İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

POLYPROPYLENE NANOCOMPOSITES: PREPARATION AND CHARACTERIZATION

M.Sc. Thesis by
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Programme : Polymer Science and Technology

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POLİPROPİLEN NANOKOMPOZİTLER: HAZIRLANMASI VE KARAKTERİZASYONU

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FOREWORD

This M.Sc. study has been done in Polymer Science and Technology Graduate Program of Institute of Science and Technology at Istanbul Technical University.

First and foremost I would like to express my indebtedness to my advisor Prof. Dr. Nurseli Uyanık who has supported and encouraged me from the beginning of this study and shared her deep knowledge and experience.

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Polymer Science and Technology

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ABBREVIATIONS

CEC	**:** Cation Exchange Capacity
PP	**:** Polypropylene
Cp	**:** Capilene Polypropylene
Bp	**:** Buplen Polypropylene
MH-418	**:** Petoplen MH-418 Polypropylene
PPNC	**:** Polypropylene Nanocomposite
PPA	**:** Polymer Processing Aid
PO	**:** Polyolefine
PE	**:** Polyethylene
NC	**:** Nanocomposite
PNC	**:** Polymer Nanocomposites
LDPE	**:** Low Density Polyethylene
LLDPE	**:** Linear Low Density Polyethylene
HDPE	**:** High Density Polyethylene
IA	**:** Itaconic Acid
MFI	**:** Melt Flow Index
MVR	**:** Melt Volume Rate
GD	**:** Grafting Degree
MAH	**:** Maleic Anhydride Grafted Polypropylene
MMT	**:** Montmorillonite

LIST OF SYMBOLS

λ = Wavelength, nm

Å = Ionic Radius

θ = Diffraction angle

$\mathbf{d_{001}}$ = Layer distance of clay platelets

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POLYPROPYLENE NANOCOMPOSITES: PREPARATION AND CHARACTERIZATION

SUMMARY

Polyolefins (PO) are the most widely used polymers and processed usually by extrusion. Nanocomposites (NCs) are a combination of two or more phases containing different compositions or structures, where at least one of the phases is in the nanoscale regime. Preparation of PO-based polymer / (organo) clay nanocomposites (PNC) is more difficult than that of any polymer, which contains polar groups in its backbone. Homogeneous dispersion of polar clay cannot be realized due to lack of PO miscibility with organically-modified clay (organoclay). Strong interaction between a non-polar polymer (e.g. PO) and polar organoclay might be achieved with addition of a compatibilizer. The convenient way of preparing a compatibilizer is functionalization of the original PO.

Polypropylene (PP) has gained an important position among other PO due to its versatile and broad range of applications. However, its applications are limited because of its poor barrier properties to oxygen, as well as it has the disadvantage of being quite brittle at room temperature and exhibiting poor resistance to crack propagation. To compete with engineering plastics, the incorporation of fillers or reinforcements to PP is often required. In particular, reinforcing this polymer with nanoclays in the adequate conditions can lead to nanomaterials with improvement mechanical, thermal, and barrier properties as well as higher dimensional stability.

In the case of PO processing by extrusion, the instabilities on the surface show generally periodic distortions do to high shear rates. Polymer processing aids (PPA) are used to overcome these surface irregularities.

In this study, the effects of polymer processing aids (PPA) on polypropylene (PP) nanocomposites (NC) were investigated. The commercial fluoropolymer PPA was used as 500 ppm in polypropylene nanocomposite (PPNC) matrix. For preparing of PPNC two kinds of compatibilizers were used: 1) PP grafted maleic anhydride that was commercial and 2) PP grafted itaconic acid which was prepared in the laboratory. The percentage of compatibilizer was taken three times of the percentage of organoclay in PPNC. PPNC materials will be synthesized by using different amounts of PPs, organoclays, PPA and compatibilizers in Mini Lab Extruder by melt extrusion.

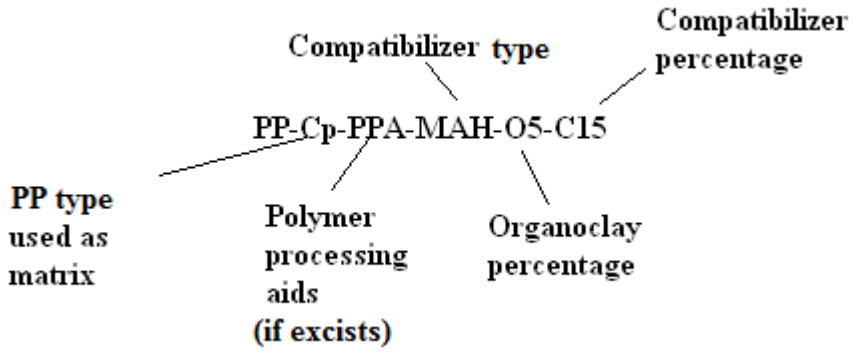
In this context firstly, itaconic acid (IA) monomer which including polar group was grafted to PP in xylene solution with 180 W input power at 8 minutes. In all experiments, the weight ratio of xylene to PP was always 10/1. Dibenzoyl peroxide (DBPO) was used an initiator and IA as the comonomer

The grafting degrees (GD) of synthesized grafted polymers were measured back titration with ethanolic KOH solution and isopropanolic HCL solution. Solution of PP-g-IA samples in xylene was extracted with 0.005 N KOH solutions and back

titrated with 0.005 N HCL solutions. Grafting of PPs with IA were provided in optimum conditions and the determined values for GDs are: 0.30 g IA/100 g Cp, 0.31g IA/100 g Bp, 0.32 g IA/100 g MH-418.

The PPNC samples were prepared by single step melt mixing. Thus, 3, 5-wt% organoclay and concentration of compatibilizers 10, 15 -wt% were mixed with PPs in Haake Mini Lab Extruder. To prevent the degradation and to provide the homogeneity of polypropylene nanocomposites during extrusion the working conditions were determined as 216 ^{o}C and 100 rpm screw speeds for 2 min. cycling time in extruder.

Each sample description refers to a specific composition involving the components used in the preparation of the samples.



The interlayer spacing of silicate layers, mechanical properties and processability of PPNC samples were investigated. The interlayer spacing of silicate layers of samples were examined by using the X-ray diffraction (XRD) (Table 1). Mechanical properties were determined by universal testing machine (Table 1). The processabilities of samples were investigated by melt flow measurements and determined by normalized values of data (Table 2).

Compatibilizers might also influence the melt properties of the polymer matrix as observed during the MFR measurements. Calculation of "normalized" MFR values helps to see the interaction of clay with the continuous PO matrix.

$$\text{Normalized melt flow rate} = \frac{\text{Melt flow rate of nanocomposite}}{\text{Melt flow rate of corresponding control unit}}$$

The Table 2 shows that n-MFR and n-MVR values of PPNC.

Table 1: Interlayer spacing and Young Modulus values of PPNC samples.

Sample Description	PP	d_{001} (Å)	E_{mod} (N/mm2	PP	d_{001} (Å)	E_{mod} (N/mm2)	PP	d_{001} (Å)	E_{mod} (N/mm2)
PP-MAH-O3-C10	Capilene SB56	27.8	1130	Buplen 6531	28.0	1085	MH-418	27.3	1320
PP-MAH-O5-C15	Capilene SB56	25.7	1100	Buplen 6531	27.0	1180	MH-418	27.9	1300
PP-PPA-MAH-O3-C10	Capilene SB56	30.4	1230	Buplen 6531	28.9	1115	MH-418	28.0	1390
PP-PPA-MAH-O5-C15	Capilene SB56	32.1	1260	Buplen 6531	28.0	1220	MH-418	39.8	1450
PP-IA-O3-C10	Capilene SB56	22.9	980	Buplen 6531	26.4	1120	MH-418	26.0	1130
PP-IA-O5-C15	Capilene SB56	38.7	1300	Buplen 6531	26.7	1210	MH-418	29.6	1280
PP-PPA-IA-O3-C10	Capilene SB56	27.8	1080	Buplen 6531	27.3	1340	MH-418	27.5	1240
PP-PPA-IA-O5-C15	Capilene SB56	39.9	1380	Buplen 6531	28.1	1300	MH-418	29.8	1300

Table 2: n-MFR and n-MVR values of PPNC samples.

Sample Description	PP	n-MFR	n-MVR	PP	n-MFR	n-MVR	PP	n-MFR	n-MVR
PP-MAH-O3-C10	Capilene SB56	0.97	0.92	Buplen 6531	0.96	1.67	MH-418	0.96	1.30
PP-MAH-O5-C15	Capilene SB56	0.83	0.79	Buplen 6531	1.07	1.19	MH-418	0.74	0.95
PP-PPA-MAH-O3-C10	Capilene SB56	1.47	1.45	Buplen 6531	0.83	0.78	MH-418	0.97	0.68
PP-PPA-MAH-O5-C15	Capilene SB56	0.81	0.80	Buplen 6531	0.96	0.95	MH-418	1.10	0.78
PP-IA-O3-C10	Capilene SB56	1.14	1.11	Buplen 6531	0.70	0.97	MH-418	0.73	0.78
PP-IA-O5-C15	Capilene SB56	1.08	0.98	Buplen 6531	0.85	0.87	MH-418	0.88	1.10
PP-PPA-IA-O3-C10	Capilene SB56	0.95	0.94	Buplen 6531	0.71	0.97	MH-418	0.78	0.82
PP-PPA-IA-O5-C15	Capilene SB56	0.89	0.96	Buplen 6531	0.63	0.62	MH-418	0.94	0.86

POLİPROPİLEN NANOKOMPOZİTLER: HAZIRLANMASI VE KARAKTERİZASYONU

ÖZET

Poliolefinler (PO) genellikle çok geniş olarak ekstrüzyon işlemlerinde kullanılan polimerlerdir. Nanokompozitler, en az bir fazın nano ölçekli olması ile iki veya daha fazla fazın bir araya gelmesi ile daha farklı bir kompozisyonun veya yapının oluşmasıdır. Poliolefin (PO) / Organokil tabanlı nanokompozitlerin hazırlanması (PNK), ana zincirinde polar grup taşıyan herhangi bir polimerin hazırlanışından daha zordur. Polar kilin homojen dağılımı, organik olarak modifiye edilmiş kil (organokil) ile poliolefinin karışabilirliği sağlanır. Polar olmayan (örnek:PO) ve polar organokil arasındaki kuvvetli etkileşim bir uyumlaştırıcının katılmasıyla yenilebilir. Bir uyumlaştırıcının hazırlanmasında en uygun yöntem, orjinal PO'nin işlevsel hale getirilmesidir. Polipropilen çok yönlü ve geniş kullanım alanıyla diğer poliolefinler arasında önemli bir yer kazanmıştır. Bununla birlikte, oksijene karşı göstermiş olduğu zayıf bariyer özelliğinden dolayı uygulama alanı sınırlıdır. Ayrıca oda sıcaklığında oldukça kırılgan olması ve çatlamaların ilerlemesine karşı zayıf direnç göstermesi dezavantajlarına da sahiptir. Mühendislik polimerleri ile karşılaştırdığımızda, polipropilenin sıklıkla dolgu maddeleri veya güçlendiriciler ile takviye edilmesi gerekmektedir. Özellikle yeterli miktarda nanokil ie bu polimerin güçlendirilmesi ile boyutsal kararlılığı ile birlikte mekanik, termal ve bariyer özellikleri geliştirilmektedir.

Ekstrüzyonda PO işlenmesi halinde, yüksek kayma hızına bağlı olarak yüzey üstünde ki kararsızlıklar genellikle periyodik deformasyonlar gösterir. Polimer işleme yardımcıları (PPA) bu yüzey düzgünsüzlüklerini yok etmek için kullanılır.

Bu çalışmada, polimer işleme yardımcılarının (PPA) polipropilen (PP) nanokompozitler (NK) üzerine etkisi araştırılmıştır. Floropolimerik PPA polipropilen nanokompozit matris içinde 500 ppm seviyesinde kullanılmıştır. Polipropilen nanokompozit hazırlanırken iki çeşit uyumlaştırıcı kullanılmıştır: 1) laboratuarda hazırlanmış, itakonik asit aşılanmış PP ve 2) ticari olarak kullanılan maleik anhidrit aşılanmış PP. Polimer nanokompozit içindeki uyumlaştırıcı miktarı organokilin üç katı olacak şekilde alınmıştır. Polimer nanokompozit malzemeler değişik miktarlarda polipropilen, organokil, PPA ve uyumlaştırıcının Mini Lab ekstrüderde eriyik ekstrüzyon yöntemi ile işlenmesiyle elde edilmiştir.

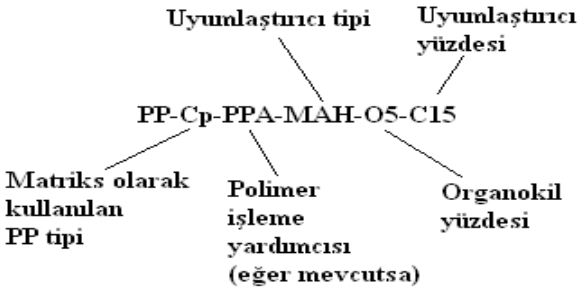
Bu amaçla önce polar grup içeren monomer, itakonik asit (IA), ksilen çözeltisinde PP'ye 180 W mikrodalga gücünde 8 dakikada aşılandı. Bütün deneylerde ksilenin poliolefine oranı 10/1 olarak alındı. Başlatıcı olarak dibenzoil peroksit (DBPO) ve komonomer olarak IA kullanıldı. Analitik yöntemle aşılanma oranları belirlendi.

Aşılanma dereceleri etanolik potasyum hidroksit (KOH) ve izopropanolik hidroklorik asit (HCL) çözeltileriyle geri titrasyon yapılarak analiz edilmiştir.

Ksilende çözünmüş olan PP-g-IA çözeltisi 0.005 N KOH ile ekstarkte edildi ve sonra 0.005 N HCL ile geri titrasyon yapıldı. Reaksiyon koşulları ve aşılanma derecesi (GD) sonuçları: 0.30 g IA/100 g Cp, 0.31g IA/100 g Bp, 0.32 g IA/100 g MH-418.

Polipropilen (PP) nanokompozitler (NK) tek basamaklı eriyik karıştırma yöntemi ile hazırlanmıştır. Bu nedenle, 3-5 % organokiller ve 10-15 % konsantrasyonlarda uyumlaştırıcılar PP ile birlikte MiniLab ekstrüderde karıştırılmışlardır. Degradasyonun olmaması ve homojen polipropilen nanokompozit elde edebilmek için Haake Mini Lab ekstrüderde çalışma koşulları 216 ^{o}C proses sıcaklığında, 100 rpm vida hızı ve 2 dakika bekleme süresi olarak karar verilmiştir.

Her örnek tanımlaması, örneklerin hazırlanılmasında kullanılan bileşenleri içerecek şekilde yapılmıştır.



Kilin tabakalar arası uzaklığı, mekanik özellikleri ve propilen (PP) nanokompozitlerin (NK) işlenebilirliği araştırıldı. Kilin tabakalar arasındaki uzaklıkları X-ışınları kırınımı analizi (XRD) ile belirlendi (Tablo1). Mekanik özellikler üniversal test cihazları kullanılarak ölçülmüştür (Tablo1). Örneklerin işlenebilirliği eriyik akış ölçümleri ile irdelenmiş ve normalize edilmiş değerler belirlenmiştir (Tablo2).

Tablo 1: PPNK örneklerinin tabakalar arası uzaklık ve Young Modul değerleri.

Örnek adı	PP	d_{001} (Å)	E_{mod} (N/mm2)	PP	d_{001} (Å)	E_{mod} (N/mm2)	PP	d_{001} (Å)	E_{mod} (N/mm2)
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PP-IA-O3-C10	Capilene SB56	22.9	980	Buplen 6531	26.4	1120	MH-418	26.0	1130
PP-IA-O5-C15	Capilene SB56	38.7	1300	Buplen 6531	26.7	1210	MH-418	29.6	1280
PP-PPA-IA-O3-C10	Capilene SB56	27.8	1080	Buplen 6531	27.3	1340	MH-418	27.5	1240
PP-PPA-IA-O5-C15	Capilene SB56	39.9	1380	Buplen 6531	28.1	1300	MH-418	29.8	1300

Tablo 2: Örneklerin n-MFR ve n-MVR sonuçları.

Örnek adı	PP	n-MFR	n-MVR	PP	n-MFR	n-MVR	PP	n-MFR	n-MVR
PP-MAH-O3-C10	Capilene SB56	0.97	0.92	Buplen 6531	0.96	1.67	MH-418	0.96	1.30
PP-MAH-O5-C15	Capilene SB56	0.83	0.79	Buplen 6531	1.07	1.19	MH-418	0.74	0.95
PP-PPA-MAH-O3-C10	Capilene SB56	1.47	1.45	Buplen 6531	0.83	0.78	MH-418	0.97	0.68
PP-PPA-MAH-O5-C15	Capilene SB56	0.81	0.80	Buplen 6531	0.96	0.95	MH-418	1.10	0.78
PP-IA-O3-C10	Capilene SB56	1.14	1.11	Buplen 6531	0.70	0.97	MH-418	0.73	0.78
PP-IA-O5-C15	Capilene SB56	1.08	0.98	Buplen 6531	0.85	0.87	MH-418	0.88	1.10
PP-PPA-IA-O3-C10	Capilene SB56	0.95	0.94	Buplen 6531	0.71	0.97	MH-418	0.78	0.82
PP-PPA-IA-O5-C15	Capilene SB56	0.89	0.96	Buplen 6531	0.63	0.62	MH-418	0.94	0.86

Uyumlaştırıcı, eriyik akış ölçümlerinde görüldüğü üzere polimer matrisin eriyik özelliklerini etkilemektedir. Normalize eriyik akış indeksinin hesaplanması kil ile polimer matris arasındaki etkileşimin irdelenmesine yardımcı olmuştur.

$$\text{Normalize eriyik akış hızı (n-MFI)} = \frac{\text{Kompozitin eriyik akış hızı}}{\text{Kontrol ünitesinin eriyik akış hızı}}$$

Polipropilen nanokompozitler'in n-MVR ve n-MVR değerleri Tablo 2'de gösterilmiştir.

1. INTRODUCTION

Polypropylene (PP) is one of the most widely used plastic because of its low cost, low density and high specific properties. Increasing demand for using them forced the scientist to improve their properties. Some mechanical and thermal properties of polymer materials can be improved by using reinforcing inorganic fillers [1].

In general, composite materials are formed by combining two or more materials that have quite different properties. The different materials work together to give the composite unique properties, but within the composite you can easily tell the different materials apart-they do not dissolve or blend into each other. The structures and properties of the composite materials are greatly influenced by the component phase morphologies and interfacial properties. Nanocomposites are based on the same principle and are formed when phase mixing occurs at a nanometer dimensional scale. As a result, nanocomposites show superior properties over their micro counterparts or conventionally filled polymers. Polymer nanocomposites (PNC) are commonly defined as the combination of the polymer matrix and additives can be one-dimensional (examples include nanotubes and fibres), two dimensional (which include layered minerals like clay) or three dimensional (including spherical particles). Polymer- clay nanocomposites have advanced significiantly in recent years. [2,3]. Polyolefins (PO) are the most widely used polymers in preparation of polymer nanocomposites (PNC) and it is more difficult than that of any polymer, which contains polar groups in its backbone [4,5]. One of most convenient and useful method to prepare PP nanocomposites is the functionalization of PP by introducing polar or polarizable groups into the polymer matrix. Thereafter, during melt blending efforts have been made to improve the mixing of clay in PP matrix by using functional oligomers [6,7] by grafting a polar component such as itaconic acid (IA) and monoesters. They can be on the nonpolar backbone [8,9]. Polymer-clay nanocomposites can be fabricated via direct polymer melt intercalations in which the polymer chains are diffused into the space between the silicate layers or galleries [10,11]. Conventional polymer processing such as

extrusion can reduce the time for nanocomposites fabrications through its ability to break up the silicate layers. Although polyolefin/clay composites are well known today and it is possible to find a large number of references on this subje, more experimental data are necessary to have a complete understand of their morphology. For example, it is well accepted the presence of both compatibilizers and polyolefins increases the clay's interlayer distance [12-14]. However, it has been reported that sometimes the opposite is found, which means that the interlayer distance decreases and the clay colapses [15,16].

Homegeneous dispersion of nano-sized fillers in the matrix provides a large interfacial area; otherwise the looosely agglomerated nanoparticles would easily result in failure of the composites when they are subjected to force. A homegeneous product, incorporation of any additives requires a serious mixing in molten state, which is primarily provided by melt blending process by means extrusion.

In this study, nanocomposites were produced by means of a co-rotating twin screw extruder in single step melt mixing method. This study was carried out to determine the effects of polymer processing aids (PPA) on polypropylene (PP) nanocomposites (NC). A strong interaction between PP and polar organoclay needs a compatibilizer to overcome the poor adhesion between polar and non-polar components. Two kinds of compatibilizer were used for this purpose: PP grafted itaconic acid which was prepared in the laboratory and PP grafted maleic anhydride that was commercial. Two different levels (3 and 5 %) of organoclay additive were used. The fluoropolymer PPA was used as 500 ppm in PNC matrix.

The interlayer spacing of silicate layers, mechanical properties and processability of samples were investigated.

2. THORETICAL PART

A composite, in general, is defined as a combination of two or more components differing in form or composition on a macro scale, with two or more distinct phases having recognizable interfaces between them [17]. Most composites have two constituent materials: a binder or matrix, and reinforcement. The reinforcement is usually much stronger and stiffer than the matrix, and gives the composite its good properties. The matrix holds the reinforcements in an orderly pattern. Because the reinforcements are usually discontinuous, the matrix also helps to transfer load among the reinforcements. Nanocomposites (NCs) are a combination of two or more phases containing different compositions or structures, where at least one of the phases is in the nanoscale regime. The matrix may be metallic, ceramic or polymeric. Depending on the matrix nature NCs may be assigned into these three categories. The nano particles are classified as; 1) lamellar, 2) fibrillar, 3) tubular, 4) spherical, and 5) others. In particular, reinforcing the polymers with nano particles in the adequate conditions can lead to nanomaterials with improved mechanical, thermal, and barrier properties as well as with higher dimensional stability [18]. In polymer nanocomposites (PNC), matrix is a single or multicomponent polymer. In this work, PP and its grafted copolymers were used as multi component matrix and the organoclays as nano particle additives. To understand the PNC structure these main components will be discussed: clay minerals and polymer matrices.

2.1. Clay Minerals

The clay minerals are a part of a general but important group within the phyllosilicates that contain large percentages of water trapped between the silicate sheets. Most clay is chemically and structurally analogous to other phyllosilicates but contains varying amounts of water and allows more substitution of their cations. Clays exhibit plasticity when mixed with water in certain proportions. When dry, clay becomes firm and when fired in a kiln, permanent physical and chemical

reactions, occur. Clays are distinguished from other fine-grained soils by differences in size and mineralogy.

2.1.1. Silicate mineral structures

Clay minerals belong to the phyllosilicate group (from Greek “phyllon”: leaf, and from the Latin “slic”: flint). While the number of their species is relatively small, clay minerals exhibit a great diversity in their composition because of their large compositional ranges of solid solutions and their ability to form polyphased crystals by interstratifications. It is useful as a point of departure to briefly describe the basic lattice common to phyllosilicates. The elementary character is the Si-O tetrahedral linkage of an essentially two-dimensional, hexagonally symmetric, network. One side of this” sheet” network is coordinated through a common oxygen atom with other cation-oxygen-hydoxyl complexes. These are linked by an important component of covalent bonding or van der Walls type bonds. The key to phyllosilicate structure is the silicon-oxygen network which determines the shape and extent of the structure. A superficial classification of the common clay minerals can be based upon the number of ions present in the octahedrally coordinated sites. There are three sites available and their occupancy is two ions in the case of dioctahedral minerals and between 2.5 and 3 ions for the “trioctahedral” minerals. There appear to be no intermediate occupancies except where lithium, or possibility certain amount of sodium, is present. These alkali minerals are rare and difficulties identify [19].

In a simple structure there might be only two kinds of boxes, representing tetrahedral and octahedral, appropriately linked together. Thus, we can change the chemical composition of a mineral by replacing all or part of the cations in one type of box by another kind of cation, such that size and valence considerations are not violated. Two divalent cations which are not very different in ionic radius, magnesium and iron, for example, can readily substitute for each other in an octahedral site [20].

2.1.2. Classification of clay minerals

There are 4 types of clay minerals which are classified by their chemical formula; Kaolin, Smectide, Illite and Clorite.

2.1.2.1 Kaolin group

The clay groups in the kaolin group consist of dioctahedral 1:1 layer structures with a general composition of $Al_2Si_2O_5(OH)_4$. (Fig 2.1) kaolinite, dickite and nacrite are polytypes. The kaolinite tacking sequence consists of identical layers with an interlayer shift of 2a/3. Dickite and nacrite have two-layer stacking sequence where the vacant site of the octahedral sheet alternates between two distinct sites.

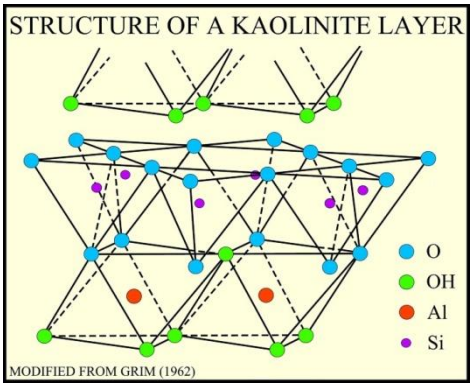


Figure 2.1: Structure of a kaolinite layer.

2.1.2.2. Illit group

Illite regarded as a species in the true (flexible) mica group. Both illite and vermiculite have a closely similar range of layer charge but illite is non-expandable and has fixed instead of exchangeable cations in the interlayer space. In reality, illites are exculisevely dioctahedral and clay-size, while vermiculites are most commonly trioctahedral and often mica-size. The charge of illite layers is $0.9/O_{10}(OH)_2$, but the overall charge is often lower than this because illite particiles are very thin.

2.1.2.3. Chlorite group

The chlorite group 2:1 phyllosilicate contains both primary and secondary minerals. The magnitude and location of the layer charge in the chlorite minerals are similar to that of the mica minerals (approximately 3:1 Si to Al in the tetrahedral layer resulting in an approximate layer charge of 1). The chlorite minerals are distinguished from the other 2:1 layer silicates by the presence of an interlayer hydroxide sheet. The interlayer sheet can be dioctahedral and dominated by $Al^{3+}[Al_2(OH)_6]$ or trioctahedral and dominated by Mg^{2+} and $Fe^{2+}[(Mg.Fe^{II})_3(OH)_6]$.

In either case, the interlayer hydroxide sheet bears charge and acts as a layer charge-neutralizing cation [19].

2.1.2.4 Smectite group

The smectite group contains the 2:1 phyllosilicates that have a layer charge between 02 and 0.6 per ½-unit cell. The layer charge in the smectites generally originates from both the tetrahedral and the octahedral layers, with one layer providing the bulk of the layer charge. The 2:1 layers are held to adjacent 2:1 layers by iyonic interactions between the negatively charged layers and interlayer cations (which reside between the 2:1 layers). Because the layer charge of the smectites is relatively low, the internal surfaces (the region between the 2:1 layers) are accessible to water molecules, and ions and molecules present in the aqueous phase. Smectites are structurally derived from pyrophyllite [$Si_8Mg_6O_{20}(OH)_4$], or talc [$Si_8Mg_6O_{20}(OH)_4$] by substitutions mainly in the octahedral layers, viz. Al can be substituted by Mg, Fe, Cr, Mn or Li. When substitutions occur between ions of unlike charge, deficit or excess charge develops on corresponding parts of the structure. Both groups of smectite are important in sandstones. Substitutions of ions of the same charge, e.g. Fe^{2+} for Mg^{2+} and Fe^{3+} for Al^{3+}, is common in octahedral positions. Substations by ions of lower charge (e.g. Al^{3+} for Si^{4+} in tetrahedral positions and Mg^{2+} for Al^{3+} or Fe^{2+} for Fe^{3+} in octahedral positions) produces a net negative charge for the tetraocta-tetrahedral sandwich. This is redressed by the presence of a limited quantity of interlayer cations, such as Na^{+} or Ca^{2+} or Mg^{2+} ions, although other cations, including organic ions also can be introduced by exchange reactions. The smectite group of clay minerals is characterized by properties of cation exchange and expandability. They have the distinctive ability to transiently take up and release water, or organic molecules, between their layers and thus expanded or contract parallel to the layers. Smectites include any clay with a basal spacing (the thickness of the 2:1 sheet plus interlayer space) that expands to 1.7 nm on treatment with ethylene glycol. Expansion by ethylene glycol is indicative of a structure in which the number of positive charges (i.e. positively charged metal ions) needed in the interlayer positions corresponds to < 0.2 to 0.5 unit per formula unit [$O_{10}(OH)_2$]. In the Al-rich smectite, montmorillonite, the need for interlayer cations is the result of substation on Mg^{2+} for AL^{3+} and the ensuring charge imbalance in the octahedral layers. In contrast beidellite (also Al-rich), the need for interlayer cations is the

result of substation of Al^{3+} for Si^{4+} in the tetrahedral layers. Smectites usually are very fine grained even by clay minerals standards (i.e. usually less than 1 μm). The smectite group includes the dioctahedral smectites (e.g. montmoillonite, beidellite, nontronite) and the trioctohedral smectites (e.g. saponite, hectorite and sauconite).

Montmorillonite is the mineral with the general formula of $Na_{0,2}$ $Ca_{0,1}$ Al_2 Si_4 O_{10} $(OH)_2$ $(H_2O)_{10}$. Montmorillonite is a fine powder which has monoclinic-pyrismatic crystal structure, a color from white to brown-green and yellow, average density of 2.35 g/cm^3, molecular weight of 549.07 g/mol and hardness of 1.5–2 (Figure 2.2). Single montmorillonite crystals are quite fine, granulated and they got random other lines. In general a montmorillonite crystal consists of 15–20 silicate units. This property is so useful for engineering projects. There are two different swelling types of montmorillonite according to expansion size of the basal space as crystallized and osmotic swelling. Crystallized swelling occurs when the water molecules enter in to the unit layers. First layer of the water molecules which are adsorbed occurs when they bind with hydrogen bonds to hexagonal oxygen atoms. Montmorillonitles whose cations are exchangeable hydrates as Na^+, Li^+ can swell to 30–40 Å. Moreover, sometimes this swelling level increases up to hundred. This type distance is called as osmotic swelling. Montmorillonits do not swell much when they got high valance cations as exchangeable cations [21, 22].

Among the several species of clays in soils, the mineral smectite is perhaps the most widely distributed member. Most soil smectites (montmorillonites) are dioctahedral. They are characteristic constituents of clays of vertiols, Mollisols, and Alfisols, and are also found in some Entiols. The high plasticity and swell-shrink potential of the mineral make these soils plastic when wet and hard when dry; whereas wide cracks will form as soils dry out. The dry soil is difficult to till and displays wide cracks. Because of the mineral's high surface area, it finds application in the paper industry for making glossy surface on paper. Apparently, smectite also has the capacity to reduce surface tension in liquids; hence it is added to latex in the production of foam rubber. The mineral is reported to be very valuable for its binding power and its strength it imparts to other material. In aqueous solution it disperses easily, forming a suspension, which will change viscosity, and exhibits thixotropy (from Greek thixis=touch, and trope=change). Up in standing, a smectite suspension turns into a gel, but is restored into a sol by shaking or stirring. Because of this characteristic,

smectite suspensions are employed in drilling fluids. The high cation exchange capacity is the reason for utilizing smectite in the purification of liquids, in bleaching oils, and in the paint industry. In the production of paint, smectite clays are called fuller's earth [23, 24].

Unlike the 1:1 phyllosilicates, which are relatively pure, the smectites are chemically complex. The ideal chemical formulae introduced up for the smectite minerals oversimplify the chemical composition of the smectites as they occur in the environment. Isomorphic substation in both the tetrahedral and octahedral layers results in somewhat complex structural formula. Further, incomplete occupation of the tetrahedral and octahedral layers may also occur. The interlayer positions also contain several different cations.

Figure 2.2: The crystal lattice structure of montmorillonite.

The reason of this situation is that gravitational forces between silicate and cation layers are higher than ion hydration thrust force [25].

Smectites are a class of layered clays that are swell able in water and contain a significant cation exchange capacity at about 80 meq/100 g (this means that there are 80 meq of exchangeable cation per 100 g of clay). The fundamental inorganic unit is comprised of two tetrahedral silicate layers that sandwich a central metal octahedral layer (Figure 2.3). Isomorphous substitution of these clays primarily within the octahedral layer which gives rise to a net negative charge on the basal

oxygen surfaces. This is compensated for by the presence of hydrated exchangeable cations in the interlayer or gallery regions, which in nature are usually alkali or alkaline earth cations. These cations are easily exchanged by larger species such as long chain alkylamonium ions, whose importance will become clear later. The distance from one basal surface to the next in registry is called the basal spacing and is measured as the lowest angle peak in X-ray powder diffraction spectra. Natural clays have a basal spacing in the range of 1.2 to 2.0 nm, depending on the type of cation and amount of water present.

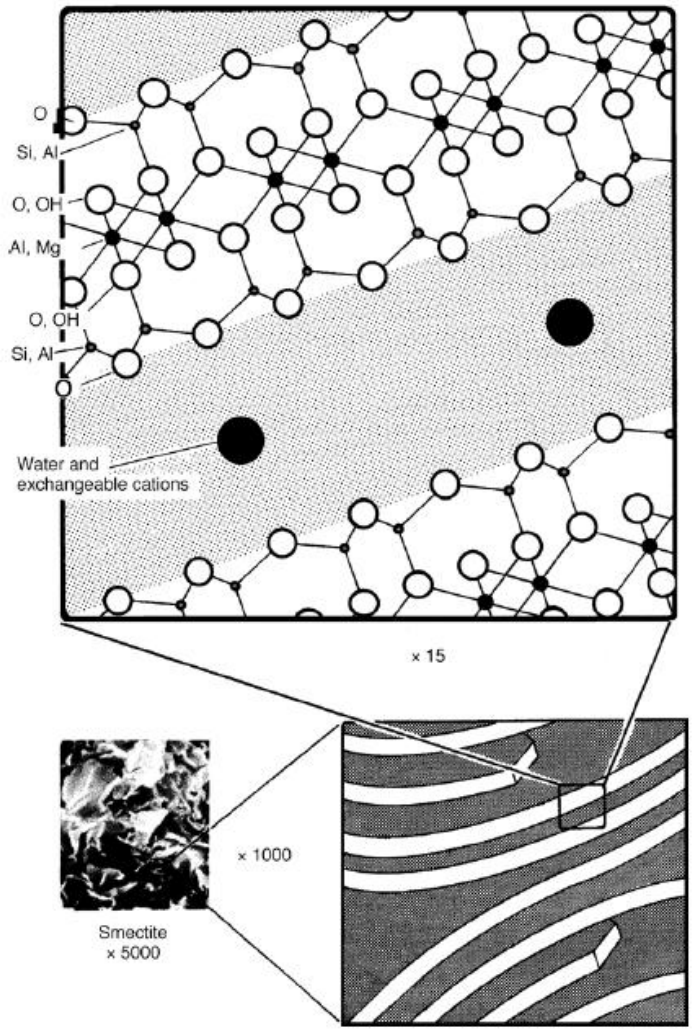


Figure 2.3: Structure of 2:1 phyllosilicates.

2.1.3 Cation exchange capacity

Cations are positively charged ions such as calcium (Ca^{2+}), magnesium (Mg^{2+}), and potassium (K^{+}), sodium (Na^{+}), Hydrogen (H^{+}), aluminum (Al^{3+}), iron (Fe^{2+}), manganese (Mn^{2+}), zinc (Zn^{2+}), and copper (Cu^{2+}). The capacity of the soil to hold

on these cations called the cation exchange capacity (CEC). These cations are held by the negatively charged clay and organic matter particles in the soil through electrostatic forces (negative soil particles attract the positive cations). The cations on the CEC of a soil represent the total amount of exchangeable cations that the soil can absorb. A low CEC means the soil the soil chemistry that are caused by land use (Table 2.1)

CEC units are usually expressed as centimoles of positive charge per kg of soil [cmol(+)/kg], which is numerically equivalent to the previously used unit of milli-equivalents per 100 g (me/100 g). CEC is usually estimated by displacing exchangeable cations (Na, Ca, Mg, K) with another strongly adsorbed cation, and then determining how much of the strongly adsorbed cation is retained by the soil. The strongly adsorbed cation is supplied by reagents such as ammonium chloride, ammonium acetate, silver thiourea, barium chloride and potassium chloride [26].

Table 2.1: Ratings for cation exchange capacity.

Rating	CEC cmol(+)/kg
Very low	<6
Low	6-12
Moderate	12-25
High	25-40
Very high	>40

Clay minerals are aluminosilicates having the major elements of oxygen, silicon, and aluminum. The crystal structure is in the form of plates or layers. The silicate layer has a tetrahedral configuration and the aluminum layer has a tetrahedral configuration and the aluminum layer has an octahedral configuration. The tetrahedron has four sides, whereas the octahedral configuration is eight sided. Silicon tetrahedra have four oxygen atoms associated with the aluminum atom.

These crystal configurations are the building blocks of clay minerals. The minimum unit that repeats itself in three dimensions to form the clay crystal structure is the ubit cell. This anologous to the monomer unit thta repeats to form an organic

polymer such as Polyethlene. Both silicon tetrahedra and aluminum octahedra form sheets by shared bonding with oxygen atoms. These sheets layer with one another to form the different clay meneal structures. The kandite mineral group has one silicon sheet and one aluminum sheet. The smectites and vermeculates have 2 silicon sheets to 1 aluminum sheet, but differ in their properties. Chlorites also have a 2:1 silicon to aluminum sheet ratio, but have a sheet of magnesium atoms between the silicon sheets [27].

The general cation exchange capacity of natural or synthetic clay minerals is between 50-200 meq/100 gr. Because of the cation exchange capacity is higher than 200, the forces between layers prevent seperation of clay layers. On the other hand, clay minerals, which cation exchange capacity lower from 50 meq/100 gr clay, could not seperate clay layers. Due to these resaons, montmorillonite which cation exchange capacity between 50-150 meq/100 g clay, are used as swelling agent in NCs [21].

2.1.4. The interlayer spacing

In order to have a stable mineral, there must be some degree of attraction between the layers making up the mineral. There is a fundamental difference between the 1:1 and 2:1 layers. The 2:1 layer is bounded on both sides by basal oxygen planes whereas the 1:1 layer has basal oxygen on one surface and hydroxyls on the other surface. The interlayer bonding for the 1:1 layer silicates whether dioctahedral or trioctahedaral, is via hydrogen bonds from one hydroxyl surface to the adjacent oxygen plane of the neighboring 1:1 layer. These are long hydrogen bonds, but there are many of them and thus their contribution to the interlayer bonding is strong. Any ionic substitution occurring in the 1:1 layer is usually such that overall electrostatic neutrality is maintained, i.e., the layer charge is always zero or very near to zero.

The 2:1 layer is more complex because it is possible to have a net layer charge. Since such a situation would be unstable because of the electrostatic repulsing between all the layers, the charge must be balanced by the presence of extra positive charge [21].

2.2. Polyolefins

The term polyolefin covers all polymers made from monomers with linear C=C double bonds. This includes polymers such as low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE) and polypropylene (PP). The different types of polyethylene derive from differences in the polymer chains, which in turn result in variations in melting points, densities, properties and therefore applications (Table 2.2) [28].

Table 2.2: Melting point and densities of common polyolefins.

Polyolefin	Melting Point (^{0}C)	Density (g/cm^3)
LDPE	115	0.92
LLDPE	123	0.92
HDPE	130	0.95
PP	170	0.90

2.2.1. Polyethylene

Polyethylene (PE) is the highest-volume polymer in the world. Its high toughness, ductility, excellent chemical resistance, low water vapor permeability, and very low water absorption, combined the ease with which it can be processed, make PE of all different density grades an attractive choice for a variety of goods.

Many types of polyethylene exist, all having essentially the same backbone of covalently linked carbon atoms with pendant hydrogen's; variations arise chiefly from branches, ranging from simple alkyl groups to acid and ester functionalities. The density of a particular grade is governed by the morphology of the backbone; long, linear, chains with very few side branches can assume a much more three-dimensionally compact, regular, crystalline structure, commercially available are LDPE (low density PE), LLDPE (linear low density PE), HDPE (high density PE), HMWPE (high molecular weight poly ethylene), UHMWPE (ultra high molecular weight polyethylene), HDXLPE (high density cross-linked PE), PEX (cross-linked PE), MDPE (medium density PE), and VLDPE (very low density PE).

2.2.1.1. Low density polyethylene (LDPE)

LDPE combines high impact strength, toughness, and ductility to make it the material of choice for packing films, which is one of the largest applications. Films range from shrink film, thin film for automatic packaging, heavy sacking, and multilayer films (both laminated and coextruded) where LDPE acts as a seal layer or water vapor barrier [29]. It has found stiff competition from LLDPE in these film applications due to LLDPE's higher melt strength. LPDE is polymerized under conditions of high temperature and high pressure. Because LDPE is processed under extreme conditions, the molecular structure is mostly amorphous. Because of the amorphous structure, the branches are very high in quantity and length (Figure 2.4) [30, 31].

Figure 2.4: Molecules of LDPE.

2.2.1.2. Linear low density polyethylene (LLDPE)

This product revolutionized the plastic industry with its enhanced tensile strength for the same density, as compared with LDPE. LLDPE is essentially a mix of HDPE and LDPE. It is created by a low pressure polymerization process much like HDPE, but has more branches much like LDPE has (Figure 2.5). These branches are long enough to prevent the molecules from being closely packed together. This results in a linear molecule structure like HDPE, but also a low density like LDPE. A homogeneous LLDPE with narrow comonomer sequence distribution as well as narrow molecular weight distribution is characterized by lower density, lower melting point, higher impact strength, sgnificiantly lower film haze, and improved film properties in the machine and transeverse direction [32, 33].

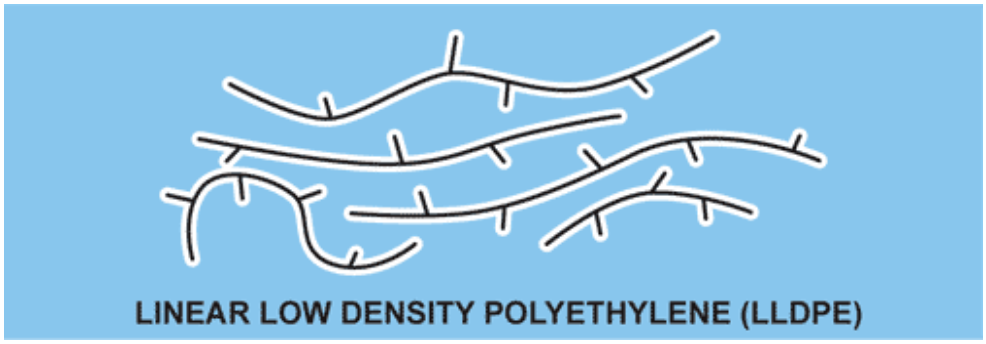


Figure 2.5: Molecules of LLDPE.

2.2.1.3. High density polyethylene (HDPE)

HDPE is the most rigit among the three common PE's and has a density ranging from 0.935-0.960 g/cm^3. HDPE is the product of limited branching that occurs when the polymerization is at low temperatures. (Figure2.6) Because of limited branching, HDPE is more crystalline; leading to the increased density. HDPE can be processed three different ways: slurry particle reactor, gas phase and metallocene catalyst. HDPE is the plastic that is used in making fuel tanks because of its low permeability and superb chemical resistance [32, 34].

Figure 2.6: Molecules of HDPE.

2.2.2. Polypropylene

Polypropylene (PP) is a lightweight plastic that is rigid and tough. Combined with its low cost, PP is used in a wide variety of applications. There are three different types of PP are used throughout the injection molding industry; isotactic, syndiotactic and atactic (Figure 2.7). The isotactic structure of PP is the most widely used of three types. Isotactic PP has a semi-crystalline structure that offers good mechanical properties such as stiffness and tensile strength [34]. When combines with different fillers such as clay, talc, calcium and glass, the mechanical properties

of PP can be dramatically enhanced. The addition of 30% short fiber glass reinforcement increases tensile strength and doubles the impact resistance [32].

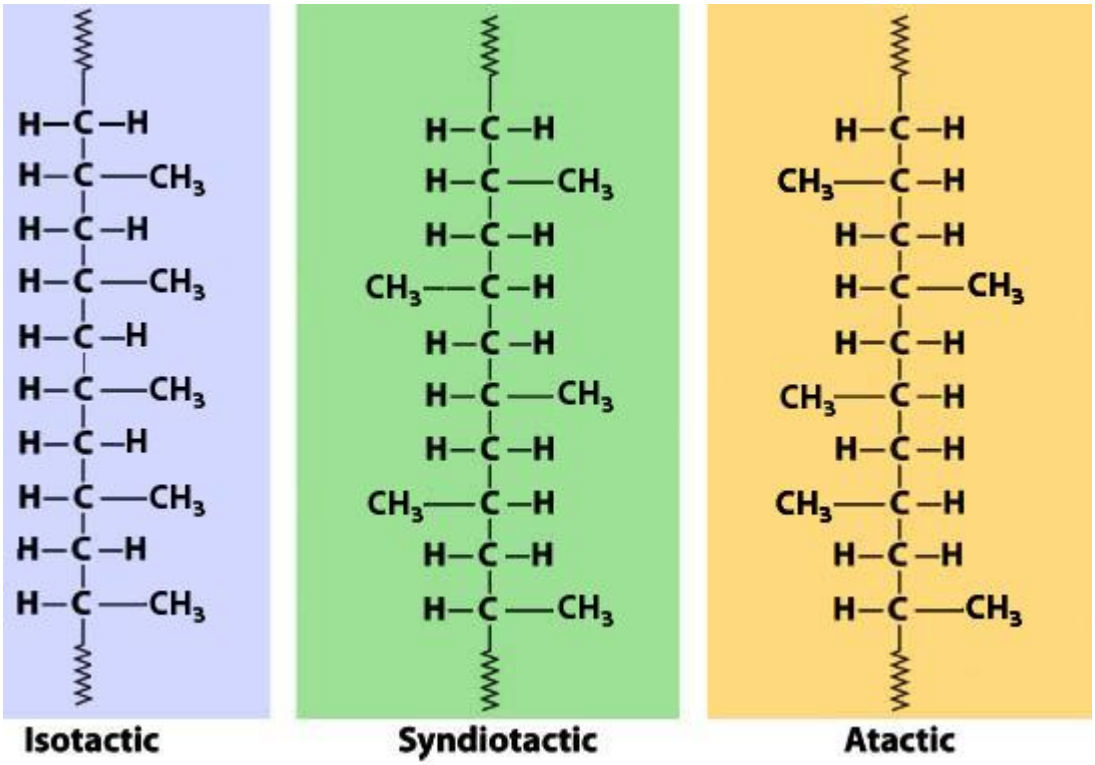


Figure 2.7: Stero-configurations of polypropylene.

In general, PP is not very flame resistant. A non-halogen flame retardant, such as magnesium hydroxide, can be added to PP to produce a low smoke, flame retardant material. The mechanism involves the creation of metals oxides and water, which smothers the flame. The down fall to placing flame retardant substances in PP is the reduction of UV resistance. Carbon black can be added to provide some protection against harmful UV rays [35, 36].

Polypropylene is often compared to polyethylene (PE) because it demonstrates many of the same characteristics as PP. There are some differences between these two plastics that will determine which plastic is better for an application. In general, PP has superior stiffness and stress cracking resistance compared to PE. Yet, PP is more sensitive to UV degradation than PE. The glass transition point and melting point are both higher in PP than PE, which also creates higher service temperatures. For this reason sterilizable medical devices and dishwasher safe containers are made of PP. In the area crack resistance due to mechanical stresses, PP out performs PE substantially. When subjected to extreme bending, PP does not blush or craze like

PE will. This is the reason PP is used glue, carpets, ropes, strapping tape and items needing internal or living hinges [32].

Polypropylene is one of the lightest plastics, with a density of 0.905. The nonpolar nature of the polymer gives PP low water absorption. Polypropylene has good chemical resistance, but liquids such as chlorinated solvents, gasoline, and xylene can affect the material PP has a low dielectric constant and is a good insulator. Difficulty in bonding to PP can be overcome by use of surface treatments to improve adhesion characteristics.

The molecular weight distribution (MWD) has important implications for processing. A PP grade with a broad MWD is more shear sensitive than a grade with a narrow MWD. Broad MWD materials will generally process better in injection molding applications. In contrast, a narrow MWD may be preferred for fiber formation [37]. Various grades of PP are available tailored to particular application. These grades can be classified by flow rate, which depends on both average molecular weight and MWD. Lower flow rate materials are used in extrusion applications. In injection molding applications, low flow rate materials are used for thick parts and high-flow- rate materials are used for thin-wall molding.

Polypropylene can be processed by methods similar to those used PE. The melt temperatures are generally in the range of 210-250 ^{0}C. Heating times should be minimized to reduce the possibility of oxidation. Blow molding of PP requires the use of higher melt temperatures and shear, but these conditions tend to accelerate the degradation of PP. Because of this, blow molding of PP is more difficult than for PE. The screw metering zone should not be too shallow to avoid excessive shear. For a 600-mm screw, the flight depths are typically about 2.25 mm, and 3.0 mm for a 90-mm screw [38]. In film application, film clarity requires careful control of the crystallization process to ensure that small crystallites are formed. This is accomplished in blow film by extruding downward into two converging boards.

Polypropylene (PP) is used as a matrix in numerous composite products because of its tensile strength, impact strength, flexural modulus and softening point. The mold shrinkage of polypropylene is less than that of the HDPE. Table2.3 furnishes some mechanical properties of PP homopolymer. Its appeal is both low density and low cost. Because PP is semi crystalline, its heat distortion temperature increases significiantly from 55 ^{0}C to 130 ^{0}C with the addition of 20 % glass fiber

reinforcement. Since polypropylene non polar, it absorbs very little water. Due to its T_g below room temperature, it exhibits good impact strength. Because of these properties polypropylene is used 90% of the time in glass mat thermoplastic sheet material for compression molding. Short and long fiber-reinforced polypropylene made by melt impregnation is available from many sources for injection molding applications.

Table 2.3: Selective properties of PP.

Property	PP homopolymer
Tensile strength, MPa	36
Elongation at break. %	350
Flexural modulus, MPa	1310
Brittle temperature, ^{0}C	+15
Softening point,^{0}C	145-150
Hardness, (R-scale)	95
Impact strength,k.m-2	24.5
MFI, g/10 min	8.7 (2.16 kg/230 ^{0}C)

2.2.2.1 Properties of polyproyplene

Polypropylene is a linear hydrocarbon polymer containing little or no unsaturation. It is therefore not surprising that PP and PE have many similarities in their properties, particularly in their swelling and solution behavior and their electrical properties. In spite of many similarities, the presence of a methyl group attached to alternate carbon atoms on the chain backbone can alter the properties of the polymer in a number of ways. For example it can cause a slight stiffening of the chain and it can interfere with the molecular symmetry. The first effect leads to increase crystalline melting point whereas the interference with molecular symmetry would

tend to depress it. The most significant influence of the methyl group is that it can lead to products of different tacticity, ranging from completely isotactic and syndiotactic structures to atactic molecules (Figure 2.4). The isotactic form is the most regular since the methyl groups are all disposed on one side of the molecule. Such molecules cannot crystallize in a planar zigzag form as do those of polyethylene because of the streric hindrance of the methyl groups but crystallize in a helix, eight three molecules being required for one turn of the helix. Both right-hand and left-hand helices occur both forms can fit into the same crystal structure. Commercial polymers are usually about 90-95 % isotactic. In these products, atactic and syndiotactic structures may be present either as complete molecules or as blocks of varying length is chains of otherwise isotactic molecules.

The influence of molecular weight on the bulk properties of polypropylene is often opposite to that experienced with most other well-known polymers. Although an increase in melt viscosity in melt viscosity and impact strength, in accord with most other polymers, it also leads to a lower yield strength, lower hardness, lower stiffness and softening point. This effect is believed to the fact that high molecular weight polymer does not crystallize so easily as lower molecular weight material and it is the differences in the degree of crystallization which affect the bulk properties. It may also be mentioned that an increase in molecular weight leads to a reduction in brittle point. (Table 2.4)

The morphological structure of polypropylene is rather complex and at least four different types of spherules have been observed. The properties of the polymer will depend on the size and type of crystal structure formed and this will in turn be dependent on relative rates of nucleation to crystal growth. The ratio of these two rates can be controlled by varying the rate of cooling and by the incorporation of nucleating agents. In general the smaller the crystal structures the greater the transparency and flex resistance and the less the rigidity and heat resistance. One unfortunate characteristic property of polypropylene is the dominating transition point which occurs at 0 ^{0}C with the result that the polymer becomes brittle as this temperature is approached. Even at room temperature the impact strength of some grades leaves something to be desired.

Table 2.4: Some mechanical and thermal properties of commercial polypropylene.

Property	Test method	Homopolymers		
Melt Flow index	load 2.16 kg at 230 ^{0}C	3.0	0.7	0.2
Tensile strength, MPa	Straining rate 18 in/min.	34	30	29
Elongation at break, %	Straining rate 18 in/min.	350	115	175
Flexural modulus, MPa	-	1310	1170	1100
Brittleness Temperature, ^{0}C	ICI/ASTM D.476	+15	0	0
Vicat softening point, ^{0}C	BS 2782	145-150	148	148
Rockwell hardness, R-scale	-	95	90	90
Impact strength, J	13.5	34	46	46

Products of improved strength and lower brittle points may be obtained by block copolymerization of PP with small amounts (4-15%) of ethylene. Such materials are widely used (known variously as polyallomers or just as propylene copolymers) and are often preferred to the homopolymer in injection moldings and bottle blowing applications [39].

2.2.2.2. Mechanical properties of polypropylene

Like other thermoplastics, polypropylene is a viscolelastic material; consequently its mechanical properties are strongly dependent on time, temperature, and stress. Furthermore, PP is a semi-crystalline material, so the degree of crystallinity and orientation also affects mechanical properties. A number of common short-term tests-tensile strength, elongation at break and strain at yield- are based on the behavior of the material in tension. That of polypropylene follows the general pattern for a hard though material, showing relatively high yield strenght and high

elongation at break. The tensile strength of PP is inferior to that of most other thermoplastics, with the exception of low density polyethylene. PP homopolymer has a higher tensile strength than copolymer, and is comparable with high density polyethylene. Flexural modulus too, is lower than most materials apart from low density polyethylene and some polyamides. PP copolymer more flexible than homopolymer.

Many polymers exhibit small secondary transitions (T_{sec}) at temperatures well below that of the glass transition temperature. In many cases these small transition can be detected and studied by compressibility measurement. A polymer above its glass transition temperature acts as a tough ductile material while below it, the material is hard and glassy. On cooling, the glass transition temperature is sometimes known as the freeze temperature. Glass transition temperature is measured using a dynamic mechanical thermal analyzer (DMTA) or differential scanning calorimeter (DSC). PP has the following transition temperatures:

- Second-order glass transition temperature at -10 ^{0}C (predicted). The actual value may be observed between 0 to 20 ^{0}C depending on the frequency/heating rate.
- Crystallization melting point between 160-170 ^{0}C depending on the grade and the frequency/heating rate.
- Recrystallization temperature on slow cooling of the melt between 115 ^{0}C and 135 ^{0}C.

Elongation at break indicates how to material fails in tension. A low elongation figure denotes a brittle rupture, while a high elongation shows that the material responds ductile manner. PP has a high elongation figure, although it is exceeded by low density polyethylene. The elongation figure for PP copolymer is substantially higher than that of homopolymer. Strain at yield is an indication of rigidity of the material within its structurally useful range of stress. The comparative ranking of thermoplastic by this criterion is quite similar to that produced by elongation at break, except that there is little difference between figures for PP homopolymer and copolymer. Impact strength is the shortest, with the load applied in less than a second whereas the time scale for the other short-term tests is measured in the low minutes. The impact performance of PP homopolymer is noticeably less than that of copolymer. Mechanical properties of PP can be substantially modified by the

inclusion of fillers, reinforcement, and modifiers. Tensile strength is not greatly affected by fillers, nor even by glass fiber reinforcement unless the fibers are chemically coupled to the polymer. Then there is a dramatic improvement due to the efficiency with which the tensile load is transferred from the PP matrix to the reinforcing fibers. Flexural modulus, or rigidity, is improved by fillers such as talc and calcium carbonate, as well as by reinforcements. Impact strength is reduced by fillers but increased a little by reinforcement and substantially so by elastomers modifiers. Impact strength increases as the temperature rises and material becomes more elastic and ductile [34].

2.2.3. Polymer processing aids

"Processing aid" is a general term that refers to several different classes of materials used to improve the processability and handling of high molecular weight polymers. The benefits are realized mainly in the melt state of the host polymer. Their use is focused on PO-based polymers. Two main groups of processing aids are lubricants and fluoropolymer based additives. Each has a distinct effect on the polymer melt and is used in a different way [40].

Lubricants are used in polymer processing to lower melt viscosity or to prevent polymers from sticking to metal surfaces. Internal lubricants act intermolecularly, making it easier for polymer chains to slip past one another. Lowering viscosity improves polymer flow, material used for lubricants include metal soaps, hydrocarbon waxes, polyethylene, amide waxes, fatty acids, fatty alcohols, and esters [41].

Fluoropolymer-based processing aids are mostly copolymers of vinylidene fluoride and hexafluoropropylene. This material is commonly referred to as "fluoroelastomer", even though it is not cross linked when used as a processing aid and, thus, has no elastomeric properties [42]. The most pronounced effect of fluoropolymer processing aids is the elimination of the melt fracture during polymer extrusion.

2.2.4. Melt flow index

MFI is an approximate indication of the molecular weight of the polymer. It gives a rough idea of how long, or short, the molecular chains are in the sample being measured. A high MFI resins generally will have a lower viscosity. That is, it flow and process more easily. However, it usually also will have poorer physical properties, such as impact strength or tensile modulus.

Table 2.5: End use indication through MFI for various grades of polypropylene.

MFI @230 ^{o}C and 5 kg load	*End use application*
2	Compression moldings, pipes
1-5	Extrusion blow moldings
5-15	Biaxially oriented films
5-15	Film tapes
5-15	Monofilaments
5-20	General injection moldings
30	High-speed injection moldings
30-40	Flat films
40-80	Stable fibers
60	Spun-bonded fabrics

The MFI of a polymer grade also governs its intended use. Products with 1.0 or less MFI for Polyolefin are usually used in blow molding and extrusion applications. A list of MFI of polypropylene for different end-use is giving in Table 2.5. More viscous resins are measured by the HLMFI test. They are used for larger-sized products where melt strength is important in processing. These products include automotive gas tanks and large diameter pipe. High MFI (5 or over) materials flow more easily. These are injection molding materials for applications ranging from caps and closures to pails. MFI is a single point test. That is, it gives only one measurement of viscosity at specific conditions. This helps make the test quick and simple, which is why MFI is widely accepted. A disadvantage is that the test provides only a limited amount of information. It does not indicate how the polymer will flow under other conditions.

2.3 Compatibilezer

Compatibilizer for polymers blends or polymer composites are interfacial agents improving compatibility between the immiscible components through their effects on wetting, dispersion and adhesion. The term compatibilizer is commonly used for immiscible polymer/polymer blends; for dispersed fillers, the terms coupling agents, surface treatments, or surface modifiers are commonly used. They are all considered as interfacial agent. The differences and similarities in the compatibilization mechanisms applicable to blends and composites are discussed along with methods of incorporation of common compatibilizers having different chemical structures.

2.3.1. Principles of compatibilization

The major difficulty in devising useful polymer blends is the general incompatibility of polymers. There is essentially no entropy of mixing for a blend of high molecular weight polymers. Thus, one major driving force for solubility that is found in mixtures of small is absent in polymer blends. Therefore, one can except that polymers will be soluble or miscible in one another only in special cases, such as in the presence of specific strong interactions between repeating units. This phenomenon has been outlined in several texts [43, 44]. Rarer still is immiscibility and compatibility at which a mixture's constituents have different properties (e.g., structure, polarity) but show some interaction, because of reactive groups, surface active agents, or compatibilizers.

Immiscibilty and compatibility are not necessarily bad. Actually, the entire technology of thoughned polymers is based on this approach, because it synergistically combines the properties of completely different polymers to form a blend with properties superior to those of the individual blend components [45, 46].

Compatibilizers that compatibilize two polymers, A and B, consist of two parts. One part interact with polymer A and the other part with polymer B, but to do so effectively, they must be concentrated at the interface between the two polymers (Figure 2.8). The result is a better dispersion of the polymer blend as shown in figure 2.9. Infinite dispersion, however, is not necessarily desirable since a minimum particle diameter exists for each system below which there will be no synergistic improvement in properties (e.g., fracture toughness)

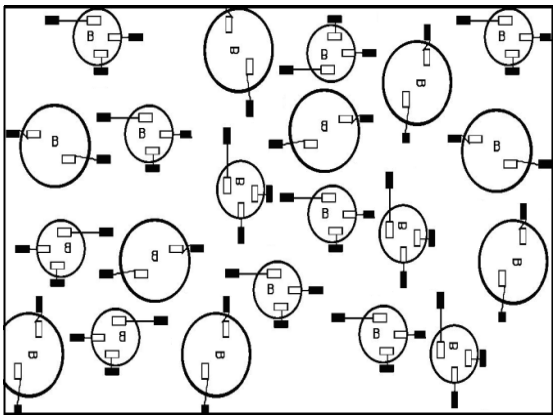


Figure 2.8: Schematic representation of an AB block copolymer compatibilizing a blend of polymers A and B.

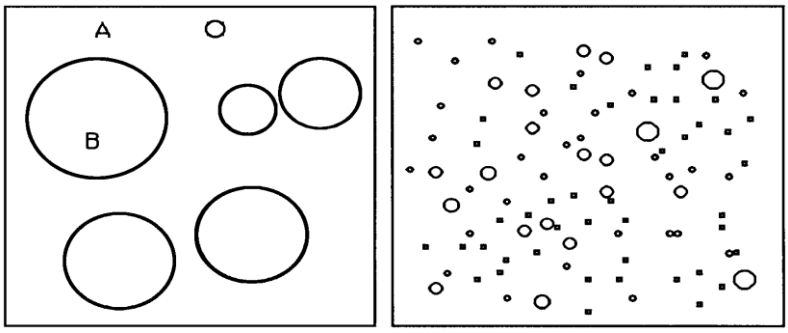


Figure 2.9: Schematic representation of a compatibilization reaction.

2.3.2. Classification of compatibilizers.

Compatibilizers can be classified in two categories: non-reactive and reactive compatibilizes; random, graft and block copolymers; and nature of their base polymers. Compatibilizers based on polyolefins will be consider seperately because multilayer structures as they are used in film packaging contain at least one component of a polyolefinic nature, which must to be compatibilized with the remainder of the structure.

Non-reactive compatibilizers, which compatibilize two polymers, A and B, consist of two parts: the first is soluble in polymer A, and second is soluble in polymer B. The compatibilizers effect derives from their solubility. Therefore, the solubility parameters of both parts should be as close as possibility to the solubility parameters of the polymer components in the polymer mixture [47, 48].

In random copolymers, the components, the base polymer B and a comonomer A, are distributed randomly along the polymer chain. Random copolymers are usually

produced in a high pressure radical polymerization process [49,50]. Random copolymers only work well as compatibilizers when the comonomer A is reactive.

In graft copolymers, either monomers or polymers are grafted onto each other. If only monomers are grafted to the backbone, the monomer should be reactive. An example is PP grafted with maleic anhydride. The exposure of the reactive monomers on the usually non-reactive base polymer backbone makes them more accessible to an attack by other polymers, transforming them into effective compatibilizers.

2.3.3. Study on IA and MAH grafting on polpropylene

There were two major findings that pioneered the revival of modified clay minerals and synthetic clays: First, the report of nylon-6/montmorillonitte material from Toyota research [51, 52] where very moderate inorganic loadings resulted in concurrent and remarkable enhancements of thermal and mechanical properties. Second Giannelis at al. found that it is possible to melt-mix polymers with clays without the use of organic solvents [53]. Because of these first works including nylon-6 and clay, compatibilizers had not necessaries. After starting to use non-polar polyolefins (PO), compatibilizers have been starting to use. Firstly MAH grafted polymers compatibilizers starting to use and after IA grafted compatibilizers have started to use.

Itaconic acid (IA) and its monoesters can be grafted onto polyolefins [8].

J.A. Trapow and coworkers worked on effect of clay content, PP/clay compatibility, and processing conditions. PP-g-MAH was used as compatibilizer in this work. They were determined that the young's modulus improved by the clay incorporation and became higher as a function of clay content. On the other hand neither the tensile strength nor the impact toughness were enhanced and this could be attributed to poor interfacial adhesion between the PP matrix and unmodified clay. XRD patterns indicated that the polymer chains were intercalated between the clay platelets, whereas no evidence of exfoliation has been found. TEM micrographs, some areas where a small amount of polymer has moved into the gallery spacing between clay platelets have clearly observed. Both results have in accordance with those of mechanical properties. Analyzing the compatibility between clay and matrix (by using different clays or PP-g-MAH), highest effect was obtained for the

most hydrophobic clay used. Nevertheless, the difference in the mechanical properties have not significant when comparing with standard deviations, except for the impact thougness where a clear increase has observed for nanocoposite with organomodified clays. The processing condition showed no important influence on degree of dispersion or the mechanical properties [54].

W. Lertwimolnun and B.Vergnes worked on PP/organoclay nanocomposites which have been prepared via direct melt intercalation in an internal mixer. PP-g-MAH was used as compatibilizer to improve the dispersability of the clay. The structures of nanocomposites have been characterized by X-ray diffraction, transmission electron microscopy and rheometry in small amplitude oscillatory shear. The effects of concentration of PP-g-MAH and processing parameters were investigated. The state of intercalation, interpreted by interlayer spacing, is globally unaffected by processing parameters. Increasing shear stress, mixing time and decreasing mixing temperature improve clay layer silicate exfoliation [55].

M. Yazdani and his co-workes worked on methyl esters of itaconic acid on PP. Firstly, they functionalized PP in the melt phase by grafting with MMI and DMI. It was found that the percentage of grafting attained depends on the initial concentration of both monomer and initiator used in the reaction. They found that the molecular weight of the grafted polymer decreased with increasing percentage of grafting. Thermal properties of the modified PP samples indicated slightly higher crystallinity of the functionalized polymers but having the same melting temperatures as PP [56].

E. Moncada and his coworkers worked with monoesters of IA and maleic anhydride (MAH) for grafting on PP. Firstly they were prepared PP/clay nanocomposites by melt mixing PP of different molecular weights with different clays as nanoparticles and by using modified PP grafted with different percentages of IA as compatibilizers. The aim of this study was to investigate the effect of both molecular weight of PP, used as polymer matrix, as well as the degree of grafting of the modified PP on the mechanical and morphological properties of nanocomposites. The degree of clay dispersion in the PP matrix and the mechanical properties of the resulting nanocomposite improved considerably by incorporation of PP-g-IA as a compatibilizer. However, this improvement depended on the grafting extent of the compatibilizer, type of clay and molecular weight of the PP used as matrix.

Secondly E. Moncada and coworkers were used PP grafted maleic anhydride (PP-g-MAH) as compatibilizer. Inferior mechanical properties were obtained for nanocomposites prepared by using this compatabilizer. Results indicated that IA-g-PP was more efficient as compatibilizer for the formation of nanocomposites than commercially available MA-g-PP [9].

2.4. Polymer Nanocomposites

A composite material is made by combining two or more materials to give a unique combination of properties. Nanocomposites technology is a newly developed field, in which nanofillers are added to a polymer to reinforce and provide novel characteristics. Nanocomposite technology is applicable to a wide range of polymers from thermoplastics and thermosets to elastomers.

2.4.1. Polymer nanocomposite preparation and synthesis

The process of synthesis of polymer/clay nanocomposites involves the uniform dispersion of agglomerates of clay particles within a polymeric matrix. Ultimately, the nanocomposites would incorporate smaller intercalated clay particles, fully exfoliated individual clay platelets, or a mixed intercalated/exfoliated system. In order to qualify as a nanocomposite, this exhibits useful mechanical, barrier, electrical, thermal, and other properties [57].

Colloid and surface chemistry play important roles in the synthesis of polymer-clay nanocomposites. Dispersion of clay layers in polymers is hindered by the inherent tendency to form face-to-face stacks in agglomerated tactoids due to high interlayer cohesive energy. There is a growing interest in the surface chemistry of clays in pursuit of nanocomposite synthesis using specific monomers, prepolymers and polymer melts. Polymers and silicates do not necessarily form a nanocomposite: the compatibility between the two phases is important [58].

In general, nanocomposites can be formed in one of three ways:

• Melt intercalation.

• Solution dispersion.

• In-situ polymerization

2.4.1.1. Melt intercalation

Melt intercalation is the most widely used method in polymer/clay nanocomposite preparation, and it has tremendous potential for industrial application. An advantage of this method over the others is that no solvent is required. The melt blending process involves mixing the layered silicate by annealing, statically or under shear, with polymer pellets while heating the mixture above the softening point of the polymer. During the annealing process, the polymer chains diffuse from bulk polymer melt into the galleries between silicate layers.

Figure 2.10 represents a schematic illustration of nanocomposite formation by direct melt intercalation structure and properties of organically modified layered silicate. This process involves annealing a mixture of the polymer and organically modified layered silicate above the softening point of the polymer, statically or under shear. While annealing, the polymer chains diffuse from the bulk polymer melt into the galleries between the silicate layers [57, 59].

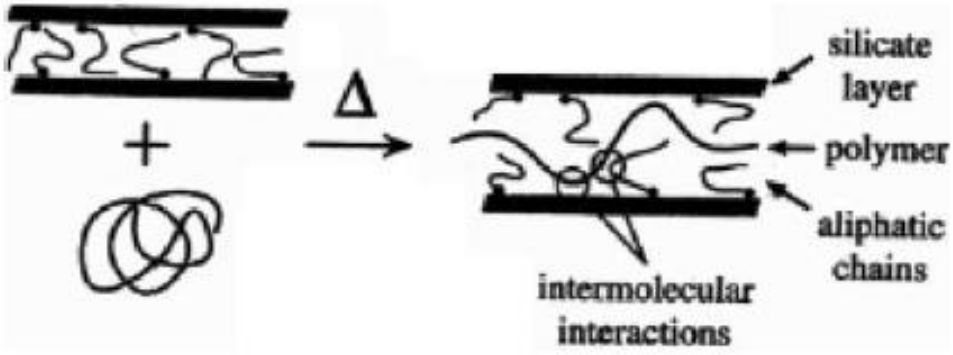


Figure 2.10: Schematic depicting the intercalation process between a polymer melt and an organically modified layered silicate.

In some cases the polymer–silicate mixture can be extruded by using (a) static melt intercalation: by mixing and grinding dried powders of polymer and organic silicate in a pestle and mortar and then heating the mixture in vacuum, and (b) extrusion melt intercalation: by extruding the mixture with twin screw extruder to produce a polymer nanocomposite from the polymer and modified clay [2, 60, 61].

2.4.1.2. Solution dispersion

The solution dispersion method involves mixing a preformed polymer solution with clay. This is based on a solvent system in which the polymer or pre-polymer is

soluble and the silicate layers are swellable. The layered silicate is first swollen in a solvent, such as water, chloroform, or toluene. When the polymer and layered silicate solutions are mixed, the polymer chains intercalate and displace the solvent within the interlayer of the silicate. Upon solvent removal, the intercalated structure remains, resulting in polymer / layered silicate nanocomposite. Using this method, intercalation only occurs for certain polymer/solvent pairs. This method is good for the intercalation of polymers with little or no polarity into layered structures, and facilities production of thin films with polymer-oriented clay intercalated layers. However, from commercial point of view, this method involves the copious use of organic solvent, which is usually environmentally unfriendly and economically prohibitive [57, 62].

2.4.1.3. In-Situ polymerization

In-situ polymerization involves the dispersion and distribution of clay layers in the monomer followed by polymerization (Figure 2.11). The layered silicate is swollen within the liquid monomer or a monomer solution so that polymer formation can occur between the intercalated sheets.

Polymerization can be initiated either by heat or by radiation, diffusion of a suitable initiator, or by an organic initiator or catalyst fixed through cation exchange inside the interlayer before the swelling step [57].

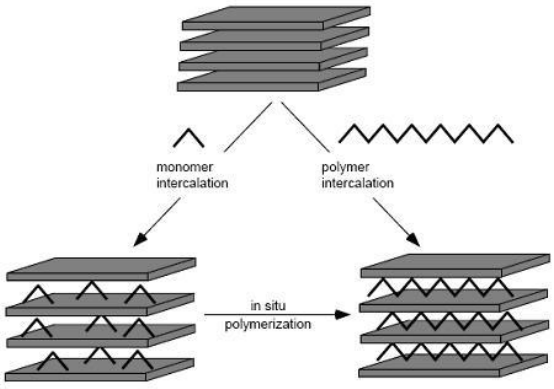


Figure 2.11: Method for creating intercalated polymer-clay architectures via direct polymer contact and via insitu polymerization of pre intercalated polymers.

2.4.2. Nanocomposite structures

Depending on the nature of the component used (layered silicate, organic cation and polymer matrix) and the method of preparation, three main types of composites may be obtained when layered clay is associated with a polymer. There are two end members that delineate the realm of structures possible in-polymer clay nanocomposites. At one end of the spectrum are well-ordered, stacked multilayers that result from intercalated polymer chains within host silicate clay layers. At the other end of the spectrum are exfoliated materials, wherein the host clay layers have lost their entire registry and are well dispersed within a continuous polymer matrix. (Figure 2.12) Exfoliated polymer-clay nanocomposites display acceptable stiffness, strength and barrier properties with far lower ceramic content than is achieved far more conventional particulate-filled polymer composites. Often, there are occasions where retention of the layered nature of a polymer–clay nanocomposite is the desired outcome. Such regular nano assemblies have the following unique characteristics and applications:

1. There are a wide variety of both host materials (clay and nonclay) and polymers.

2. Anisotropic arrangements of polymers in two-dimensional microenvironments occur.

3. The variable gallery spacing is adaptable to polymer size.

4. Microenvironments can induce spatial chemistry and host surface chemistry effects.

5. Rigid host layers provide enhancements to structural, chemical, and thermal stabilities to more fragile guest polymers.

Two primary methods are utilized to prepare intercalated polymer-clay materials. The former route is limited because the types of polymers that can be intercalated directly are limited. The latter route, while more universal, results in a loss of control over the molecular weight of the final polymer.

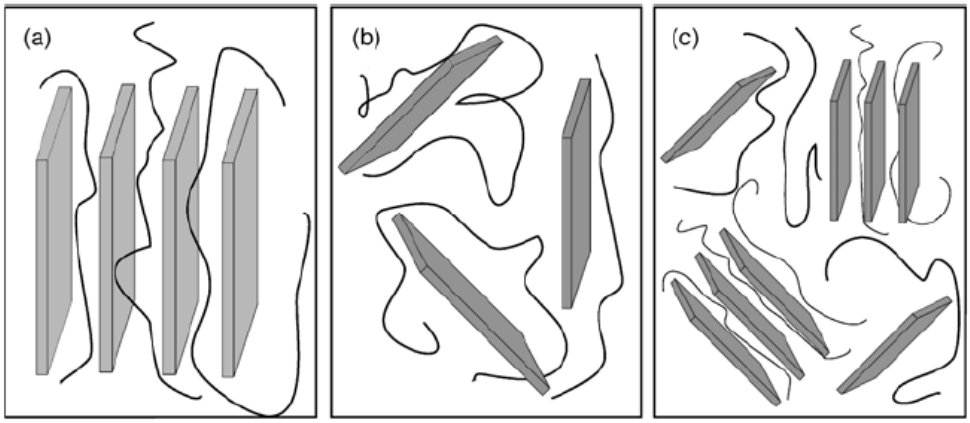


Figure 2.12: Schematic representation of the various PNC architectures: (a) intercalated, (b) exfoliated, and (c) mixed intercalated-exfoliated.

Some of the PNC systems are created in a unique way where in the clay layers are crystallized from a silicate sol-gel in direct contact with a polymer solution. In the majority of intercalated PNC cases, the linear macromolecules are in nearly fully extended conformation. Another way to intercalate polymers directly is through a melt method, where the polymers are heated with pre-exfoliated (in most cases) clay. In this way, a conventional polymer extrusion process can often be utilized. The formation of PNCs via melt intercalation depends on the thermodynamic interaction between polymer chains and host layers, and also on the diffusion of polymer chains from bulk to interlayers. For more hydrophobic polymers, however, the clays must be rendered more organophilic to enhance their compatibility.

Probably the most successful route to creating PNCs in general has been the in situ process, wherein monomers are polymerized in the presence of clay mineral layers. In terms of well-ordered polymer–clay intercalates, using in situ polymerization have included polyacrylamide, nylon, polyaniline, polycaprolactone, polyimide, PMMA, polystyrene, polyurethane, polyethynylpyridine, and epoxy resins. If conditions are varied, many of these polymers can also be induced to form exfoliated PNC architectures.

The dispersion of mineral reinforcing components to a polymeric matrix has been utilized for many decades. Inactive fillers or extenders act to simply reduce costs, and their chemistry is less important than factors such as particle size, shape, morphology, distribution, and, of course, cost. Active fillers are reinforcing materials and require at least some compatibility between polymer and inorganic,

and they must often undergo a surface modification process to insure this. In contrast to conventionally scaled composites on the micrometer level, nanocomposites exhibit changes in composition and structure over the nanometer length scale. Individual clay layers fall into this realm because they have a thickness on the order of 1 nm. Clays such as kaolinite, mica, and talc have been important plate-shaped conventional fillers in the past. However, preparation of a true nanocomposite requires complete dispersion, or exfoliation, of the elementary clay layers within the polymer matrix, without any aggregation into larger units such as tactoids or intercalation products. This is a serious challenge that has been addressed well since the first pioneering research was published in 1987 from Toyota workers. There are very few successful reports of making fully exfoliated PNCs from dissolved polymer solutions. This is because even when dispersions of fully exfoliated clays are exposed to macromolecular solutions, the strong interactions between macromolecules and silicate layers often just reaggregate the layers. There is a report that polysulfone exfoliates organoclays via a "solution dispersion" technique. More success for making the better PNCs has occurred using the melt mixing method concerning superior composite properties, including more exfoliation. In a study of PNC synthesis, the PNC structure can also be investigated in the differences in melt rheology and in the crystalline morphology. As in the case for intercalated materials, the clays need to be pre modified by reaction with alkylammonium ions in order to make them more compatible with the hydrophobic polymers. The most successful process for making exfoliated PNCs has been through the polymerization of monomers that are in the presence of clay minerals. Conditions must be optimized to promote a polymerization that causes the uniform dispersion of silicate layers within the polymer matrix. The heat of reaction evolved (enthalpy) during polymerization provides an essential component to the exfoliation. Therefore, exfoliation is enhanced with increasing amounts of intercalated monomers and with decreasing layer charge on the clay surface. In-situ polymerizations (emulsion, thermal, photo, free radical, etc.) that employ organoclays and lead to truly exfoliated PNCs.

The main reason for these improved properties in nanocomposites is the interfacial interaction between the matrix and layered silicate, as opposed to conventional composites [4]. Layered silicates have layer thickness onthe order of 1 nm, and very

high aspect ratios (e.g. 10~1,000). A few weight percent of layered silicate particles that are properly dispersed throughout the matrix can thus create a much larger surface area for polymer filler interactions than do conventional composites.

PP has no polar groups in the chain, direct intercalation of PP in the silicate galleries is impossible. To overcome this difficulty, Usiki et al. first reported a novel approach to prepare PP/nanocomposites using a functional oligomer (PP-OH) with polar telechelic OH groups as a compatilizer. In this approach, PP-OH was intercalated between the layers of $2C_{18}$-MMT, and then it was melt mixed with PP to obtain the nanocomposite with intercalated structure. Kawasumi et al. reported the preparation of PP/MMT nanocomposites obtained by melt blending of PP, a maleic anhydride grafted PP oligomer (PP-g-MAH), and clays modified with stearylammonium using a twin screw extruder. This study used two different types of maleic anhydride modified PP oligomer with different amounts of maleic anhydride groups and two types of organically modified clays to understand the miscibility effect of the oligomers on the dispersibility of the organo modified layered silicate in the PP matrix. In addition, they also studied the effect of hybridization on the mechanical properties when compared with neat PP and PP/nanocomposites without oligomers. WAXD analyses and TEM observations established the intercalated structure for all nanocomposites. On the basis of WAXD patterns and TEM images, they proposed a possible mechanism for dispersion of intercalated clay layers in the PP matrix.

2.4.3. Characterization of PNCs

Generally, the structure of nanocomposites has typically been established using WAXD analysis and transmission electron micrographic (TEM) observation. Due to its easiness and availability WAXD is most commonly used to probe the nanocomposite structure [2, 3] and occasionally to study the kinetics of the polymer melt intercalation [63]. By monitoring the position, shape, and intensity of the basal reflections from the distributed silicate layers, the nanocomposite structure (intercalated or exfoliated) may be identified. Although WAXD offers a convenient method to determine the interlayer spacing of the silicate layers in the original layered silicates and in the intercalated nanocomposites (within 1-4 nm), little can be said about the spatial distribution of the silicate layers or any structural non-

homogeneties in nanocomposites. Additionally, some layered silicates initially do not exhibit well defined basal reflections.

X-ray diffraction allows the determination of the spaces between structural layers of silicate utilizing Bragg's law: $\sin\theta = n\lambda /2d$. Intercalation and delamination change the dimensions of the gaps between the silicate layers, so an increase in layer distance indicates that a nanocomposite has formed. A reduction in the diffraction angle corresponds to an increase in the silicate layer distance. Generally, diffraction peaks observed in the low angle region (2θ = 3–9°) indicate the d-spacing (basal spacing, d_{001}) of ordered intercalated and ordered-delaminated structures. If the nanocomposites are disordered, no peaks are observed in the XRD due to loss of structure of the layers, the large d-spacing (>10nm), or both. In general, the following relationship between the composite and the X-ray diffraction pattern hold [60, 64].

Therefore, conclusions concerning the mechanism of nanocomposites formation and their structure based on WAXD patterns are only temporary. On the other hand, TEM allows a qualitative understanding of the internal structure, spatial distribution of the various phases, and views of the defect structure through direct visualization. However, special care must be exercised to guarantee a representative cross-section of the sample [65].

Information about the macrostructure of a polymer such as the dimensions and packing of crystallites, spherulites, lamellae, separated phases, and voids; particle size and shape in solution or colloids; and information on branched polymers and the deformation and annealing of polymers can be obtained from small-angle Xray scattering (SAXS). The reflections that lie very close to the beam stop are necessary for this information. To obtain sufficient clarity synchrotron radiation is often used. If the sample is reactive under high intensity X-radiation, this method is unsuitable. The morphological properties of PNC samples were investigated by the scanning electron microscope (SEM) which is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity.

The types of signals made by an SEM can include secondary electrons, back scattered electrons, characteristic x-rays and light (cathodoluminescence). These signals come from the beam of electrons striking the surface of the specimen and interacting with the sample at or near its surface. In its primary detection mode, secondary electron imaging, the SEM can produce very high-resolution images of a sample surface, revealing details about 1 to 5 nm in size. Due to the way these images are created, SEM micrographs have a very large depth of focus yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. This great depth of field and the wide range of magnifications (commonly from about 25 times to 250,000 times) are available in the most common imaging mode for specimens in the SEM, secondary electron imaging, such as the micrograph taken of pollen shown to the right. Characteristic x-rays are the second most common imaging mode for an SEM. X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher energy electron to fill the shell and give off energy. These characteristic x-rays are used to identify the elemental composition of the sample. Back-scattered electrons (BSE) that come from the sample may also be used to form an image. BSE images are often used in analytical SEM along with the spectra made from the characteristic x-rays as clues to the elemental composition of the sample.

2.4.4. Works on PNC including IA/MAH grafting polypropylene

Polymer-layered silicate nanocomposites were first reported in the literature as early as 1961, when Blumstein demonstrated polymerization of vinyl monomers intercalated into montmorillonite (MMT) clay [66]. At the time it was not known that these were nanocomposites and, indeed, the term did not yet exist. In the early 1990's researchers at Toyota prepared a polyamide-6 material by polymerization of caprolactam in the presence of montmorillonite clay and found a remarkable enhancement in several properties [67, 68]. The nanocomposites prepared PA 6 possessed excellent mechanical and thermal properties at very low filler content offering economical solution in several fields of application. The main advantages are light weight, high modulus and strength, decreased gas permeability, increased thermal stability. Their mechanical properties are superior to unidirectional fibre reinforcement from the inorganic layers will occur in two rather than in one dimension [64]. Because of the length scale involved that minimizes scattering,

nanocomposites are usually transparent [69]. They also exhibit significant increases in thermal stability as well as a self-extinguishing character. In polymer-layered silicates, composite properties are achieved at a much lower volume fraction of reinforcement in comparison with conventional fiber or mineral-reinforced polymers. They can be processed by such techniques as extrusion and casting common to polymers which are superior to the costly and cumbersome techniques used for conventional fiber and mineral-reinforced composites and furthermore are adaptable to films, fibers and monoliths. Most of the work in this area is at present at the experimental stage, although some commercial explanation has been reported. For example, the Toyota Motor Company is using an automotive timing-belt cover made from a nylon-layered silicate nanocomposite. Potential applications are barrier films for food packaging, aero plane interiors, fuel tanks and components in electrical or electronic parts, brakes and tires [2].

Denis and his co-workers concluded that increasing the mean residence time and shear intensity generally improved delamination and dispersion, although they noted that increasing the shear intensity generally improved delamination and dispersion, although they noted that increasing the shear intensity beyond an optimal level led to poorer exfoliation and dispersion [70].

Leia and co-workers reported the effect of clay chemistry on processing and properties of the polypropylene nanocompoistes. They fabricate nanocomposites using clays cloisite Na^{+}- MMT, cloisite 15A, cloisite 20A, cloisite 30B, and nanocor 130E, 131PS and found that addition of nanoclay in the polypropylene shows improvement in crystallization temperature indicating the nucleating effect of the nano-clays in the crystallization of PP. The extent of crystallization temperature (T_c), varied slightly with the types of clay. However, on the other hand the melting temperature of the polypropylene decreases on addition of organoclay. They reported that the introduction of low molecular weight surface surfactants in the clays leads to the decrease in melting temperature. The addition of nanoclay also shows better improvement in storage modulus and softening temperature [71].

Lili and his co-workers produced clay polypropylene nanocomposites using melt processing technique. They reported that addition of organo-modified MMT in nano composites causes a ceramic like compact char during combustion test and this is an important factor for flame retardancy of polymer/layered silicate composites. The

addition of MMT also increases the decomposition temperature of PP. They reported that the improvement was not only due to the barrier effects of the MMT and also due to the physic-chemical adsorption of volatile degradation products on the silicates [72].

M. Yazdani and his co-workers worked on melt functionalization of PP with methyl esters of itaconic acid. They were found that the percentage of grafting depends on both, monomer and initiator concentrations. Also they found that the moleculer weight of the grafted polymer decreased with increasing percentage of grafting. The degredation of PP was attributed to the well known β-scisson process, induced by the peroxide used as radical initiator. It was concluded that MMI and/or DMI were grafted onto PP as short polymeric chains and that the chain end grafting could take place [56].

M.D Read and his co-worker studied on development of structure in melt blended PP organoclay nanocomposite and they found that number of larger agglomerates was reduced down the length of the extruder, but the degree of fine dispersion (number of layers per stack in a clay tactoid) was approximately constant. This suggest that the final level of dispersion at the smallest scale defined by the number of layer per stack, was reached in the first melting section but was not reduced with additional shear or residence time. On a larger length scale, the number of large agglomerates was reduced with longer residence time and number of mixing sections [73].

M. Modesti and co-worker worked on thermal behavior of compatibilized PP nanocomposite. They found that the presence of organo-clay causes a great increase of the crystanillity because the fillers act as nucleating agents, thus promoting heterogeneous crystallization. They concluded that the nanoclay influences the crystalline domains of the material, because the crystallinty degree increases, while the amorphous region are not influenced by its presence, as the glass transition temperature is not any variation and nanoclays brought an increase of thermal stability in oxidizing atmosphere of PP. Thermal properties and fire behavior of PP nanocoposites are better in presence of maleic anhydride as compatibilizer. They obtained better results for 5 wt % filled materials [18].

C. K. Hong and co-worker studied on effects of PP-g-(maleic anhydride/styrene) compatibilizer on mechanical and rheological properties of PP/clay nanocomposites.

They prepared PP/clay nanocomposites by melt mixing by presence of PP-g-(MA/ST) as a compatibilizer. They found from XRD peaks of plane of (0 0 1) the organo-modified montmorillonite in the nanocomposites were shifted to lower angles by addition of PP-g-(MA/ST), indicating the intercalation capability of PP-g-(MA-ST) in the silicate layers. TEM photographs showed that the organo-modified montmorillonite was intercalated and partly exfoliated in the presence of PP-g-(MA/ST) during melt mixing also they found that the extent of organo-modified montmorillonite intercalation was also dependent on the mixing sequences and addition of PP-g-(MA/ST) with organo-modified montmorillonite improved the thermal stability , tensile and rheological properties of the nanocomposites [74].

Moncada E. and his coworkers worked with monoesters of IA and maleic anhydride (MAH) for grafting on PP. Firstly they were prepared PP/clay nanocomposites by melt mixing PP of different molecular weights with different clays as nanoparticles and by using modified PP grafted with different percentages of IA as compatibilizers. The aim of this study was to investigate the effect of both molecular weight of PP, used as polymer matrix, as well as the degree of grafting of the modified PP on the mechanical and morphological properties of nanocomposites. The degree of clay dispersion in the PP matrix and the mechanical properties of the resulting nanocomposite improved considerably by incorporation of PP-g-IA as a compatibilizer. However, this improvement depended on the grafting extent of the compatibilizer, type of clay and molecular weight of the PP used as matrix.

Moncada E. and coworkers were also used PP grafted maleic anhydride (PP-g-MAH) as compatibilizer. Inferior mechanical properties were obtained for nanocomposites prepared by using this compatibilizer. Results indicated that IA-g-PP was more efficient as compatibilizer for the formation of nanocomposites than commercially available MA-g-PP [9].

3. EXPERIMENTAL PART

3.1. Chemicals Used

3.1.1. Polypropylenes (PP)

Commercial PP samples with different molecular weights and properties used as polymer matrix for the preparation of nanocomposites.

3.1.1.1. Capilene SB56 (Cp)

Impact copolymer was obtained from Carmel olefins. Capilene SB56 is a low melt flow rate impact copolymer intended for pipe extrusion. Capilene SB56 Melt flow index (MFI) =0.35 g/10 min, flexural modulus=1050 MPa.

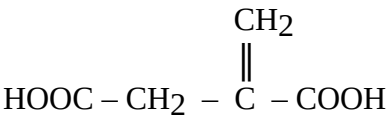
3.1.1.2. Buplen 6531 (Bp)

PP homopolymer was obtained from Lukoil Bulgaria Ltd. 6531 (MFI) =3.0 to 5.0 g/10 min, specific gravity=0.898-0.905 g/cm^3, flexural modulus >1100 MPa.

3.1.1.3. Petoplen MH-418 (MH-418)

Isotactic polypropylene (MH-418) was obtained from PETKIM Petrochemical Co. Its number averaged and weight averaged molecular weights were 53300 g/mol and 565700 g/mol, respectively. Specific gravity=0.905 g/cm^3, MFI=4.0 to 6.0 g/10 min. flexural modulus =1420 MPa.

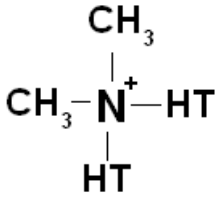
3.1.2. Itaconic acid (IA)



Systematic name, 2-methylene succinic acid, was the product of Fluka A. G. With a 99% purification, was used without any purification procedure. (m.p. = 165- 167 ^{0}C)

3.1.3. Montmorillonite (MMT)

The layered silicate was Nanofil 8 which is an organically modified nanodispersible layered silicate based on a natural bentonite. The surface treatment is a dimethyldi (hydrogenated tallow) alkyl ammonium salt.



Typical properties of Nanofil 8 is:

Product Form	:	Powder
Color	:	Off White
Bulk Density	:	270 g/l
Median Particle Size	:	5 μm
LOI	:	43 %
Moisture Content	:	1,6 %
Modifier Content	:	125 meq/100g clay
Interlayer Spacing	:	3.5 nm

3.1.4. Polymer processing additive (PPA)

Fluorinated polymers based processing aids were supplied by Aksoy Plastics Corp. PP/F 108151 is a masterbatch consisting 5% Dyneon FX 5911 PPA and 95% carrier PP reported usage level 1%, reported benefits are to prevent melt fractures, die build-up, gel formations and surface defects. The PPA Dyneon FX 5911 used as proposed and the resulting rate was 500 ppm in PNC matrix.

3.1.5. Maleic anhydride grafted PP (PP-g-MAH)

It was used as one of the commercial compatibilizers which is a maleic anhydride functionalized polypropylene (PP-g-MAH), containing 1 wt% of maleic anhydride. Acid value is 41 mg KOH/g. Density and viscosity of PP-g-MAH are 0.93 g/cm^3 (at 23 ^{o}C) and 1100 mPa.s, respectively. Also softening point is approximately 161 ^{o}C.

3.1.6. Dibenzoyl peroxide (DBPO)

It was used as the initiator, which is a product of Peroxide Chemie GmbH (München, Germany).

3.1.7. Xylene

It was used as the solvent, which is a product of Merck A.G.,

3.1.8. Isopropyl alcohol

It was used for analytical measurements as the solvent, which is a product of Merck A.G.

3.1.9. Methyl alcohol

It was used for precipitation of reacted samples, obtained from Merck A.G.

3.1.10. Ethyl alcohol

It was used for analytical measurements as the solvent, which is a product of Merck A.G.

3.1.11. Potasium hydroxide (KOH)

It was used for analytical measurements purchased from Merck A.G.

3.1.12. Hydrochloric acid (HCl)

% 37 HCl solution, which is a product of Merck A.G., was used for analytical measurements.

3.1.13. Sodium carbonate ($Na_2CO_3. H_2O$)

It was used for analytical measurements purchased from Merck A.G.

3.1.14. Bromothymol blue

It was used as the indicator for back titration of product samples.

3.1.15. Methylene red

It was used as the indicator for standardizing titration solutions.

3.2. Equipment Used

3.2.1. Magnetic stirrer with heater

It was used for heating and mixing of product sample in xylene solvent for analytical measurement work. This instrument has a maximum mixing rate of 1250 rpm and it can be heated to a maximum temperature of 300°C.

3.2.2. Microwave oven

Beko MD 1585 model MW applicator has the energy outgoing power as 1300 W and MW frequency as 2.45 GHz. All experiments were run 180 W power and 8 min.

3.2.3. Extruder

We used MiniLab extruder to prepare the polymer nanocomposites by melt mixing method. This MiniLab extruder is HAAKE MiniLab Micro Compounder which is ensured from Thermo Electron Company. Counter-rotating twin screw extruder motor power of is 400W, screw speed range is 1-360 rpm, and maximum torque is 5 Nm/screw. Maximum internal temperature of extruder is 350 ^{0}C. Barrel internal value is 3.5 cm^{3} and total volume of cycle capacity is 5.5 cm^{3}.

Figure 3.1: HAAKE MiniLab micro compounder.

3.2.4. Mechanical test device

To obtain mechanical properties of polymer nanocomposites, mechanical tests were made by using Zwick/Roell Z0.5 TH universal testing machine

Grips	: Zwick 8195 1 kN pneumatic grips.
Loadcell	: 500 N
Pre-load	: 1 Mpa
Speed E-modulus	: 20 mm/min.
Test speed	: 50 mm/min.

3.2.5. Melt flow index device

Melt flow index (MFI) is a value which consists of melt flow rate (MFR) and melt volume rate (MVR) values. MFR is the weight of flowed sample in a certain time (g/10 min.) MVR is the volume of flowed sample in a certain time (cm^3/10 min.) under 2.16 kg load. HAAKE Melt Flow MT is used to measure MFR and MVR values of sample. (Figure 3.2)

Figure 3.2: "Melt Flow Index" MFI device.

3.2.6 XRD analysis

X-ray diffraction analysis (XRD) is a nondestructive method for the structure analysis of crystals. The sample is irradiated with monochromatic X-ray light and stray radiation recorded. An important field of application is the identification of crystalline fractions in samples. Measurement were made by using Shimadzu XRD 6000 Model and used wave length is λ=1.5405 Å.

3.3. Experimental Procedure

3.3.1. Preparation and purification of grafted polypropylene

All grafting reactions were carried out at 180 W at 8 minute microwave input power. Polypropylene was dissolved in xylene then was mixed together with DBPO and monomer in a certain proportion. In all experiments, the weight ratio of xylene to polypropylene is always 10/1.

A little amount of ethanol was added to mixture in order to dissolve monomers better in the reaction solution. The mixtures are put into the microwave applicator, irradiated for the expected time, and then removed. The samples were purified by dissolving in xylene and precipitating in methyl alcohol two times to be sure of the removal of un-reacted monomers, and then dried in vacuum at 60 ^{0}C. The products were used to determine the grafting degree (GD).

Graft copolymers which were used as compatibilizers were obtained by grafting PP with IA.

3.3.2. Preparation of polymer nanocomposites (PNC)

The organoclay Nanofil 8 is dried in air circulating oven at 110 ^{o}C for 4 hours prior to compounding. In this experiment two different levels of filler (3 and 5 %) and compatibilizers (10 and 15 %) were also used. Polypropylene grafted itaconic acid (PP-g-IA) and polypropylene grafted maleic anhydride (PP-g-MAH) have been used as compatibilizer. Polymer processing aids containing experiments were prepared with Dyneon FX 5911 PPA masterbatch. It was used as 1% in PNC matrix.

Single step melt mixing method was used to prepare PNCs for all samples. For this purpose, optimization conditions were determined at different temperatures, cycling time and rotational speed for single step melt mixing in Mini Lab twin screw

extruder. During the optimization, the important criteria were to prevent the degredated polymer structure and shark skin effect, and to provide the homogeneity of polymer nanocomposites.

Several extruder temperatures were tried between 200-235 °C to determine an optimum temperature. It was shown that at high set temperatures, polymer nanocomposites underwent to degredation, while at low temperatures homogeneous polymer nanocomposites could not be achieved. The suitable extruder temperatures are 216 °C kept constant for all PP samples. For determining the rotational screw speed, the experiments were done within the range of 80-150 rpm screw speeds for 216 °C and 3 min. cycling time. The suitable screw speed for the processing of PNC was determined as 100 rpm for all PP samples.

A cycling time was optimized for the process to provide a homogeneous dispersion of organoclay in matrix and prevent degradation of PNC. In addition, it was important to choose a short cycling time to increase out-put of the process. In the pre-works, to determine the influence of the cycling time on homogeneity, surface appearance and out-put, the experiments were done within the range of 2-7 min.

Consequently, optimization conditions were determined as 216 °C set temperature for all polypropylene samples, and screw speed for all samples are 100 rpm. Cycling time for all PP samples was taken as 2 min.

3.4. Tests and Analyses

3.4.1. Measurement of grafting degree by analytical method

A small amount (0.2-0.4g) of grafted polyolefin was dissolved and heated to 110 °C with reflux in 100 mL xylene for 30 min, followed by cooling to 60 °C. 30 milliliters 0.005 N potassium hydroxide (KOH)/ethanol solution was added, and the mixture was heated under reflux for 15 min. The alkali concentration was determined by acid titration using 0.005 N hydro-chloride (HCl)/isopropanol solution. The indicator was 0.1% bromothymol blue/ethanol solution. A blank was carried out by the same method.

Grafting degree is expressed by the following equation:

$$GD = \frac{N(V_0 - V) \times MW}{n \times W \times 1000} X100\%$$

Where N is the concentration of HCl/isopropanol (mol/L), W is quantity of sample (g), V is the volume of HCl/isopropanol used by titration, V_0 is the volume of HCl/ isopropanol used in a blank assay, MW is the molecular weight of monomer and n is the number of carboxyl group on the monomer.

3.4.2. Mechanical test

From the measured stress and strain values, elastic modulus, maximum stress, young modulus, and stress at break were calculated from the average of at least 4 specimens tested. For the comparing of the mechanical improvements on the PNCs, mechanical properties of original PP's were measured and calculated. 50 mm/min. test speed and 1 MPa Pre-Load were used for the measurements.

3.4.3. Melt flow index test

Determination of the melt flow rate, MFR, measurements followed DIN 1133 at 230 ^{0}C. The effects of compatibilizer on the melt flow properties of the PNCs were determined by calculating the normalized values of MFR (n-MFR) and MVR (n-MVR) [75].

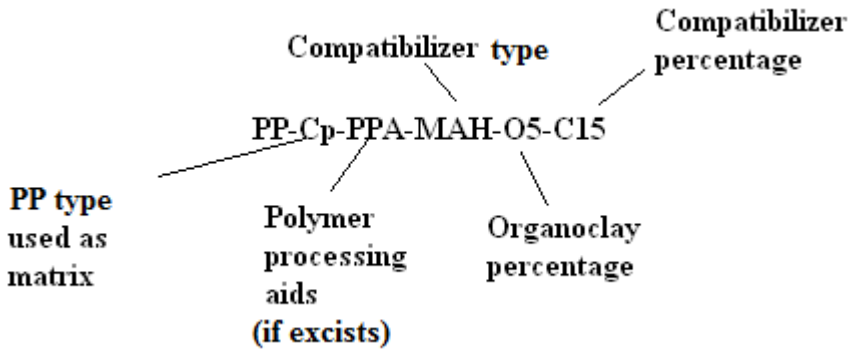
For this purpose, MFR and MVR measurement techniques were also applied to control units. The corresponding control units contained matrix polyolefin and the different percentages of compatibilizers. The normalized MFR and MVR values calculated by equation given as follows:

$$\text{Normalized melt flow rate} = \frac{\text{Melt flow rate of nanocomposite}}{\text{Melt flow rate of corresponding control unit}}$$

4. RESULTS AND DISCUSSION

In this work, polymer nanocomposites (PNC) which contain compatibilizer, polymer processing aid (PPA) and organoclay in polypropylene (PP) matrix were synthesized. For preparing PPNCs, organically modified clay was mixed with PP and compatibilizer in counter rotating twin screw extruder by a single step method. Pre-works were done in order to determine the optimum extrusion conditions in minilab extruder of samples. The effects of PPA on the properties of PPNC samples were also investigated.

Each sample description refers to a specific composition involving the components used in the preparation of the samples.



The compatibilizer can be generally used in polyolefin NC preparation to overcome the poor adhesion between a nonpolar PP and polar organoclay. In this work, two kinds of compatibilizers were used for this purpose: PP grafted maleic anhydride (PP-g-MAH) that was commercial and PP grafted itaconic acid (PP-g-IA) which was prepared in the laboratory. The percentage of compatibilizer was taken three times of the percentage of organoclay in PPNC. The preparation procedure of PP-g-IA compatibilizers was given in Section 3.3.1. and their grafting degrees were also tabulated (Table 6.1).

4.1 The Optimization of compounding Conditions

Optimization experiments for PPNC compounding were done at different temperatures, cycling times and rotational speeds to determine optimum conditions for single step melt-mixing method in MiniLab extruder. The important criteria chosen for determining of the optimization conditions were to investigate the degradation and shark skin effect. High temperatures and long cycling times cause to degradation while high rotational speeds cause to shark skin appearance. Several processing temperatures were tried between 200-235 ^{0}C to determine an optimum temperature to provide the homogeneity of PPNCs. One of trial was done 235 ^{0}C and we observed that samples colors were turn to brown color and we understood that at this temperature is not suitable for working extruder. We decreased temperature of extruder 1 ^{0}C in every trial. Also when we did trial at 200 ^{0}C , observed that not good dispersion and also shark skin effect on samples. It was shown that at high set temperatures, polymer nanocomposites underwent to degradation, while at low temperatures homogeneous polymer nanocomposites could not be achieved. For determining the rotational screw speed, the experiments were done within the range of 80-150 rpm screw speeds. When started to work 80 rpm screw speed, dispersion of clay in PP matrix was not good and PP ribbon was bold and appeared shark skin on samples. If we work 150 rpm, PP nanocomposites ribbons were so thin which were not good as we required. The suitable screw speed for the processing of all PPNC was determined as 100 rpm, because this was the limit speeds of for shark skin effect. A cycling time was optimized for the process to provide a homogeneous dispersion of organoclay in PO matrix and prevent the degradation of PPNC. For higher values than this value, the degradation occurred. In addition, it was important to choose a short cycling time to increase out-put of the process. In the pre-works, to determine the influence of the cycling time on homogeneity, surface appearance and out-put, the experiments were done within the range of 2-7 min. cycling time.

Consequently, optimization conditions were determined as 216 ^{0}C mixing temperature, 100 rpm screw speed with 2 min. cycling time for all PP samples.

4.2. Synthesis Conditions for Characterization of Samples

The 24 nanocomposite samples were prepared by using 3 different types of PPs (Capilene SB56, Buplen 6531 and MH-418), 1 type of organoclays with two levels, 1 type and a single percentage polymer processing aid and 2 type of compatibilizer. The percentage of compatibilizer was taken three times of the percentage of organoclay in PPNC. The experimental techniques for the preparation and characterization of compatibilizers were explained in Section 3.3.1. The grafting degrees (GD) of the IA in the compatibilizer were given in Table A.1. Initiator concentration [DBPO] were arranged to keep nearly the same GD for different PP types. The methods used for the preparation of PPNC samples were given in Section 3.3.2. The PPNCs contained two different levels (3-5-wt %) of organoclay and two different compatibilizer (PP-g-MAH and PP-g-IA) whose percentage was taken three times of the percentage of organoclay in PPNC. The fluoropolymer PPA (Dyneon FX 5911) was used as 500 ppm in PP matrix.

4.3. XRD Analysis Results

The results of the XRD measurements of samples are given in Table A.3., A.4., and A.5. From the diffraction values, the distance between clay layers (d_{001}) of original clay Nanofil 8 was calculated from the Bragg equation ($n\lambda=2d \sin \theta$) as 12.9 Å.

In Cp containing PPNC samples (Table A.4.), 5% organoclay addition (with 15% compatibilizer) is really effective to increase the interlayer spacing than that of 3% organoclay (with 10% compatibilizer) for both type of compatibilizer. On the other hand, PPA addition is more effective in PP-g-MAH containing samples that of PP-g-IA. However the sample no. PP-Cp-PPA-IA-O5-C15 exhibits the highest interlayer spacing in this series.

In Bp containing PPNC samples (Table A.5.), the nanoadditive percentage and PPA addition were no distinct effect on the increasing of the interlayer spacing.

In MH-418 containing PPNC samples (Table A.6.), although, generally, the effects of the nanoadditive percentage were not prominent, the addition of PPA to the 5% organoclay with PP-g-MAH containing PPNC samples showed a big layer distance.

4.4. Mechanical Characterization Results

4.4.1. Tensile results

Tensile test were applied to polymer nanocomposite samples by using universal testing machine (Section 3.4.2.). Young's modulus, maximum strength, strength of break and percent elongation to break of PPNC samples were obtained at least from the 4 samples averaged. The calculated results were given in Table A.6, A.7, and A.8. According to these values, mechanical properties results for the samples with and without PPA containing PPNCs showed different tendencies depending on the PP type. The young modulus results were consistent with the XRD results.

In Cp containing PPNC samples (Table A.6.), the measured Young modulus values of samples 5% organoclay addition (with 15% compatibilizer) is effective than that of 3% organoclay (with 10% compatibilizer) for both type of compatibilizer. PPA addition is more effective in PP-g-MAH containing samples that that of PP-g-IA. However, the sample no. PP-Cp-PPA-IA-O5-C15 exhibits the highest Young modulus value in this series.

In Bp containing PPNC samples (Table A.7.), the nanoadditive percentage and PPA addition were no distinct effect on the mechanical properties. The best results were taken from the sample PP-Bp-PPA-IA-O5-C15.

In MH-418 containing PPNC samples (Table A.8.), although, the effects of the nanoadditive percentage were not clear, generally. PP-g-MAH containing PPNC samples showed the best mechanical properties in this series. The biggest interlayer spacing posses sample showed the highest Young modulus value.

Generally, Young modulus of samples increases with increasing of their maximum strength and strength of break, but lowering the percent elongation.

4.5. Melt Flow Index Results

The influences to the processability of different types of compatibilizers with varying percentages to the polymer nanocomposites were observed by melt index measurements. MFR and MVR values of PPNC samples were given in Table A.9.

MFI is a pressure-imposed, capillary flow experiment and was used to study the relationship between low strain rate shear flow properties and clay structure in nanocomposites and the interaction between clay and matrix of PPNC samples.

In the interaction between clay and bulk PP, the "control" polymer matrix effect should be excluded to investigate the effect of compatibilizers and clay percentage on PPNC. For this purpose, normalized MFI (n-MFI) values were calculated and then the results were compared (Section 3.4.3.). The corresponding control units contained matrix polyolefin and the different percentages of compatibilizers. MFI measurements involved MFR and MVR measurement. MFR and MVR measurements were also applied to the control units.

Control units were prepared in the extruder, with 10% and 15% w/w compatibilizer without containing any organoclay.

The normalized values of with and without PPA containing samples showed different tendencies depending on the PP type. On the other hand, the normalized MFR values of PPNC samples close to 1.0 means that there is no appreciable effects of nanoadditive on processing, generally.

5. CONCLUSION

Polymer nanocomposite (PNC) samples containing polypropylenes (PP) were prepared. The PPNC samples were prepared by using different types of PP and the compatibilizer with a commercial organoclay. The polymer processing aid (PPA) was added to investigate its effects to the properties of PPNC samples.

The PNC samples were prepared in MiniLab twin screw extruder at 216 ^{0}C mixing temperature, 100 rpm screw speed with 2 min. cycling time. Two different levels (3 and 5%) of organoclay nanoadditive were used. PP-g-MAH and PP-g-IA compatibilizers were used at amounts of three times of organoclay content. The fluoropolymer PPA was used as 500 ppm in PPNC matrix.

The prepared 24 samples were investigated structural by XRD, mechanical by universal testing machine and processability by using MFR measurements points of view.

The distances between clay layers (d_{001}) of the samples show the better results for 5 % organoclay loaded samples. In between the samples, Sample No. PP-Cp-PPA-IA-O5-C15 and PP-MH-418-PPA-MAH-O5-C15 showed the better results. In Bp containing samples, there is no sample like these ones.

Mechanical properties of the PPNC samples were also investigated and the same tendencies were found in E_{mod} values. E_{mod} values of Sample No. PP-Cp-PPA-IA-O5-C15 and PP-MH-418-PPA-MAH-O5-C15 showed the best results.

Processabilities of PPNC samples were measured by MFR measurement technique and n-MFR values were calculated. n- MFR values of PPNC samples close to 1.0 means that there is no appreciable effects of nanoadditive on processing, generally.

It was found that the resulted samples were intercalated to exfoliated depending on its composition.

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APPENDICES

Table A.1: Grafting degree (GD) of PP samples with IA.
(MW power = 180 W, t= 8 min)

Monomer	Polypropylene	DBPO % (g/100 g PP)	GD, % (g/100 g PP)
IA	CAPILENE SB56	1.1	0.30
IA	BUPLEN 6531	1.0	0.31
IA	MH-418	1.0	0.32

Table A.2: Sample descriptions and contents of samples, which contain PP.

Sample Description	**Compatiblizer**	**Organoclay %**	**Compatibilizer %**
PP-Cp-O0-C0	---	0	0
PP-Cp-MAH-O0-C10	PP-g-MAH	0	10
PP-Cp-MAH-O0-C15	PP-g-MAH	0	15
PP-Cp-MAH-O3-C10	PP-g-MAH	3	10
PP-Cp-MAH-O5-C15	PP-g-MAH	5	15
PP-Cp-PPA-MAH-O0-C10	PP-g-MAH	0	10
PP-Cp-PPA-MAH-O0-C15	PP-g-MAH	0	15
PP-Cp-PPA-MAH-O3-C10	PP-g-MAH	3	15
PP-Cp-PPA-MAH-O5-C15	PP-g-MAH	5	15
PP-Cp-IA-O0-C10	PP-g-IA	0	10
PP-Cp-IA-O0-C15	PP-g-IA	0	15
PP-Cp-IA-O3-C10	PP-g-IA	3	10
PP-Cp-IA-O5-C15	PP-g-IA	5	15
PP-Cp-PPA-IA-O0-C10	PP-g-IA	0	10
PP-Cp-PPA-IA-O0-C15	PP-g-IA	0	15
PP-Cp-PPA-IA-O3-C10	PP-g-IA	3	15
PP-Cp-PPA-IA-O5-C15	PP-g-IA	5	15
PP-Bp-O0-C0	---	0	0

Table A.2 (contd.): Sample descriptions and contents of samples, which contain PP.

Sample Description	Compatiblizer	Organoclay %	Compatibilizer %
PP-Bp-MAH-O0-C10	PP-g-MAH	0	10
PP-Bp-MAH-O0-C15	PP-g-MAH	0	15
PP-Bp-MAH-O3-C10	PP-g-MAH	3	10
PP-Bp-MAH-O5-C15	PP-g-MAH	5	15
PP-Bp-PPA-MAH-O0-C10	PP-g-MAH	0	10
PP-Bp-PPA-MAH-O0-C15	PP-g-MAH	0	15
PP-Bp-PPA-MAH-O3-C10	PP-g-MAH	3	10
PP-Bp-PPA-MAH-O5-C15	PP-g-MAH	5	15
PP-Bp-IA-O0-C10	PP-g-IA	0	10
PP-Bp-IA-O0-C15	PP-g-IA	0	15
PP-Bp-IA-O3-C10	PP-g-IA	3	10
PP-Bp-IA-O5-C15	PP-g-IA	5	15
PP-Bp-PPA-IA-O0-C10	PP-g-IA	0	10
PP-Bp-PPA-IA-O0-C15	PP-g-IA	0	15
PP-Bp-PPA-IA-O3-C10	PP-g-IA	3	10
PP-Bp-PPA-IA-O5-C15	PP-g-IA	5	15
PP-MH-418-O0-C0	---	0	0
PP-MH-418-MAH-O0-C10	PP-g-MAH	0	10
PP-MH-418-MAH-O0-C15	PP-g-MAH	0	15
PP-MH-418-MAH-O3-C10	PP-g-MAH	3	10
PP-MH-418-MAH-O5-C15	PP-g-MAH	5	15
PP-MH-418-PPA-MAH-O0-C10	PP-g-MAH	0	10
PP-MH-418-PPA-MAH-O0-C15	PP-g-MAH	0	15
PP-MH-418-PPA-MAH-O3-C10	PP-g-MAH	3	10
PP-MH-418-PPA-MAH-O5-C15	PP-g-MAH	5	15
PP-MH-418-IA-O0-C10	PP-g-IA	0	10
PP-MH-418-IA-O0-C15	PP-g-IA	0	15
PP-MH-418-IA-O3-C10	PP-g-IA	3	10
PP-MH-418-IA-O5-C15	PP-g-IA	5	15
PP-MH-418-PPA-IA-O0-C10	PP-g-IA	0	10
PP-MH-418-PPA-IA-O0-C15	PP-g-IA	0	15
PP-MH-418-PPA-IA-O3-C10	PP-g-IA	3	10
PP-MH-418-PPA-IA-O5-C15	PP-g-IA	5	15

Table A.3: XRD results of CAPILENE SB56 PP containing samples.

Sample Description	2Θ	d_{001} (Å)
Nanofil 8	6.86	12.9
PP-Cp-MAH-O3-C10	3.18	27.8
PP-Cp-MAH-O5-C15	3.43	25.7
PP-Cp-PPA-MAH-O3-C10	2.90	30.4
PP-Cp-PPA-MAH-O5-C15	2.75	32.1
PP-Cp-IA-O3-C10	3.85	22.9
PP-Cp-IA-O5-C15	2.28	38.7
PP-Cp-PPA-IA-O3-C10	3.18	27.8
PP-Cp-PPA-IA-O5-C15	2.21	39.9

Table A.4: XRD results of BUPLENE 6531 PP containing samples.

Sample Description	2Θ	d_{001} (Å)
Nanofil 8	6.86	12.9
PP-Bp-MAH-O3-C10	3.15	28.0
PP-Bp-MAH-O5-C15	3.27	27.0
PP-Bp-PPA-MAH-O3-C10	3.06	28.9
PP-Bp-PPA-MAH-O5-C15	3.15	28.0
PP-Bp-IA-O3-C10	3.34	26.4
PP-Bp-IA-O5-C15	3.31	26.7
PP-Bp-PPA-IA-O3-C10	3.24	27.3
PP-Bp-PPA-IA-O5-C15	3.14	28.1

Table A.5: XRD results of MH-418 PP containing samples.

Sample Description	2Θ	d_{001} (Å)
Nanofil 8	6.86	12.9
PP-MH-418-MAH-O3-C10	3.24	27.3
PP-MH-418-MAH-O5-C15	3.16	27.9
PP-MH-418-PPA-MAH-O3-C10	3.15	28.0
PP-MH-418-PPA-MAH-O5-C15	2.22	39.8
PP-MH-418-IA-O3-C10	3.39	26.0
PP-MH-418-IA-O5-C15	2.98	29.6
PP-MH-418-PPA-IA-O3-C10	3.21	27.5
PP-MH-418-PPA-IA-O5-C15	2.96	29.8

Table A.6: Mechanical measurements of CAPILENE SB56 PP containing samples.

Sample Description	E_{mod}(N/mm^2)	σ M(N/mm^2)	σ B(N/mm^2)	ε B(%)
PP-Cp-O0-C0	1080	42.7	42.7	926
PP-Cp-MAH-O3-C10	1130	34.5	15.0	350
PP-Cp-MAH-O5-C15	1100	30.0	18.0	443
PP-Cp-PPA-MAH-O3-C10	1230	32.0	31.0	910
PP-Cp-PPA-MAH-O5-C15	1260	33.1	28.0	158
PP-Cp-IA-O3-C10	980	39.5	38.0	890
PP-Cp-IA-O5-C15	1300	38.4	38.2	850
PP-Cp-PPA-IA-O3-C10	1080	30.5	29.6	785
PP-Cp-PPA-IA-O5-C15	1380	29.0	29.0	755

Table A.7: Mechanical measurements of BUPLENE 6531 PP containing samples.

Sample Description	E_{mod}(N/mm^2)	σ M(N/mm^2)	σ B(N/mm^2)	ε B(%)
PP-Bp-O0-C0	925	33.5	22.0	750
PP-Bp-MAH-O3-C10	1085	34.5	31.2	385
PP-Bp-MAH-O5-C15	1180	34.7	20.0	310
PP-Bp-PPA-MAH-O3-C10	1115	36.5	22.0	300
PP-Bp-PPA-MAH-O5-C15	1220	33.7	22.0	345
PP-Bp-IA-O3-C10	1120	31.5	12.0	130
PP-Bp-IA-O5-C15	1210	34.3	20.0	310
PP-Bp-PPA-IA-O3-C10	1340	35.0	15.0	210
PP-Bp-PPA-IA-O5-C15	1300	35.8	21.0	325

Table A.8: Mechanical measurements of MH-418 PP containing samples.

Sample Description	E_{mod}(N/mm^2)	σ M(N/mm^2)	σ B(N/mm^2)	ε B(%)
PP-MH-418-O0-C0	1120	33.0	19.0	345
PP-MH-418-MAH-O3-C10	1320	33.0	29.0	290
PP-MH-418-MAH-O5-C15	1300	33.5	24.5	115
PP-MH-418-PPA-MAH-O3-C10	1390	34.0	16.0	315
PP-MH-418-PPA-MAH-O5-C15	1450	34.5	31.6	175
PP-MH-418-IA-O3-C10	1130	28.5	11.0	140
PP-MH-418-IA-O5-C15	1280	32.2	16.0	155
PP-MH-418-PPA-IA-O3-C10	1240	33.0	13.5	210
PP-MH-418-PPA-IA-O5-C15	1300	35.2	18.5	280

Table A.9: MFR, MVR, n-MFR and n-MVR values of PP samples.

Sample Description	MFR(g/10min.)	n-MFR	MVR(cm^3/10min.)	n-MVR
PP-Cp-O0-C0	0.47	----------	0.53	----------
PP-Cp-MAH-O0-C10	0.97	----------	1.06	----------
PP-Cp-MAH-O0-C15	1.15	----------	1.27	----------
PP-Cp-MAH-O3-C10	0.94	0.97	0.97	0.92
PP-Cp-MAH-O5-C15	0.96	0.83	1.00	0.79
PP-Cp-PPA-MAH-O0-C10	0.89	----------	1.02	----------
PP-Cp-PPA-MAH-O0-C15	1.23	----------	1.34	----------
PP-Cp-PPA-MAH-O3-C10	1.30	1.47	1.49	1.45
PP-Cp-PPA-MAH-O5-C15	1.00	0.81	1.08	0.80
PP-Cp-IA-O0-C10	0.70	----------	0.79	----------
PP-Cp-IA-O0-C15	0.72	----------	0.84	----------
PP-Cp-IA-O3-C10	0.80	1.14	0.88	1.11
PP-Cp-IA-O5-C15	0.78	1.08	0.83	0.98
PP-Cp-PPA-IA-O0-C10	0.76	----------	0.83	----------
PP-Cp-PPA-IA-O0-C15	0.80	----------	0.79	----------
PP-Cp-PPA-IA-O3-C10	0.72	0.95	0.78	0.94
PP-Cp-PPA-IA-O5-C15	0.71	0.89	0.76	0.96
PP-Bp-O0-C0	3.94	----------	5.78	----------
PP-Bp-MAH-O0-C10	7.28	----------	6.60	----------
PP-Bp-MAH-O0-C15	8.50	----------	8.82	----------
PP-Bp-MAH-O3-C10	6.98	0.96	11.05	1.67
PP-Bp-MAH-O5-C15	9.12	1.07	10.51	1.19
PP-Bp-PPA-MAH-O0-C10	8.52	----------	9.13	----------
PP-Bp-PPA-MAH-O0-C15	8.61	----------	8.12	----------
PP-Bp-PPA-MAH-O3-C10	7.07	0.83	7.11	0.78
PP-Bp-PPA-MAH-O5-C15	8.25	0.96	7.71	0.95
PP-Bp-IA-O0-C10	8.05	----------	5.57	----------
PP-Bp-IA-O0-C15	6.50	----------	6.89	----------
PP-Bp-IA-O3-C10	5.64	0.70	5.43	0.97
PP-Bp-IA-O5-C15	5.55	0.85	6.02	0.87
PP-Bp-PPA-IA-O0-C10	7.92	----------	7.03	----------
PP-Bp-PPA-IA-O0-C15	9.40	----------	9.14	----------

Table A.9 (contd.): MFR, MVR, n-MFR and n-MVR values of PP samples.

Sample Description	MFR(g/10min.)	n-MFR	MVR(cm^3/10min.)	n-MVR
PP-Bp-PPA-IA-O3-C10	5.66	0.71	5.42	0.97
PP-Bp-PPA-IA-O5-C15	5.93	0.63	5.62	0.62
PP-MH-418-O0-C0	4.67	----------	5.11	----------
PP-MH-418-MAH-O0-C10	6.16	----------	5.90	----------
PP-MH-418-MAH-O0-C15	8.47	----------	8.53	----------
PP-MH-418-MAH-O3-C10	7.48	0.96	7.65	1.30
PP-MH-418-MAH-O5-C15	6.50	0.74	8.08	0.95
PP-MH-418-PPA-MAH-O0-C10	9.74	----------	12.81	----------
PP-MH-418-PPA-MAH-O0-C15	8.11	----------	12.50	----------
PP-MH-418-PPA-MAH-O3-C10	9.49	0.97	8.70	0.68
PP-MH-418-PPA-MAH-O5-C15	8.92	1.10	9.74	0.78
PP-MH-418-IA-O0-C10	9.54	----------	1.04	----------
PP-MH-418-IA-O0-C15	7.10	----------	6.90	----------
PP-MH-418-IA-O3-C10	6.97	0.73	7.85	0.78
PP-MH-418-IA-O5-C15	6.25	0.88	7.60	1.10
PP-MH-418-PPA-IA-O0-C10	7.80	----------	7.86	----------
PP-MH-418-PPA-IA-O0-C15	7.15	----------	8.07	----------
PP-MH-418-PPA-IA-O3-C10	6.05	0.78	6.44	0.82
PP-MH-418-PPA-IA-O5-C15	6.70	0.94	6.95	0.86

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He was born 1974 in Istanbul. He graduated from Vehbi Koc High School in 1993 and attempted to Chemical Engineering Department of Ege university in 1994.In 2000 he graduated from university. He worked AK-AL Textile Company as dye-house department responsible between 2000 and 2010. He was accepted as a master student to Istanbul Technical University, Polymer Science and Technology interdisciplinary graduate programme and he is still completing his master education.