5% and PMMA/GNPs 2% Nanocomposites.

Figure 2.6 demonstrates some stages of synthesis PMMA/GNPs 1.5% nanocomposite. After adding EBIB into the solution, the mixture was started to heat on the magnetic stirrer (Figure 2.6 a). Figure 2.6 b exhibits the nanocomposite under pressure during the vacuum.

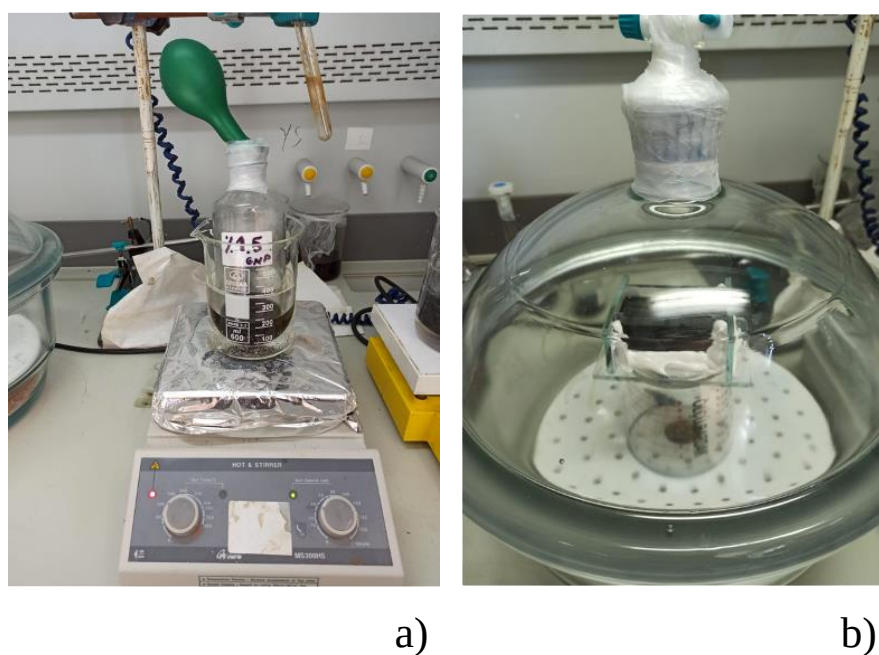


Figure 2.6 The Synthesis of PMMA/GNPs 1.5% Nanocomposite.

Fig. 2.7 exhibits some stages of synthesis base PMMA. After the weighing process of components, the mixtures were heated on the magnetic stirrer (Figure 2.7 a). The rotary stirrer was used to mix the solution homogeneously during the heating process (Figure 2.7 b). Figure 2.7 c demonstrates the base PMMA under pressure during the vacuum.

For all samples, the manufacturing process and their steps are similar. However, the duration of the manufacturing process is dependent on the content of the nanocomposite. The end of the pourable stage of the solution is significant in all. Therefore, determining the right time to pour the mixture into the molds is critical. The manufacturing process dictates the most properties of the nanocomposites.

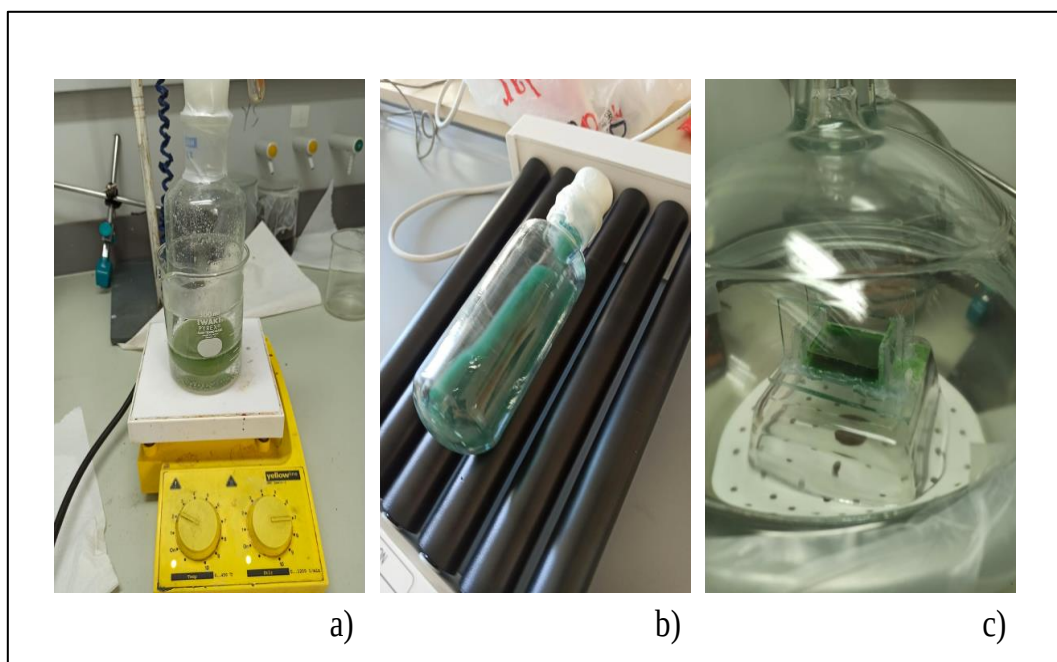


Figure 2.7 The Synthesis of base PMMA

2.3 Characterization of PMMA/GNPs Nanocomposites and Base PMMA

2.3.1 Scanning electron microscope (SEM) analysis of PMMA/GNPs nanocomposites

PMMA/GNPs nanocomposites morphological characterization is made by Scanning Electron Microscope (FEI - Quanta FEG 250 Model) (shown in Figure 2.8) at ITU National Research Center on Membrane Technologies (MEM-TEK). PMMA/GNPs nanocomposites micro structure as a function of concentration of GNPs are utilized to study GNPs distribution and dispersion quality in the PMMA polymer matrix. Material polymer matrix GNPs dispersion and distribution quality is an important parameter that affects the PMMA/GNPs nanocomposites performance.

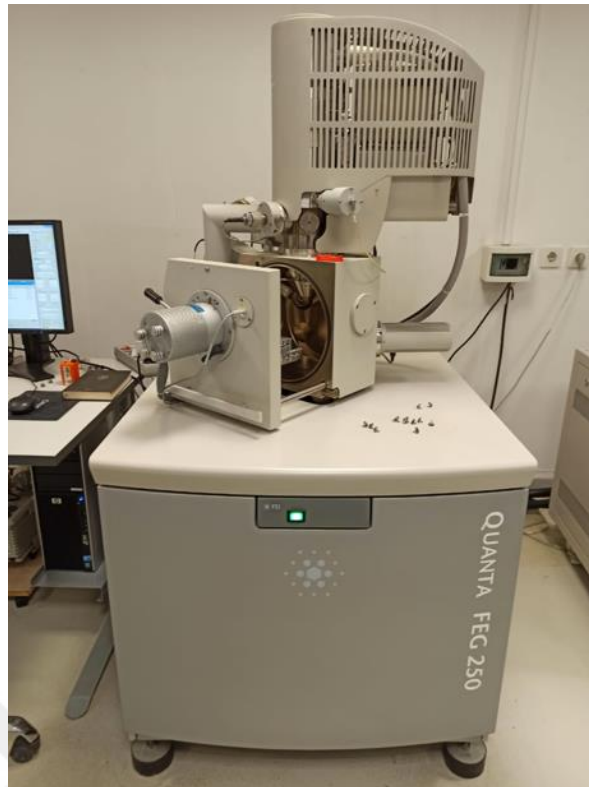


Figure 2.8 The scanning electron microscope (SEM).

Figure 2.9 shows the preparation of the samples and Figure 2.10 shows the coating device that they were placed in before characterization. After that, plasma coating technique cotes small samples. Thanks to that SEM is able to get high-quality morphology images. Then, in an evacuated scanning electron microscope chamber (Figure 2.11) the samples are placed. After that, in order to get surface morphology, the samples are put through a 15 kilos volt highly focused electron beam. Finally, the samples morphology image is displayed on the screen.



Figure 2.9 SEM samples preparation.



Figure 2.10 Coating Device used in this study.

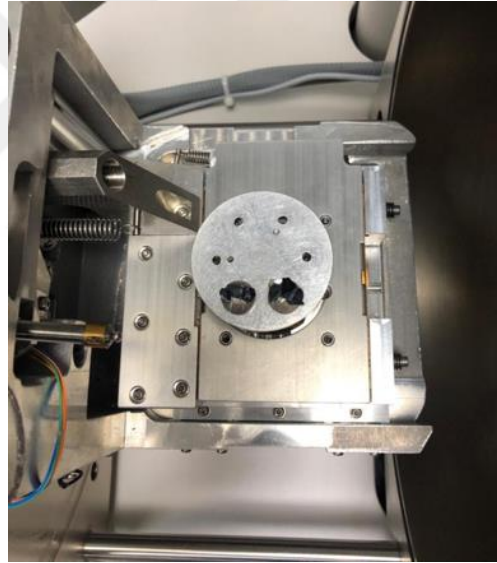


Figure 2.11 PMMA/GNPs Nanocomposite samples in the evacuated scanning electron microscope chamber.

2.3.2 X-Ray Diffraction (XRD) analysis of PMMA/GNPs nanocomposites and base PMMA

PMMA's GNPs amount rise in the nanocomposite structure effect on the crystalline properties was examined using X-Ray Diffraction (XRD). The study was taken place in ITU Prof. Dr. Adnan Tekin Applied Research Center of Materials Science and Production Technologies (ATUM) using X'pert pro device (Figure 2.12). XRD was operating at 40mA and 40 kV and a 2°/min scanning speed and with Cu Ka radiation ($k = 1.541 \text{ \AA}$).



Figure 2.12 XRD diffractometer.

2.3.3 Fourier Transform Infrared Spectroscopy (FTIR) analysis of PMMA/GNPs nanocomposites and base PMMA

FTIR Spectroscopy was applied to examine chemical structures of PMMA/GNPs nanocomposites such as chemical bonds, functional groups. Infrared spectroscopy is also beneficial to identify the quality of nanocomposites.

The FTIR measurements were achieved using an FTIR Spectrometer device branded PerkinElmer- Spectrum 100 (in Figure 2.13) at ITU National Research Center on Membrane Technologies (MEM-TEK).

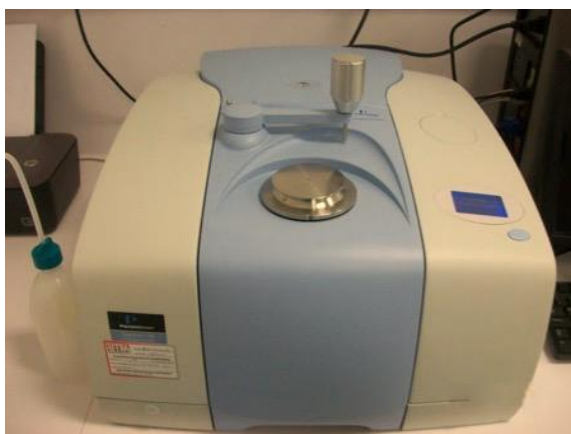


Figure 2.13 Fourier Transform Infrared Spectroscopy.

2.3.4 Thermogravimetric Analysis (TGA) of PMMA/GNPs nanocomposites and base PMMA

Thermogravimetric Analysis (TGA) is one of the thermal analysis methods and was utilized to examine the thermal stability of the nanocomposites. Temperature increasing

(in a certain rate) results in the sample mass weight change thus obtaining Thermogravimetric analysis (TGA). Thermogravimetric analysis (TGA) measurements were achieved utilizing a TGA-DSC device branded Likron SDT-Q600 (showed in Figure 2.14) at ITU Materials Production and Preparation Laboratory.



Figure 2.14 TGA-DSC.

2.3.5 Raman spectroscopy analysis of base PMMA and PMMA/GNPs

Raman spectroscopy is a carbon structure characterization advanced analysis technique. GNPs exfoliation extent, PMMA GNPs interaction, crystalline properties of GNPs and GNPs concentration change was examined in this study using Raman spectroscopy. Raman Spectroscopy Analysis was performed via Kaiser Optical model Raman Spectrometer (in Figure 2.15) at ITU Chemical and Metallurgical Engineering Faculty Crystallization Laboratory.



Figure 2.15 Raman Spectrometer.

2.3.6 X-ray Photoelectron Spectroscopy (XPS) analysis of PMMA/GNPs

X-ray Photoelectron Spectroscopy (XPS) is an analytic method that identifies the specific electrons evicted from the superficial of an example. The method is exceedingly surface-delicate by the detection depth ~ 5 nm. This analysis method was used to examine the PMMA/GNPs nanocomposites' surface chemistry. X-ray Photoelectron Spectroscopy (XPS) Analysis was achieved via Thermo K-Alpha X-ray Photoelectron Spectrometer (in Figure 2.16) at Koç University Surface Science and Technology Center (KUYTAM).



Figure 2.16 Thermo K-Alpha X-ray Photoelectron Spectrometer.

2.3.7 Stereo microscope measurement of PMMA/GNPs

In order to get 3D samples surface information, the surface topographies were viewed using a stereo microscope. Stereo Microscope Measurement was taken place with a LEICA Stereo Microscope device (in Figure 2.17) at ITU Chemical and Metallurgical Engineering Faculty Sol-Gel Laboratory.



Figure 2.17 LEICA Stereo Microscope.

2.3.8 Static contact angle measurement of PMMA/GNPs nanocomposites

Static Contact Angle Measurement of PMMA/GNPs was achieved using a Contact Angle Measurement device branded KSV CAM 200 (shown in Figure 2.18) in Mechanical Metallurgy and Heat Treatment Laboratory at ITU Faculty of Chemical and Metallurgical Engineering. KSV CAM 200 is a powerful computer toll that automatically analysis images video capture for measuring liquids absorption into porous materials, surface free energies, liquids surface or interfacial tensions and static/dynamic contact angles.

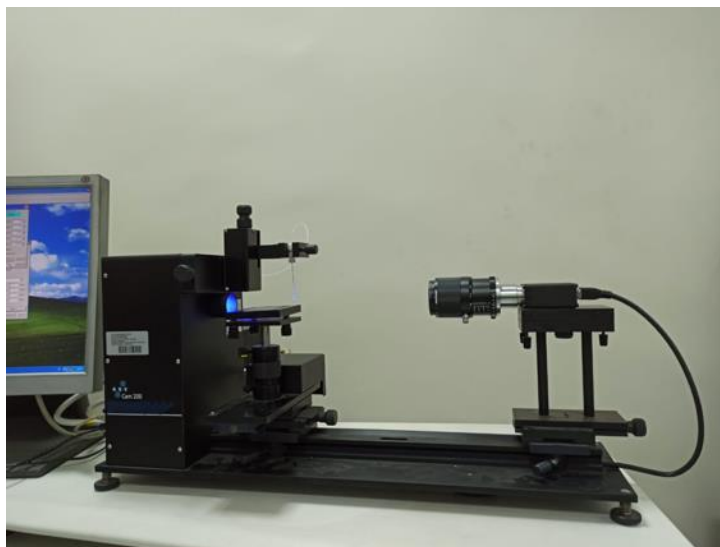


Figure 2.18 KSV CAM 200 Contact Angle Measurement device.

Static Contact Angle Measurement was carried out to analyze the strength of contact, wettability, and hydrophobicity in the interaction between solid and liquid.

This technique has a simple process. A water drop is poured onto the surface of the material. When the liquid contacts with a solid face of the material, forms the contact angle (Figure 2.19). Contact angle provides to measure the wettability of a matter. During the static contact angle measurement, the contact area between solid and liquid was not altered by an external effect. On a hydrophilic surface, water drop flattens out, however, on a hydrophobic, it balls up.

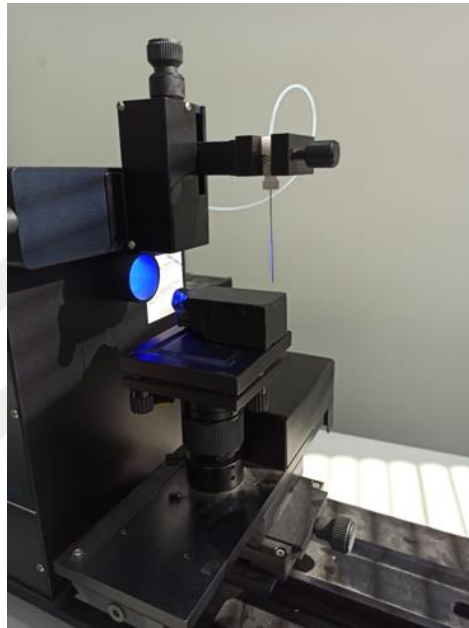


Figure 2.19 Static contact angle analysis of PMMA/GNPs 3% Nanocomposite.

2.3.9 Ultrasonic test

Samples' microhardness, shear modulus and young modulus were found by determining the PMMA/GNPs homogeneity by using the ultrasonic test method.

Figure 2.20 shows the ultrasonic testing device Krautkramer USM 25 which was used in the study to measure the velocity. Room temperature is necessary to achieve the measurements. In the aim of monitoring echo amplitudes pulse echo technique were utilized in the ultrasonic test. The PMMA/GNPs nanocomposite longitudinal wave velocity changes according to GNPs concentration were determined using a 4 MHz frequency ultrasonic probe.



Figure 2.20 Ultrasonic testing device.

The samples reference velocity was 3248 m/s which is the calibration steel block velocity, which was determined before the longitudinal wave's measurements. Reference material range was 50 mm. Figure 2.21 shows the MB4S probe used to measure the longitudinal wave's velocity.

The characterization test was carried out at Çekmece Nuclear Research and Training Center in Küçükçekmece Istanbul.



Figure 2.21 Measurement of the longitudinal wave of PMMA/GNPs 1% Nanocomposite with MB4S probe.

2.3.10 Density measurement of PMMA/GNPs by using gas Pycnometry technique

PMMA/GNPs nanocomposite elastic parameters changes according to GNPs concentration rise were determined by obtaining the samples densities by a Gas Pycnometer.

Gas pycnometry is a powerful technique to obtain accurate density and volume. In order to measure the volume this technique utilize the method of gas displacement so it is nondestructive. The displacement medium is an inert gas like nitrogen or helium. The density measurement was performed via Gas Pycnometer device branded Micromeritics™ AccuPyc II 1340 (Figure 2.22) at ITU Chemical and Metallurgical Engineering Faculty Phase Analysis Laboratory. The pycnometer of AccuPyc II 1340 is a rapid device which gives accurate density and volume measurements.



Figure 2.22 Gas Pycnometer.



3 EXPERIMENTAL RESULTS

In the aim of determining the interactions of materials, several methods were used to characterize the materials' structural and chemical properties: SEM, XRD, FTIR, TGA, Raman Spectroscopy and XPS analysis, Static Contact Angle measurement, and Ultrasonic test.

3.1 Scanning Electron Microscope (SEM) Analysis of PMMA/GNPs Nanocomposites

Scanning electron microscope (SEM) was utilized to analyze the nanocomposite surface morphologies. The figure 3.1 shows PMMA/GNPs drawing.

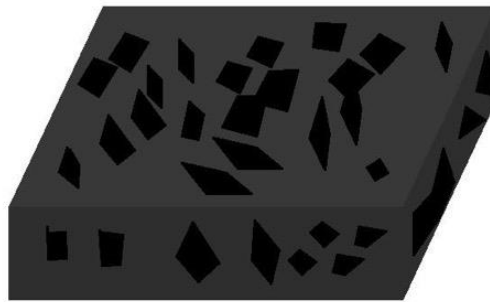


Figure 3.1 PMMA/GNPs drawing[86].

A mechanical reinforcement essential factor is an excellent nanofiller dispersion because of GNPs agglomerates forming tendency owing to π - π interaction, big surface area, and also powerful Van Der Waals attraction[87].

PMMA GNPs dispersion and adhesion improvement can attribute the nanofillers properties like decreasing crystallite size, increasing surface roughness among nanopores and increasing surface area. Random dispersion and well adhesion of GNPs particles in the matrix of PMMA is obvious. Approximately similar diameters of some microns and irregular geometry are properties that GNPs particles possess. GNPs interface and polymer holes and voids lack indicate GNPs excellent adhesion in the PMMA matrix. In the analysis of scanning electron microscopy, micron scale lack of huge agglomerates shows outstanding dispersion of GNPs in the PMMA matrix. There

were no GNPs aggregates neither dark phase seen, that shows that there was no release of irregular energy and no asymmetrical done by heterogeneous morphology. Excellent exfoliation and outstanding dispersion are possible in GNPs solution compounding. Aggregate's formation causes even dispersion decrease of GNPs in the matrix of PMMA which can lead to undesirable mechanical properties.

Increasing GNP content up to 3 wt. % makes the surface much smoother and there are no surface cavities, but some tiny scratches. At the highest content of GNP (3 wt. %), there are rectangular cracks at the surface without any cavities. Both surface and internal examination of the composites revealed that GNP addition from 0.2 to 3 wt. % significantly affects the composite morphology. In this context, the GNP content should be optimized to satisfy the desired needs which are determined by surface and internal morphologies of the composite.

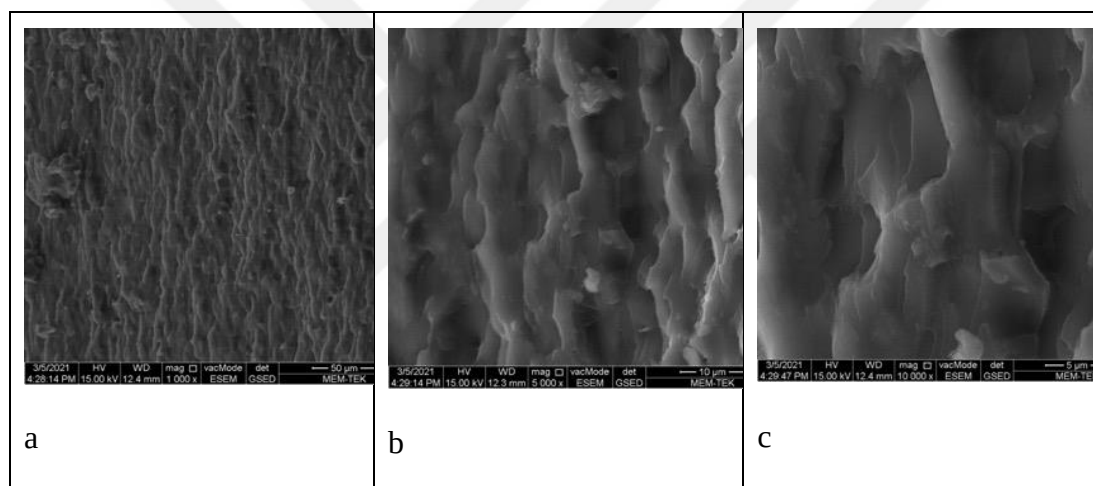


Figure 3.2 SEM images of 0.2 wt. % PMMA/GNPs nanocomposite at (a) 1 000 x, (b) 5 000 x, (c) 10 000 x magnifications.

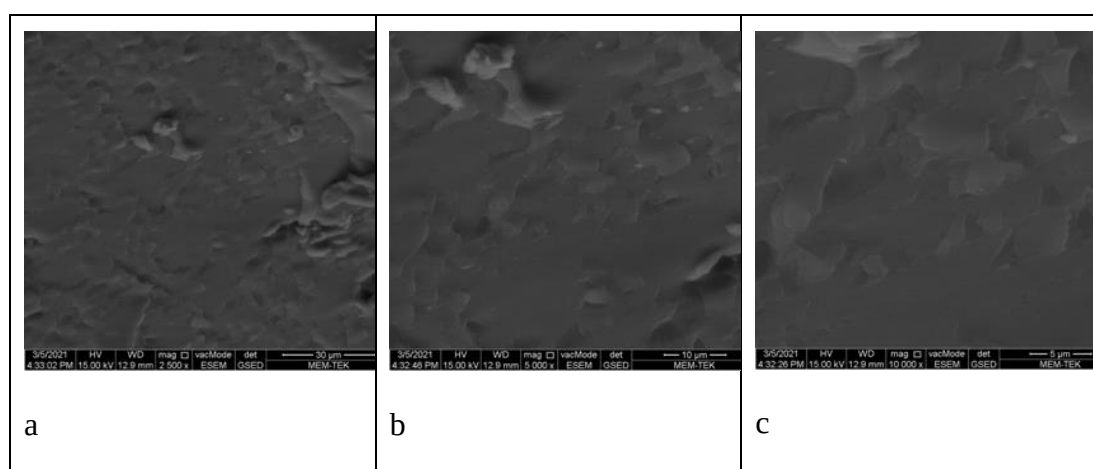


Figure 3.3 SEM images of 0.5 wt. % PMMA/GNPs nanocomposite at (a) 2 500 x, (b) 5 000 x, (c) 10 000 x magnifications.

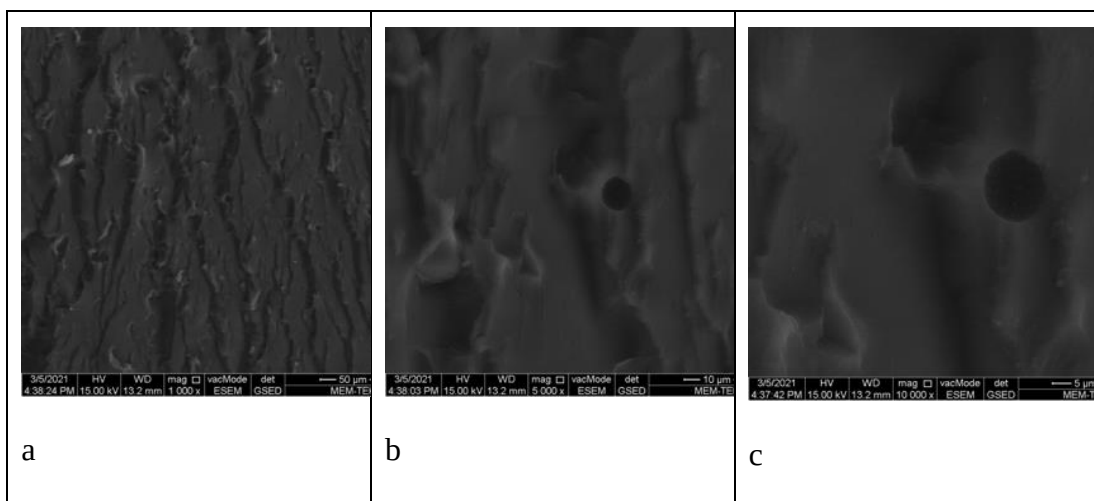


Figure 3.4 SEM images of 1 wt. % PMMA/GNPs nanocomposite at (a) 1 000 x, (b) 5 000 x, (c) 10 000 x magnifications.

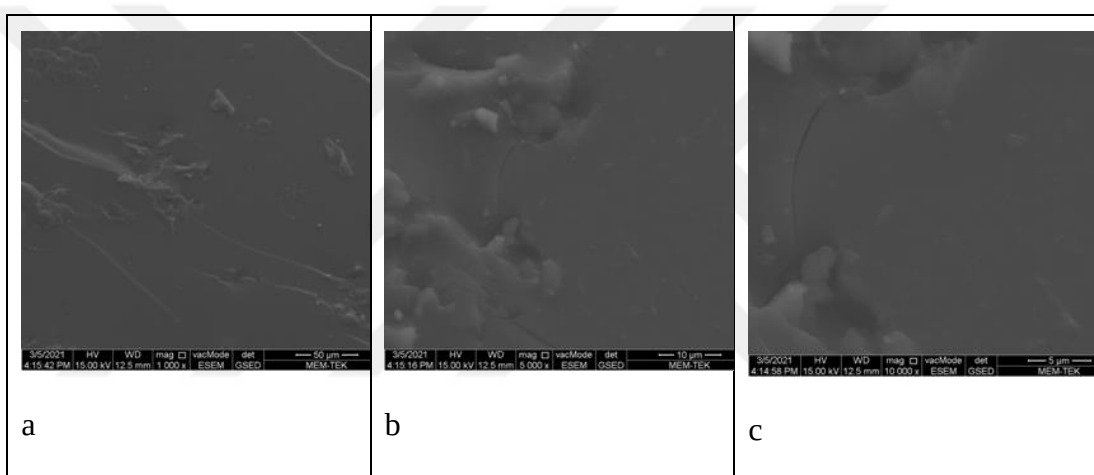


Figure 3.5 SEM images of 1.5 wt. % PMMA/GNPs nanocomposite at (a) 1 000 x, (b) 5 000 x, (c) 10 000 x magnifications.

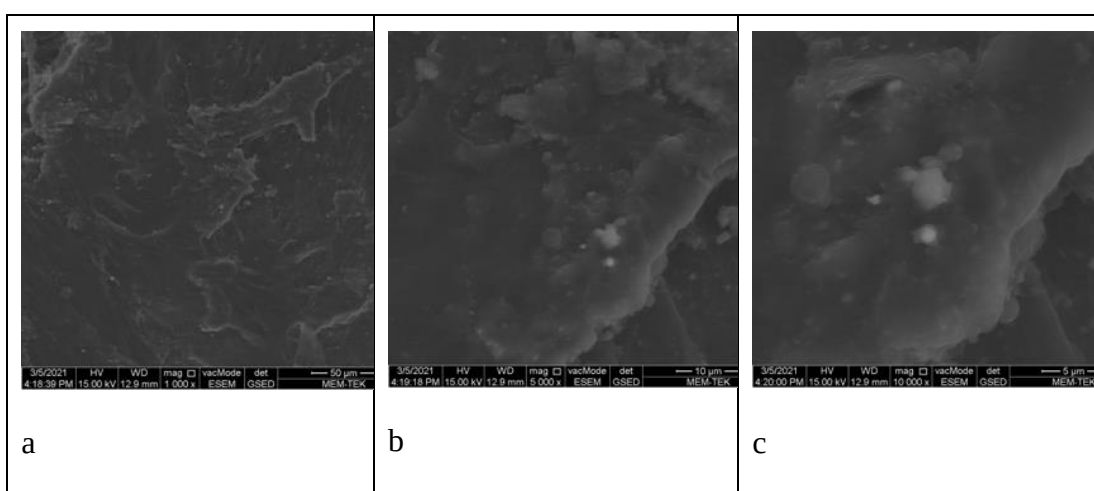


Figure 3.6 SEM images of 2 wt. % PMMA/GNPs nanocomposite at (a) 1 000 x, (b) 5 000 x, (c) 10 000 x magnifications.

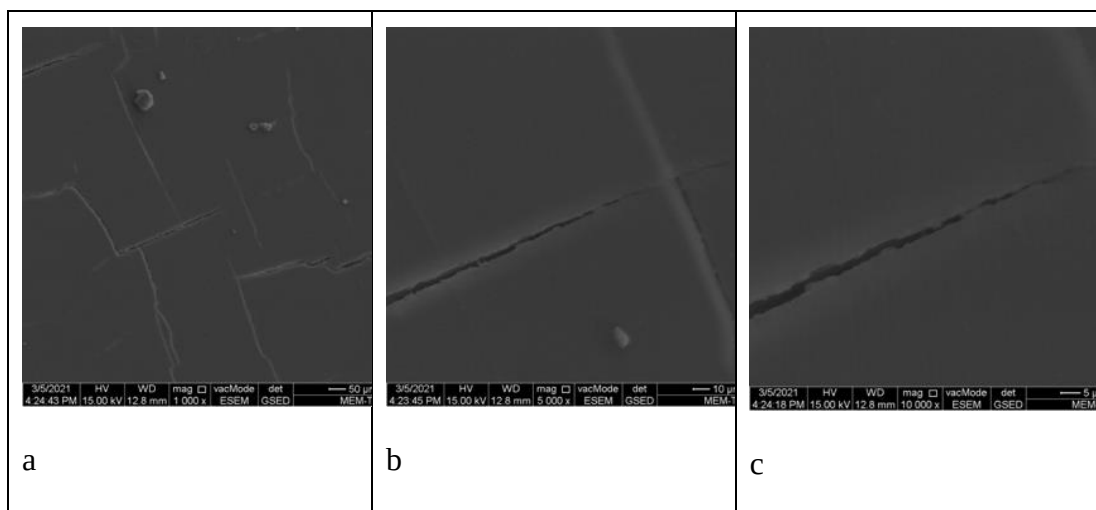


Figure 3.7 SEM images of 3 wt. % PMMA/GNPs nanocomposite at (a) 1 000 x, (b) 5 000 x, (c) 10 000 x magnifications.

3.2 X-Ray Diffraction (XRD) Analysis of PMMA/GNPs Nanocomposites and Base PMMA

Figure 3.8 shows patterns of XRD for the graphene nanocomposites. Diffraction intensity reduction order 0.2% <.... <5%.

Figure 3.8 shows the wide diffraction peak at $2\theta=14.43$ which demonstrate amorphous nature of PMMA. Non-exchangeable PMMA cause a peak of $\sim 14.43^\circ$ for all GNPs concentrations[88].

XRD diffraction patterns of the nanocomposite displays characteristic peak at $\sim 26.5^\circ$. Around $\sim 26.5^\circ$, the sharp diffraction peaks represent the GNPs (002) diffraction plane [89, 90].

Excellent ordered 0.34 nm interlayer spaced graphene composed graphite plane are shown by the $2\theta = 26^\circ$ peak[91].

However, there is a barely noticeable GNPs peak at low concentration samples. At GNPs concentration of 0.5% and 0.2%, GNPs characteristic peak of $\sim 26.5^\circ$ was also barely noticed.

Lowering the peaks of nanocomposites depict the polymer and nanofillers interaction. 5% GNPs samples had an increase in crystallinity. (002) diffraction plane had an increase in the intensity of peaks.

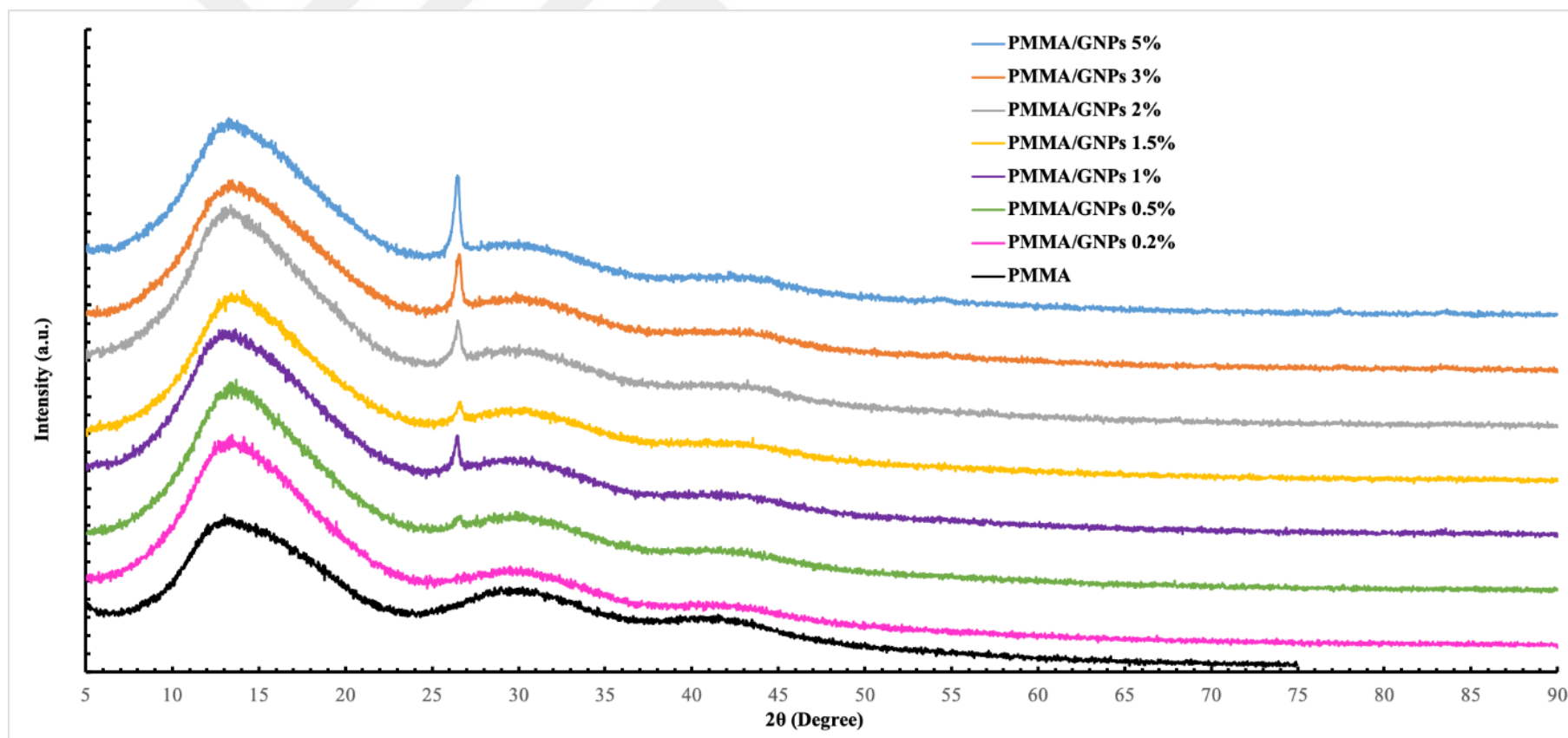


Figure 3.8 XRD analysis graph of PMMA/GNPs and Pure PMMA [86].

GNPs surface and PMMA excellent polymerization was confirmed by the results.

Consequently, nanocomposite samples crystallinity could affect the mechanical properties. Nanocomposite crystalline properties were affected by the small GNPs amount increase.

Improving crystallinity with the addition of GNPs results in enhancement in the mechanical properties of polymer nanocomposites as well[92-94].

3.3 Fourier Transform Infrared Spectroscopy (FTIR) Analysis of PMMA/GNPs Nanocomposites and Base PMMA

Nanocomposite and GNPs interface enhancement are important. Better improvements of toughness of fracture and resistance of absorption can be obtained from manufacturing an excellent interface between graphene and PMMA composites because that will make the GNPs dispersion and exfoliation better distributed in the polymer matrix[95].

Figure 3.9 presents the analysis of FTIR results for the samples of nanocomposite of GNPs/PMMA and pure PMMA both[96]. The wavenumber (cm^{-1}) is represented by the horizontal axis and the transmittance (T%) is represented by the vertical axes.

At 753 cm^{-1} (C=O bending), 1145 cm^{-1} (CH_2 bending), 1189 cm^{-1} (C–O–C bending), 1238 cm^{-1} (C–C–O stretching), 1382 cm^{-1} (C– CH_3 bending), 1434 cm^{-1} (O– CH_3 bending), 1729 cm^{-1} (C=O stretching), 2948 cm^{-1} (C– CH_3 , C–H stretching) and 2992 cm^{-1} (O– CH_3 , C–H stretching) nanocomposites of GNPs/PMMA can be seen[97, 98].

GNPs PMMA weak interaction is indicated by the spectra similarity of pure PMMA and PMMA/GNPs nanocomposites[99].

Furthermore, during the polymerization process composite components had no chemical reaction, that is indicated by the lack of new functional groups for PMMA/GNPs composite spectrum compared to the pure PMMA spectra[100].

Moreover, low GNPs% samples incorporation leads to lack of bands corresponding GNPs vibration absorption.

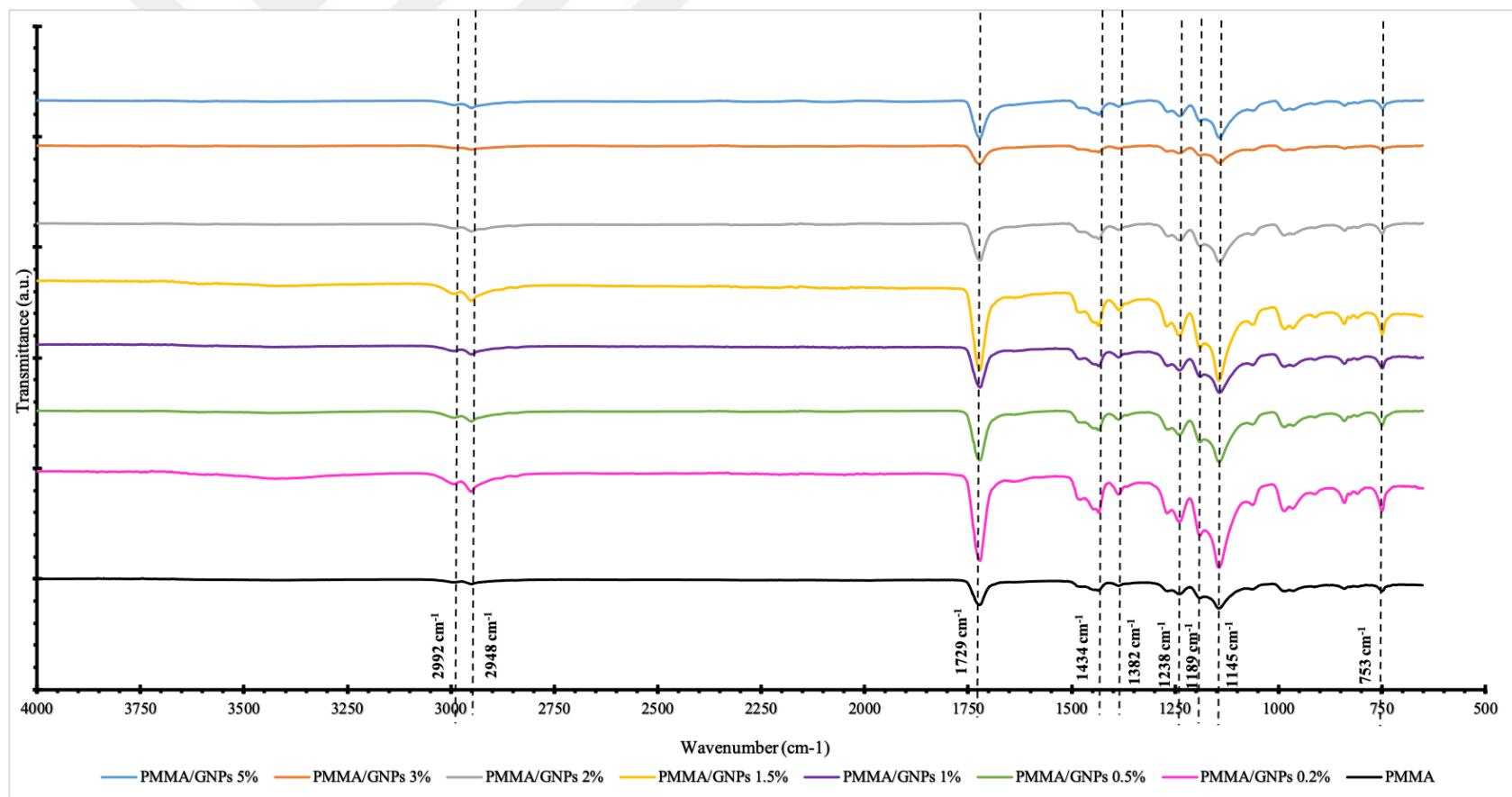


Figure 3.9 FTIR spectra of PMMA /GNPs nanocomposites and Pure PMMA [96].

In GNPs several concentrations the PMMA/GNPs bonding interaction variations leads to absorption peaks that are same for all the manufactured nanocomposites of the PMMA/GNPs. In accordance with the results of the FTIR test when GNP hits 5 weight% interaction of the among the polymer matrix of PMMA and the nanofiller (GNP) indicates minor modification in the nanocomposite of PMMA/GNPs spectrum of FTIR. No change in the distribution of the electrons in the molecular bonds did occur which is pointed out by the fact that in any concentration no position shift occurred for the peak.

3.4 Thermogravimetric Analysis of PMMA/GNPs Nanocomposites and Base PMMA

Figure 3.10 shows thermogravimetric analysis (TGA) composites' and base sample's thermogram. TGA analysis heating rate was 10 °C/min.

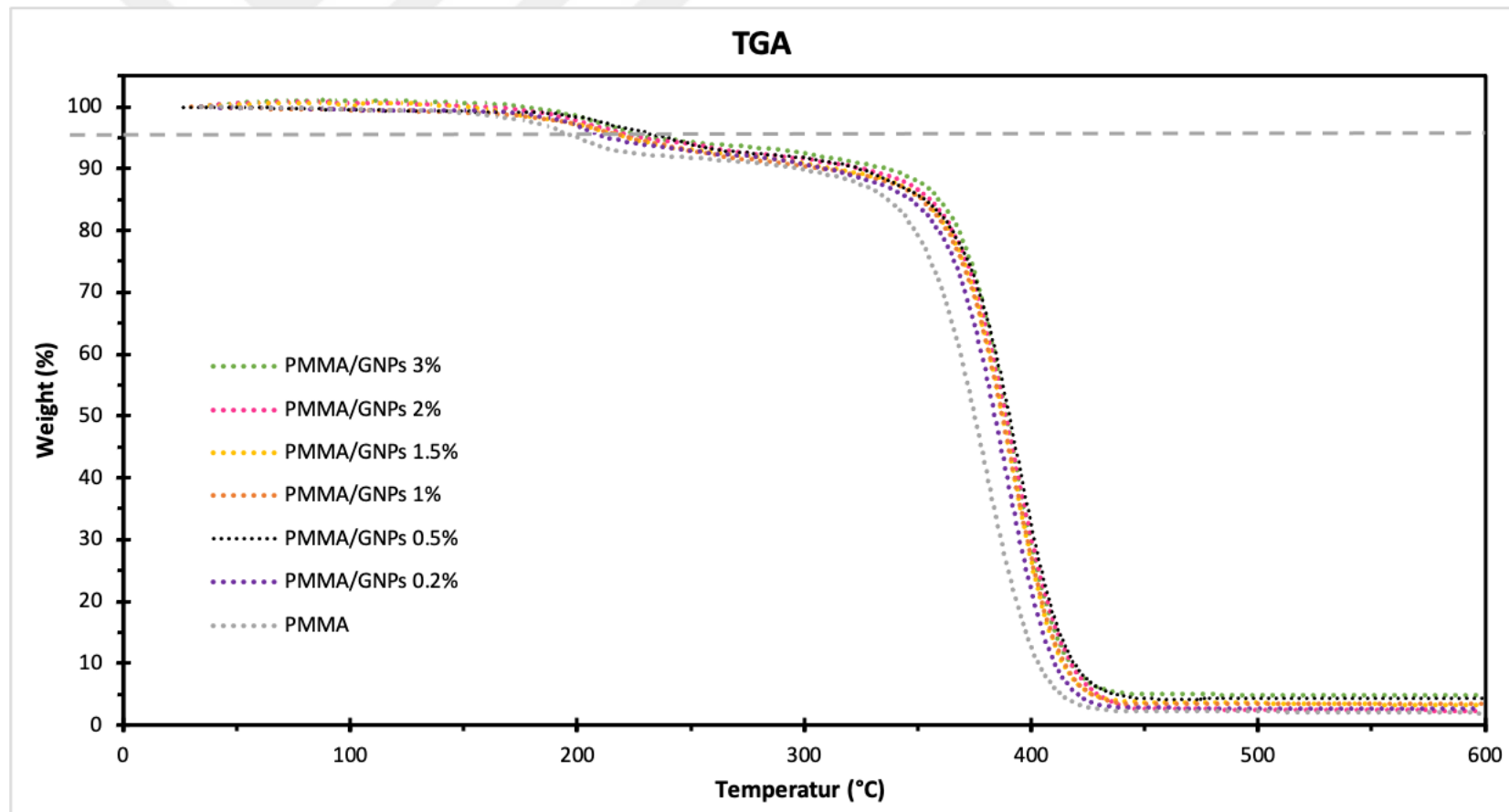


Figure 3.10 TGA curves of pure PMMA and PMMA/GNPs nanocomposites.

Base PMMA, PMMA/GNPs 0.2%, PMMA/GNPs 0.5%, PMMA/GNPs 1%, PMMA/GNPs 1.5%, PMMA/GNPs 2% and PMMA/GNPs 3%, 5%, 10%, 20% and 30% weight loss temperatures were given in Table 3.1. TGA analysis was utilized to measure the change of mass associated with temperature increase (Thermal stability is indicated by this loss).

Table 3.1 5%, 10%, 20% and 30% weight loss temperatures of pure PMMA and PMMA/GNPs nanocomposites.

Samples	~5% weight loss temperatures (°C)	~10% weight loss temperatures (°C)	~20% weight loss temperatures (°C)	~30% weight loss temperatures (°C)
Base PMMA	198.69 °C	295.88 °C	330.7 °C	356.65 °C
PMMA/GNPs 0.2%	200.34 °C	297.64 °C	348.73 °C	360.94 °C
PMMA/GNPs 0.5%	213.82 °C	309.23 °C	359.21 °C	370.93 °C
PMMA/GNPs 1%	222.63 °C	313.77 °C	362.91 °C	374.36 °C
PMMA/GNPs 1.5%	228.07 °C	325.96 °C	365.34 °C	375.70 °C
PMMA/GNPs 2%	238.96 °C	324.30 °C	365.12 °C	377.22 °C
PMMA/GNPs 3%	245.68 °C	335.87 °C	368.09 °C	378.19 °C

Around 200°C the first serious sample mass loss was noticed by an examination to the composite and base samples TGA analysis. The structure moisture evaporation was the reason of that. At 200 °C the mass loss was noted as 5% because of moisture evaporation. Also, the samples state change is represented by the 350- 450 °C dramatic mass loss. Polymeric materials ability to process is very dependent on thermal stability. Polymers thermal stability can be significantly improved by graphene which is considered as one of the most effective fillers[101-103].

It is noted that graphene nanoplates content increase enhanced the samples thermal stability. This shows that the nanocomposites thermal stability is affected positively

by the graphene nanolayers. The nanocomposites thermal stability GNPs positive influence is revealed by the TGA analysis results.

The influence reason is showed by the following:

(i) heat and mass transfer was blocked by a layer of compacted carbon which is formed by the GNPs during heating.

(ii) PMMA macromolecules thermal motion was restricted by GNPs PMMA interfacial adhesion because of GNPs surface functional groups[78].

3.5 Raman Spectroscopy Analysis of Base PMMA and PMMA/GNPs

PMMA GNPs exfoliation and interaction can be evaluated by Raman spectroscopy. Raman spectra can see GNPs crystalline properties, that is a structurally carbon characterization advanced method[104].

GNP concentration depended main three peaks similar changes was shown in Figure 11. (~ 1350 , ~ 1580 and $\sim 2700\text{ cm}^{-1}$)[105].

Electron-phonon and electronic structure interactions evolution is reflected by Raman peaks change in relative intensity, position and shape with GNPs concentration change[106].

Disordered sp^3 -hybridized carbon atoms attribute the D band. Sp^2 -hybridized carbon atoms attribute the G band. Oxidation degree is indicated by graphitic lattice sp^3 and sp^2 hybridization carbon atoms G band and D band area ratio (I_D/I_G)[78].

The D band is at $\sim 1350\text{ cm}^{-1}$. The G band is at $\sim 1580\text{ cm}^{-1}$. The 2D band is at $\sim 2700\text{ cm}^{-1}$. The area ratio of the D band to the G band (I_D/I_G) has the value is 0.85. The value of I_{2D}/I_G Ratio is equals to 0.17. The value of I_D/I_G and I_{2D}/I_G suggests the existence of multi-layer graphene[106, 107].

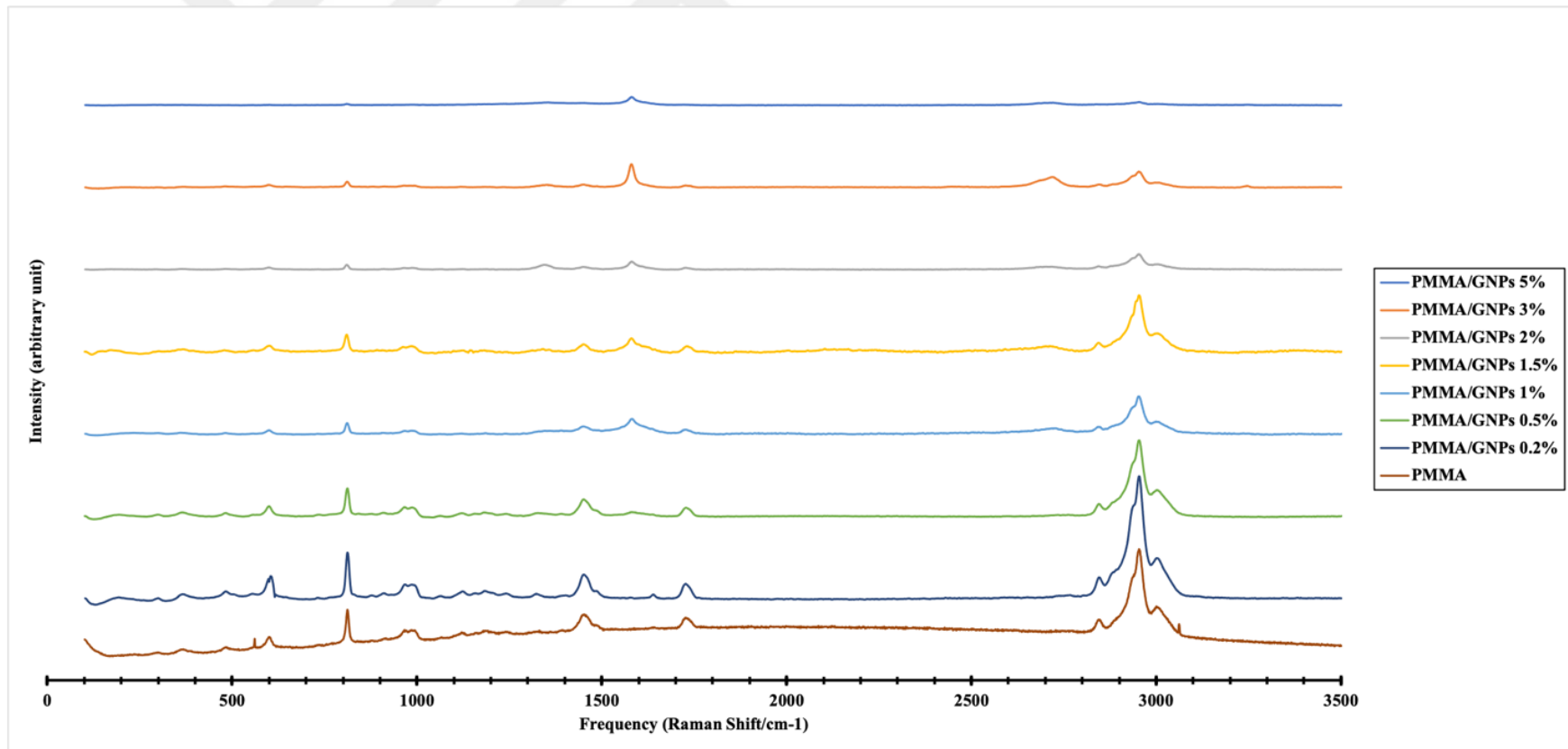


Figure 3.11 Raman spectra of PMMA/ GNPs nanocomposite samples and Pure PMMA [105].

GNPs high thermal conductivity is led by the few GNP defect and impurities which is indicated by the low I_D/I_G area ratio[108].

The sample single-layer graphene high proportion is indicated by a I_{2D}/I_G ratio increase (GNP starting material average ratio of I_{2D}/I_G is 0.49 ± 0.03).

After the functionalization, graphene layers excellent exfoliation is indicated by PMMA grafted samples higher ratio of I_{2D}/I_G [109].

All of the Raman peaks slight decrease of intensity is caused by the increase of graphene layer amount[86].

When the weight percentage of GNPs in PMMA increases, D band becomes invisible nearly which means the crystalline properties of nanocomposites increases. At the GNPs% the approximate 1350 cm^{-1} D band deduced GNPs excellent crystallinity, which is shown by the excellent carbon materials structural characterization Raman spectra method[104].

The Raman spectra of PMMA/GNPs nanocomposites are not similar to the D, G and 2D bands of GNPs. By contrast with the peak intensities in X-ray diffraction (Figure 3.8 X-ray analysis), the intensity of the Raman bands is not dependent systematically on the volume fraction of the GNP filler. That is the reason is that the lateral dimensions of the particles are bigger than the Raman laser spot[110].

3.6 X-ray Photoelectron Spectroscopy (XPS) Analysis of PMMA/GNPs

XPS analysis method was used to examine the PMMA/GNPs nanocomposites' surface chemistry and change of chemical composition. Figure 3.12 displays the results which contain C1s and O1s peaks. The XPS spectrum displayed higher intensity of C1s and O1s peaks with GNPs amount increase.

GNPs groups that contain oxygen C and O types coordinates can be identified furtherly by XPS. Main peaks of O1s and C1s relative intensities can obtain O and C atomic percentage[111].

With the concentration of GNPs rising, functional groups of O-C=O and C-O-C existence variations are addressed by the spectrum of C1s and the functional groups of C-O and C=O existence of oxygen change is indicated by the peak of Q1s. Core level of O1s and C1s emitted photoelectrons generated 533 and $\sim 285\text{ eV}$ binding energy peaks, respectively. The locations of these peaks in this study were almost identical

with the locations of the peaks (with the other Polymer/GNPs structures) in the literature[112, 113].

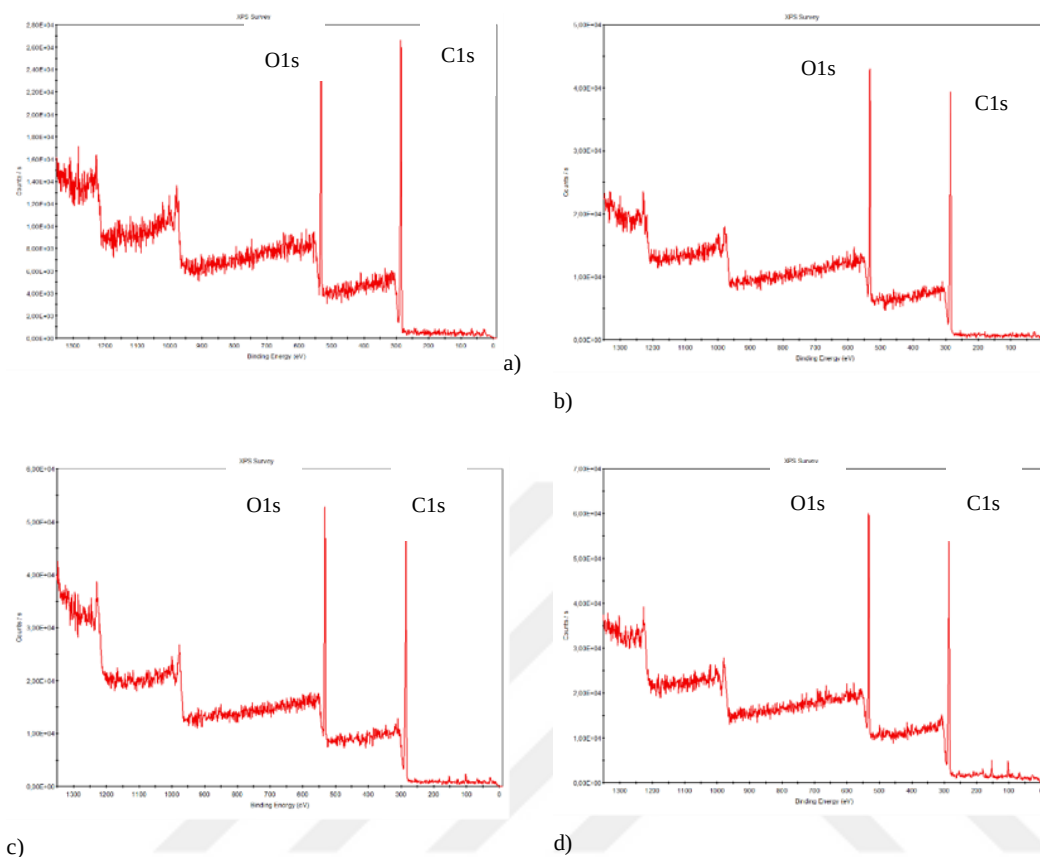


Figure 3.12 a) pure PMMA b) PMMA/GNPs 0.2% c) PMMA/GNPs 1% PMMA/GNPs 2% XPS analysis spectrum[96].

3.7 Stereo Microscope Measurement of PMMA/GNPs

The stereo microscope Images of the PMMA/GNPs done in this study can be seen in the Table 3.2.

Table 3.2 Stereo Microscope Images of PMMA/GNPs

Sample	Zoom	Image
0.2 wt. % PMMA/GNPs	10X	
0.5 wt. % PMMA/GNPs	10X	
1 wt. % PMMA/GNPs	10X	
1.5 wt. % PMMA/GNPs	10X	

Table 3.2 (continued) Stereo Microscope Images of PMMA/GNPs

Sample	Zoom	Image
2 wt. % PMMA/GNPs	10X	
3 wt. % PMMA/GNPs	10X	

3.8 Static Contact Angle (CA) Measurement of PMMA/GNPs

Solid-liquid interaction's contact strength, hydrophobicity and wettability is identified by the method of water contact angle.

Generally, when an angle is smaller than 90° of an intrinsic water contact angle the material can be called hydrophilic, and when an angle is bigger than 90° the material can be called hydrophobic[114-116].

Roughness and surface chemistry both determine wettability of the surface.

When a certain size is reached by the droplet, it will slide down in shape that is asymmetric, then the back contact angle (driving force opposite direction) and the front one (driving force direction) deference is named as the contact angle hysteresis[117].

Solid surface heterogeneity and roughness can cause contact angle hysteresis. Young equation terms the contact angles that are measured are meaningless when the primary cause is roughness. Chemically identical smooth surfaces contact angles are smaller than the rough surfaces ones[118].

PMMA is a polymer that is hydrophilic with an approximately 68° water contact angle. Anyway, it is possible to prepare a nano-structured surface PMMA that is very hydrophobic[119].

GNPs is considered as a hydrophobic material. Average Contact Angle of Graphene is ~92°[120].

Graphene wetting properties affect polymer graphene flake dispersion. Graphene is a nanomaterial that is hydrophobic. Anyway, its wetting properties is still unknown. Thus, it is an investigation topic of a crucial importance[121].

In this study, GNPs' effect on the water contact angle of PMMA was investigated. The three-phase contact line point changes and contact angle localization lead to measurements of contact angle that is erroneous led by roughness increase, all of that is suggested in the results. In this study, the nanocomposites contact angle has increased slightly with the nanofillers addition.

Table 3.3 Static Contact Angle Images of PMMA/GNPs.

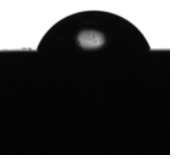
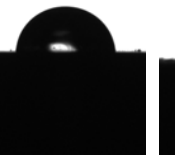
0.2 wt. % PMMA/GN Ps	0.5 wt. % PMMA/GN Ps	1 wt. % PMMA/GN Ps	1.5 wt. % PMMA/GN Ps	2 wt. % PMMA/GN Ps	3 wt. % PMMA/GN Ps
					
					

Table 3.4 Static Contact Angles (CA) of PMMA/GNPs.

Sample	Contact angle (°)
0.2 wt. % PMMA/GNPs	73.6
0.5 wt. % PMMA/GNPs	75.2
1 wt. % PMMA/GNPs	77.6
1.5 wt. % PMMA/GNPs	80.2
2 wt. % PMMA/GNPs	81.4
3 wt. % PMMA/GNPs	82.4

3.9 Ultrasonic Tests

Elastic properties of PMMA/GNPs nanocomposites were examined by ultrasonic tests. Density measurement of PMMA/GNPs was carried out by using Gas Pycnometry technique. The rise in the elastic properties in the nanocomposites was analyzed via Das et al. and Chang et al[122, 123].

The ultrasonic velocity of longitudinal waves (C_L) and ultrasonic thickness of PMMA/GNPs nanocomposites were measured via Ultrasonic testing device. Transverse Velocity (C_T) of PMMA/GNPs was calculated by using the ultrasonic thickness, physical thickness and a reference velocity (3248 m/s).

The elastic properties of pure PMMA shown in Table 3.5 was taken from Muhammettursun et al[105].

Table 3.5 The elastic properties of PMMA[105].

Sample	PMMA
ρ density (kg/m ³)	1180.890
C_L Longitudinal Velocity (m/s)	2663.508
C_T Transverse Velocity(m/s)	1322.011
ν Poisson's ratio	0.337
G Shear modulus (Gpa)	2.064
E Young's modulus (Gpa)	5.517
H Hardness (Gpa)	0.225

The Poisson's ratio (ν), Shear modulus (G), Young's modulus (E) and Microhardness (H) of PMMA/GNPs were computed and shown in Table 3.6.

Concentration of GNPs rise increased all of the values, that is observed in Table 3.6. With the GNPs 3% addition PMMA had a 18.22%, 17.54% and 17.63% increase in Microhardness, Young's modulus and Shear modulus values respectively.



Table 3.6 Ultrasonic test results.

Samples (Wt. %)	ρ Density (kg/m ³)	C_L Longitudinal Velocity (m/s)	Ultrasonic Thickness (mm)	Physical Thickness (mm)	C_T Transverse Velocity (m/s)	ν Poisson's ratio	G Shear modulus (Gpa)	E Young's modulus (Gpa)	H Hardness (Gpa)
0.2 wt. % PMMA/GNPs	1201.9	2726	50	21	1364	0.332	2.236	5.962	0.249
0.5 wt. % PMMA/GNPs	1203.6	2756	52	22	1374	0.334	2.272	6.066	0.250
1 wt. % PMMA/GNPs	1206.9	2763	59	25	1376	0.335	2.286	6.103	0.251
1.5 wt. % PMMA/GNPs	1211.1	2795	49	21	1392	0.335	2.346	6.266	0.258
2 wt. % PMMA/GNPs	1213.4	2825	46.1	20	1409	0.334	2.409	6.429	0.265
3 wt. % PMMA/GNPs	1217.9	2836	50.6	22	1412	0.335	2.428	6.485	0.266

Figure 3.13, 3.14 and 3.15 illustrate that the GNPs are beneficial and effective nano fillers to increase the mechanical properties of PMMA.

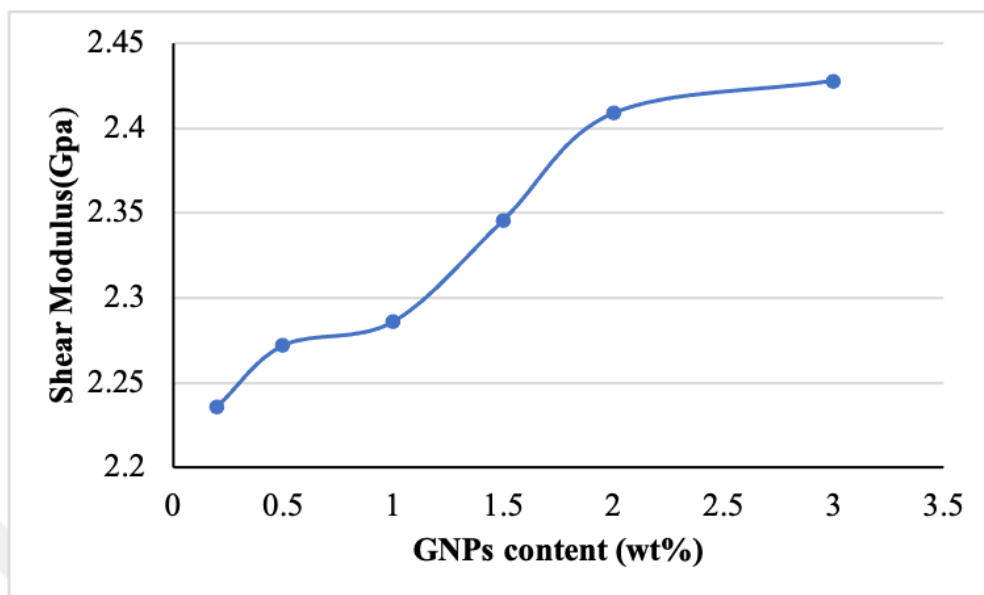


Figure 3.13 Shear modulus improvement with GNPs content increase.

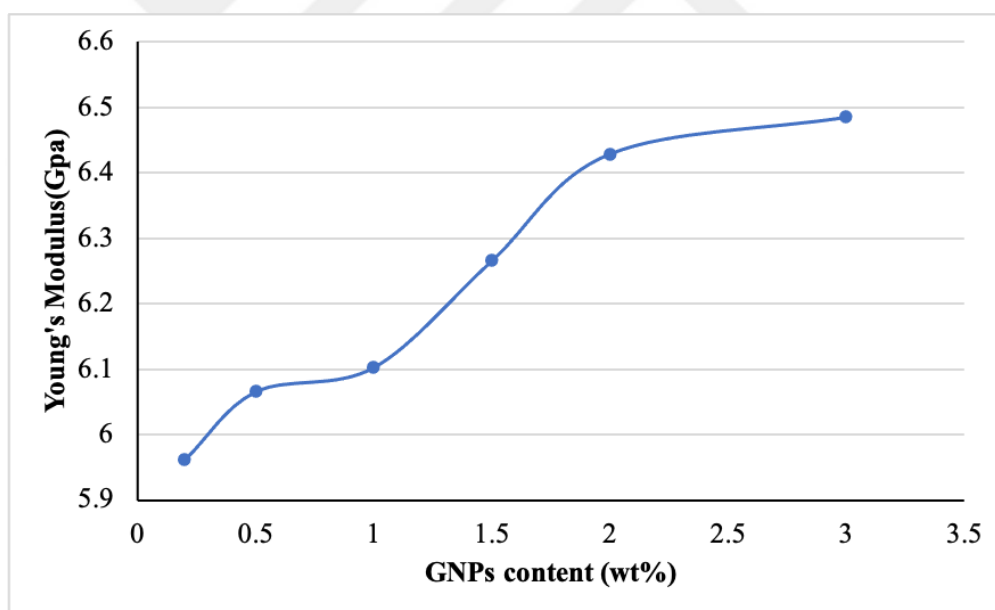


Figure 3.14 Young's modulus improvement with GNPs content increase.

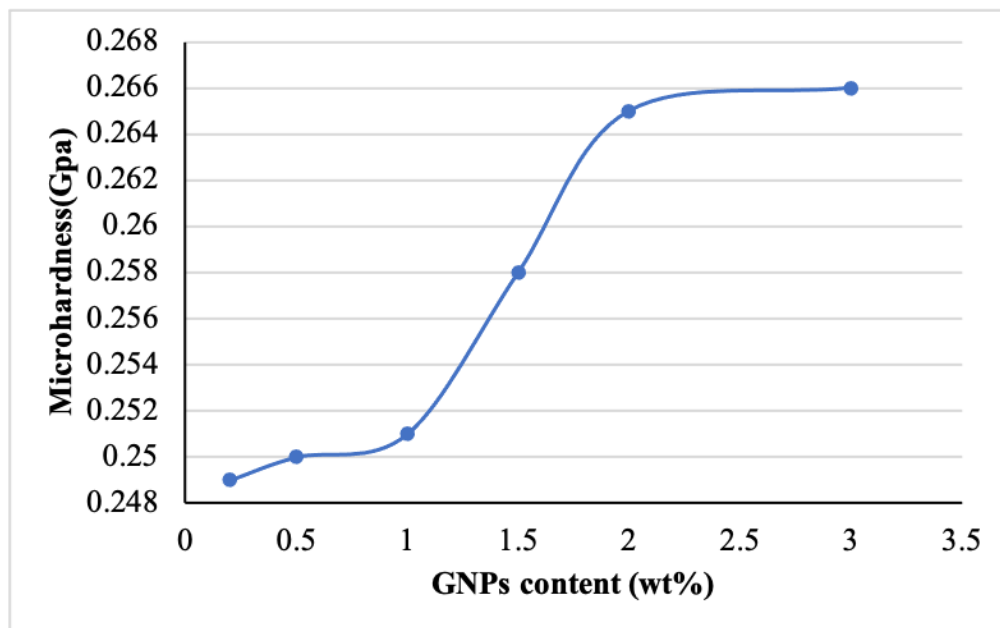


Figure 3.15 Microhardness improvement with GNPs content increase.

4 DISCUSSIONS

ATRP is a novel materials synthesis and design essential tool. Several applications requirements are met thanks to the materials synthesized by ATRP[31].

GNPs is considered a hydrophobic material. The Average Contact Angle of Graphene is $\sim 92^\circ$. Table 4.1 shows the literature comparison of Static Contact Angles (CA) of other Polymer/GNPs. In this study the nanocomposites contact angle has increased with the GNPs addition.

Table 4.1 Comparison of contact angle of PMMA/GNPs between the other Polymer/GNPs's contact angles.

Polymer/GNPs	GNPs content	Contact angle ($^\circ$)	References
Regenerated cellulose/GNP	5 wt%	57.1	[124]
Poly(lactic acid) (PLA)/GNP	0.5 wt%	88	[125]
Poly(lactic acid) (PLA)/GNPs	9 wt %	84.2	[126]
Polyvinylidene fluoride(PVDF)/Graphene oxide (GO)	0.5 wt%	61	[127]
PMMA/GNPs	3 wt %	82.4	This study

Table 4.2 shows the literature comparison of pure PMMA physical properties observed changes. To other literature comparison in this study the utilized in situ ATRP technique physical properties enhancements are shown on the table. The PMMA matrix mechanical and thermal enhancements can contributed to the PMMA matrix and GNPs fillers excellent interfacial interactions. In this study at GNPs 3% the results had obtained the maximum ATRP technique produced PMMA mechanical properties enhancements. Thought PMMA/GNPs pores, cracks and agglomerates, the study obtained an excellent PMMA and GNPs interaction. The preparation of all the sample was argon ambient performed and the results could be because of that.

Table 4.2 This study's ATRP technique produced samples of PMMA/GNPs physical properties comparison.

Team member	Technique applied	Thermal resistivity	Mechanical improvement
Zhang et al [128]	In situ fast polymerization	Utilizing graphene nanosheets at GNPs 2% a ~41 °C heat increase and weight loss of 5%	At GNPs 0.3%, in pure PMMA comparison a ~14% enhancement on the elastic modulus
Wang et al. [129]	In situ polymerization	Utilizing graphene nanosheets at GNPs 1% a ~40 °C heat increase and weight loss of 5%	
Gil et al. [130]	Solution mixing	Utilizing graphene oxide at GNPs 2% a ~50 °C heat increase and weight loss of 10%	At GNPs 1%, in pure PMMA comparison a ~16% enhancement on the elastic modulus

Table 4.2 (continued) This study's ATRP technique produced samples of PMMA/GNPs physical properties comparison.

Team member	Technique applied	Thermal resistivity	Mechanical improvement
Valles et al. [131]	'Grafting to' functionalization approach	At GNPs 2% the thermal degradation temperature (T_d) had maximally a 16 °C increase	At GNPs 2%, in pure PMMA comparison a ~ 24% enhancement on the elastic modulus
Yuan et al. [132]	In-situ bulk polymerization	At GNPs 1.5% a ~32 °C heat increase and weight loss of 5%	At GNPs 2%, ~16.6%, ~14.2% and ~16.8%
Muhammettursun et al. [105]	In situ ATRP polymerization	At GNPs 2% a ~46 °C heat increase and weight loss of 5%	enhancements on the Shear modulus, Microhardness and Elastic modulus respectively
This study	In situ ATRP polymerization	At GNPs 3% a ~ 47°C heat increase and weight loss of 5%	At GNPs 3%, in pure PMMA comparison a ~ 17.63%, ~18.22% and ~17.54% enhancements on the Shear modulus, Microhardness and Elastic modulus respectively



5 CONCLUSION

The polymer synthesis was made by an extensive utilization of ATRP with architecture, composition, well-defined functionality and narrow molar mass distribution. Nanotechnology field applications has got a wide range opened by PMMA utilization advances. Polymer applications, modification and synthesis has got several new enhancements contributed by PMMA properties knowledge. Recently, material science has got a lot of new interesting area opened by polymer matrix and graphene particles nano level dispersion developments. Virgin polymers or conventional composites could not have normally achieved these properties enhancements without the graphene nanofillers applied. The polymer matrix graphene nanofillers dispersion excellent degree has directly led to the dramatic enhancements. In spite the polymer matrix very low loading of nanofillers several enhancements had been gained by the composite and this aspect is very beneficial.

In this study, varying concentrations of GNPs nanofillers have been added to the PMMA polymer with the aim of improving the polymer properties. ATRP method was utilized to produce the PMMA polymer. In situ polymerization is the most efficient technique to disperse the GNPs nanofillers.

In situ synthesis was successful with the particles of PMMA-GNPs which is showed in the analysis of SEM, XRD, FTIR, TGA and Raman Spectroscopy Analysis.

Stereo Microscope and SEM techniques were utilized to examine the nanocomposites surface morphology. In the analysis of scanning electron microscopy, micron scale lack of huge agglomerates shows outstanding dispersion of GNPs in the PMMA matrix. There was no dark phase, GNPs aggregates, observed and this means that there was no asymmetrical neither irregular energy release implied by heterogeneous morphology.

By utilizing the XRD analysis the polymer nanofillers effect was examined in order to carry out the nanocomposite's structural characterizations. The nanocomposite XRD

diffraction patterns had a $\sim 26.5^\circ$ peak, which corresponded to the 0.34 nm distance graphene layers stacking. The peak intensity has increased with the rise of the nanofillers concentration. The polymer nanocomposites mechanical properties improve with the graphene addition and crystallinity enhancements.

FTIR was utilized to investigate the polymer nanocomposites' chemical structure. In accordance with the results of the FTIR test when GNP hits 5 weight% interaction of the among the polymer matrix of PMMA and the nanofiller (GNP) indicates minor modification in the nanocomposite of PMMA/GNPs spectrum of FTIR. Pure PMMA spectra was similar to the spectra of the nanocomposites, indicating that the polymer and nanofiller interaction was successful.

Nanocomposites thermal stability can be enhanced by a GNPs excellent dispersion which is showed in the TGA analysis results. There was a $\sim 47^\circ\text{C}$ heat increase and weight loss of 5% at GNPs 3% compared to pure PMMA.

Raman spectroscopy was used to evaluate the GNPs bonding interaction and exfoliation extent with PMMA. Raman spectra of PMMA/ GNPs nanocomposite samples and Pure PMMA have shown the similar changes of the main three peaks which depends on the concentration of GNP (~ 1350 , ~ 2700 and $\sim 1580\text{ cm}^{-1}$). All of the Raman peaks slight decrease of intensity was caused by the increase of graphene layer amount.

XPS analysis method was used to examine the PMMA/GNPs nanocomposites' surface chemistry and change of chemical composition. XPS is an exceedingly surface-delicate technique by the detection depth $\sim 5\text{ nm}$. The XPS spectrum displayed higher intensity of C1s and O1s peaks with GNPs amount increase. According to XPS analysis results, PMMA/GNPs nanocomposites possess a homogeneous structure at a nano size. The locations of these peaks in this study were almost identical with the locations of the peaks (with the other Polymer/GNPs structures) in the literature.

By measuring the contact angle of a distilled water drop which was deposited on the polymer's surfaces, the determination of the nanocomposite wettability was carried out. At GNPs 0.2% a 73.6° contact angle was measured and at GNPs 3% was 82.4° . In this study the nanocomposites contact angle has increased with the nanofillers addition.

By utilizing ultrasonic tests, the examination of the nanocomposite structure discontinuous or volumetric changes and the nanofillers dispersion quality was carried out. The polymer matrix nanofillers excellent homogenous dispersion was proved by the results of this study. The nanocomposite mechanical properties detailed information about the enhancements were gained by utilizing the ultrasonic nondestructive test. At GNPs 3% the optimum values of Microhardness, Young's modulus and Shear modulus were achieved. In comparison to the pure PMMA a 18.22%, 17.54% and 17.63% respectively enhancement rate was gained. With the concentration increase of GNPs the elastic properties got slightly improved. In spite of using very low amounts of graphene the nanocomposite mechanical and thermal properties were improved dramatically.

Thanks to the improved homogenous dispersion and interfacial interaction of the nanofillers in the polymer matrix the nano-reinforcement was successful in spite of the low amount of graphene used. Finally, thanks to all of that, a state-of-the-art material that is useful in several aerospace and medical fields were successfully obtained.

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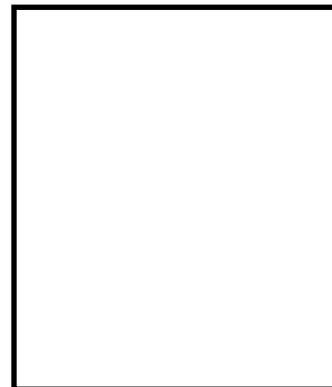
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