

## 4

# Influence of Filler Surface Modification on the Properties of PP Composites

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### 4.1

#### Introduction

Functionalization of polypropylene, nucleating effect of fillers on polypropylene crystallization, adding nucleating agents to obtain  $\beta$ -crystals in PP, modification of fillers by silane coupling agents, grafting with polypropylene, and coating by fatty acids are the methods to disperse fillers in polypropylene, to enhance the interfacial bonding and mechanical properties of polypropylene matrix composites. In this chapter, the fillers have been grouped as silica, glass, silicates, magnesium hydroxide and eggshell, cellulose and carbon, and their surface modification techniques have been reported. The effects of the surface modification of fillers on the properties of composite materials having polypropylene as the matrix are explained.

### 4.2

#### Silica Modification

Silica particles are modified by different methods for better dispersion, interfacial adhesion, and mechanical properties in composites. Table 4.1 shows the coupling agents and compatibilizers used for PP–silica composites and their effects on their properties. Silica particles were used as fillers [1–3] and surface modifiers for glass fibers (GFs) [4] in polypropylene matrix composites. Graphene oxide [1], polyurethane (PU) elastomer [2], foaming agents [3], and dimethyl chlorosilane were the surface modifiers used for silica.

Since each modification method was very specific and it had different effects on the properties of the PP–silica composites, they are reported in detail below.

Graphene oxide can be coated on silica particles. Luo *et al.* [2] synthesized novel core–shell structured hybrid sub-microparticles of graphene oxide–encapsulated silica (GO-SiO<sub>2</sub>). GO-SiO<sub>2</sub> was uniformly dispersed in maleated polypropylene (PP-*g*-Ma). The composites had enhanced interfacial adhesion and improved mechanical properties.

**Table 4.1** Effects of surface modifiers and compatibilizers on the properties of PP–silica composites.

Silica type	Surface modifier	Compatibilizer	Property change	References
Submicron silica	Graphene oxide	PP- <i>g</i> -Ma	Enhanced adhesion Improved mechanical properties	[2]
Nano silica	Polyurethane elastomer	PP- <i>g</i> -NH <sub>2</sub>	Higher impact strength	[1]
Nano silica	Poly( <i>p</i> -vinylphenyl-sulfonylhydrazide)	—	Higher impact strength	[3]
	Poly( <i>p</i> -vinylphenyl-sulfonylhydrazide- <i>co</i> -butyl acrylate)		Better foaming	
Nano silica	Dimethylchlorosilane	PP- <i>g</i> -Ma	Higher interfacial Shear strength	[4]

PU elastomer was used to bind the PP matrix and silica [1]. Chen *et al.* produced nano-SiO<sub>2</sub>/polypropylene (PP) composites by *in situ* reactive processing. The nanoparticles were covalently bonded to the matrix polymer via PU elastomer and PP-*g*-NH<sub>2</sub>. Hexamethylenediamine (HMDA) and PP-*g*-Ma were reacted to form PP-*g*-NH<sub>2</sub>. A synergetic toughening effect was observed by a rubber-type grafting polymer (i.e., PU) and interfacial reactive compatibilization with PP-*g*-NH<sub>2</sub>, for the PP nanocomposites. Very low concentrations of nano-SiO<sub>2</sub> (1.5–2.5 vol%) and PU (<4 vol%) were sufficient to greatly increase notched impact strength of PP and to slightly increase the tensile properties of the nanocomposites [2].

Nanoparticles of silica coated with foaming agents can be used to prevent agglomeration of silica in polymer melt [3]. Poly(*p*-vinylphenylsulfonylhydrazide) and poly(*p*-vinylphenylsulfonylhydrazide-*co*-butyl acrylate) were grafted onto nanosilica by Cai *et al.* [3]. Nanosilica, nanosilica grafted with poly(*p*-vinylphenylsulfonylhydrazide) and nanosilica grafted with poly(*p*-vinylphenylsulfonylhydrazide-*co*-butyl acrylate) were mixed separately with polypropylene and test samples were prepared by injection molding. The polymeric foaming agent containing soft segments (i.e., poly(*p*-vinylphenylsulfonylhydrazide-*co*-butyl acrylate)) grafted onto the surface of nano-SiO<sub>2</sub> induced localized bubble-stretching effect, pulling apart agglomerates of nanoparticles during melt blending with polypropylene. Compared to the composites containing rigid macromolecular foaming agent, grafted nano-SiO<sub>2</sub> (i.e., poly(*p*-vinylphenylsulfonylhydrazide)-grafted nano-SiO<sub>2</sub>/PP), the flexible macromolecular foaming agent (i.e., poly(*p*-vinylphenylsulfonylhydrazide-*co*-butyl acrylate)-grafted nano-SiO<sub>2</sub>/PP) shows much greater increment in notched impact strength without expense of lowering the tensile strength. This is due to increase in the ductility of the interlayer by the poly(butyl acrylate) units in the grafted copolymer.

Nano silica can be used to increase the fiber/matrix adhesion in glass fiber–PP composites. Pedrazzoli and Pegoretti [4] evaluated fiber–matrix interfacial

shear strength (IFSS) by the single-fiber fragmentation tests on polypropylene–glass fiber microcomposites filled with various types and amounts of silica nanoparticles. In particular, both non-functionalized and dimethyldichlorosilane-functionalized silica nanoparticles were added up to a weight content of 7%. They investigated the effect of various amounts of maleic anhydride (MA)–modified polypropylene (PP-*g*-Ma) on the fiber/matrix adhesion by including some selected formulations containing both PP-*g*-Ma and silica nanoparticles. IFSS, elastic modulus, and creep stability of the composites were found to remarkably increase with respect to the case of neat polypropylene matrix. The observed effect was explained by considering that silica nanoparticles increased the work of adhesion of polypropylene with respect to glass, as proven by contact angle measurements in different liquids.

### 4.3 Glass

Glass fibers and glass beads were treated with coupling agents and compatibilizers and nucleating agents were used in preparation of the PP–glass composites [5–8]. Modification methods and their effects are summarized in Table 4.2. Since the modification methods were very specific and had different effects on the

**Table 4.2** Effects of surface modifiers and compatibilizers on the properties of PP–glass composites.

Glass type	Surface modifier	Compatibilizer	Property change	References
Short glass fiber	3-(Aminopropyl) triethoxy silane	PP- <i>g</i> -Ma (Adipic acid, disodium phthalate, nucleator)	Tensile Impact Flexural strength Crystallinity increased	[5]
Glass fiber	<i>In situ</i> polymerization of PP on the fibers	—	Strength Toughness Adhesion increase	[6]
Glass bead	Encapsulated with poly(styrene- <i>b</i> -ethylene- <i>co</i> -butylene- <i>b</i> -styrene) Poly(styrene- <i>b</i> -ethylene- <i>co</i> -butylene- <i>b</i> -styrene) copolymer grafted with maleic anhydride	—	Increased interfacial adhesion Change in flow properties	[7]
Glass fiber	Nano zinc oxide treated with KA550 coupling agent	—	Crystallization temperature Crystallization rate Tensile strength Toughness increased	[8]

properties of the PP–glass composites, they are reported in detail below. Silane coupling agents [5], grafting PP on fibers [6], encapsulating with MA grafted copolymers [7], and KA550 coupling agent–treated nano zinc oxide [8] were used in surface modification of glass fibers.

Coupling agents and nucleators can be used to improve the properties of glass fiber–PP composites. Xie *et al.* [5] investigated the enhancement of tensile strength, impact strength, and flexural strength of polypropylene/short glass fiber composites by treating the glass fibers with coupling agent, mixing with maleated polypropylene (PP-*g*-Ma) for compatibilization and adhesion, and with nucleating agent for improvement of polypropylene crystallization. Alkyl trimethoxy silane (WD-10),  $\gamma$ -methacryloxypropyl trimethoxysilane (WD-70), and *N*-( $\beta$ -aminoethyl)- $\gamma$ -aminopropyl trimethoxysilane (WD-52) were used as coupling agents and adipic acid and disodium phthalate were used as nucleating agents to increase the crystallinity of PP. They showed that both the silane coupling agent and PP-*g*-Ma enhance tensile strength, impact strength, and flexural strength.

Glass fibers with grown PP chains in their surface can be used to enhance the interfacial properties of glass fiber–PP composites. Etcheverry and Barbosa [6] proposed a new modification method based on *in situ* polymerization of PP onto GFs. This method involved the modification of fibers with an aluminum alkyl and hydroxy- $\alpha$ -olefin and PP chains were grown using direct metallocenic copolymerization. The adhesion improvements were further proved by the fragmentation test, as well as by measurement of the mechanical properties. The strength and toughness increases three times and the interfacial strength duplicates in PP–GF composites prepared with *in situ* polymerized fibers.

Glass beads coated with elastomers behaved neither as elastomers nor rigid particles in molten polypropylene [7]. Balkan and Ezdesir [7] investigated rheological behaviors of polypropylene/glass bead (PP/GB) and polypropylene/wollastonite (PP/W) melts modified with thermoplastic elastomers, poly(styrene-*b*-ethylene-*co*-butylene-*b*-styrene) copolymer (SEBS), and the corresponding block copolymer grafted with MA (SEBS-*g*-Ma). Core–shell microstructure developed with strong interfacial adhesion by adding SEBS-*g*-Ma elastomer and the filler particles encapsulated with the thick SEBS-*g*-Ma elastomer interlayer (i.e., core–shell particles) acted neither like big elastomer particles nor like individual rigid particles in melt-state.

The flowability of glass fiber and PP melts can be improved by adding nano zinc oxide treated with KA550 [8]. Cui *et al.* [8] introduced nano-ZnO treated by KH550 coupling agent and GFs to PP in order to improve the mechanical performance and flowability of PP. The crystallization behavior and microstructure of nano-ZnO/GFs/PP hybrid composites were analyzed and the effect of crystallization behavior on the mechanical properties of the nanocomposites was investigated. The results indicated that nano-ZnO surface-coupled by KH550 could be uniformly dispersed in the PP matrix. The incorporation of nano-ZnO and GFs resulted in increases of the crystallization temperature and crystallization rate of PP and a decrease of the crystallization degree. The introduction of nano-ZnO

and GFs also enhanced the tensile strength and impact toughness of the hybrid composites and improved their fluidity. Composites containing 2% of nano-ZnO and 40% of GFs possessed the optimum mechanical properties.

#### 4.4

##### Silicates

Silicates such as feldspar [9, 10], bentonite [11], kaoline [12], natural zeolite [13–17], attapulgite (ATP) [18], and montmorillonite [19] were used as fillers for PP composites. Fly ash (FA), rich in silica and calcium oxide, has also been included in this section [20]. There are many different modification techniques and each modification affects the properties of the PP matrix composites differently. The silicate fillers, modification methods, and their effects are summarized in Table 4.3 and explained below. In most cases, compatibilizers were used simultaneously with surface modification. Silane coupling agents [9, 13, 15–17], polyethylene glycol (PEG) [14, 16], quaternary ammonium compounds (QACs) [12, 19], sodiumhexametaphosphate [12], oxidized polyethylene emulsion [18], and furfuryl palmitate [20] were the surface modifiers for silicates.

Silane coupling agents can improve the mechanical properties of feldspar–PP composites [9]. Ansari and İsmail [9] showed the effect of the silane coupling agent, 3-(aminopropyl) triethoxy silane (3-APE) on mechanical properties of feldspar-filled PP composites. The tensile strength and elongation at break were improved owing to enhancement of the interfacial adhesion between feldspar and PP matrix. In another study, Ansari and İsmail [10] investigated the effect of compatibilizers on the mechanical, water absorption, and morphological properties of feldspar–PP composites. Polyethylene *co*-acrylic acid (PEAA) and PP-*g*-Ma were used. The tensile strength, elongation at break, Young's modulus, and impact strength increased with the presence of both compatibilizers. Morphological investigation using scanning electron microscopy (SEM) revealed that the improvement in tensile strength and elongation at break were due to enhancement of the interfacial adhesion between feldspar and PP. A lower percentage of water absorption was observed in feldspar–PP composites with PP-*g*-Ma than the feldspar–PP composites with PEAA and control composites (without compatibilizers).

Fatty acids can be used in surface modification of bentonites [11]. Othman *et al.* [11] investigated the effect of palm oil fatty acid additive (POFA) and PP-*g*-Ma compatibilizers on the properties of bentonite-filled polypropylene composites. The mixing of the composites was improved with the addition of POFA. The impact strength and elongation at break increased with the presence of both compatibilizers while, tensile strength and Young's modulus improved only with the addition of PP-*g*-Ma. The improvement in impact strength and elongation at break was due to enhancement of the interfacial adhesion between bentonite and PP as shown by SEM. The thermal stability of bentonite-filled PP was improved

Table 4.3 Effects of surface modifiers and compatibilizers on the properties of PP-silicate composites.

Silicate type	Surface modifier	Compatibilizer	Property change	References
Feldspar	3-(Aminopropyl)triethoxy silane	—	Tensile strength Elongation at break increased Water absorption decreased, interfacial adhesion	[9]
Feldspar	—	Polyethylene <i>co</i> -acrylic acid	Impact strength	[10]
Bentonite	Palm oil fatty acid	PP- <i>g</i> -Ma PP- <i>g</i> -Ma	Interfacial adhesion improved Improved mixing Impact strength	[11]
Kaolin	Quaternary ammonium compound Sodium hexametaphosphate Sodium hydroxide	—	Elongation at break Thermal stability Less water absorption Better dispersion of kaolin	[12]
Natural zeolite	Polypropylene-grafted maleic anhydride 3-Aminopropyltriethoxysilane methyltriethoxysilane 3-Mercaptopropyltrimethoxysilane	PP- <i>g</i> -Ma	Higher impact strength Increase in melt flow index Increased crystallinity No change in melting and thermal degradation	[13]
Natural zeolite	PEG 4000	—	Increase in crystallization temperature And crystallinity	[14]
Natural zeolite	3-Aminopropyltriethoxysilane	—	Lower yield strength Reduced agglomerate size	[15]
Natural zeolite	Glycidoxypropyltrimethoxysilane	—	Increase in hardness Increased Yield strength Impact strength Stiffness	[15]

Natural zeolite	Polyethylene glycol aminopropyltriethoxysilane methyltriethoxysilane (MTES) 3-Mercaptopropyltrimethoxysilane (MPTMS)		Improved mechanical properties	[16]
Natural zeolite in intumescent system	3-(Trimethoxysilyl)-1-propanethiol (3-aminopropyl)-triethoxysilane	PP- <i>g</i> -Ma	Better dispersion  Increased LOI values PP- <i>g</i> -Ma addition enhanced tensile stress Coupling agents did not improve the tensile strength	[17]
Attapulgite	Oxidized polyethylene emulsion		Increased elongation at break Higher impact strength Flexural strength Better dispersion Increase in crystallization temperature Crystallinity	[18]
Montmorillonite	Dimethyldioctadecylammonium ions	PP- <i>g</i> -Ma1 PP- <i>g</i> -Ma2 PP- <i>b</i> -gPPG	Increased exfoliation Tensile modulus Oxygen permeability increased or unchanged Increased yield stress Tensile stress	[19]
Fly ash	Furfuryl palmitate	—	Increase in flexural strength Breaking energy Modulus	[20]

with the incorporation of POFA and PP-*g*-Ma. A lower percentage of water absorption has been observed in the PP–bentonite system with PP-*g*-Ma.

Ariffin *et al.* [12] investigated the surface treatment of kaolin on the mechanical, morphological, and thermal properties of polypropylene–kaolin composites. The composites were prepared using the Brabender internal mixer (50 rpm, 190 °C) and molded using a compression mold (190 °C) to form test samples. The agglomeration tendency of the kaolin particles was very high and composites with low strength and rigidity but fairly good toughness were obtained. To prevent agglomeration of kaolin particles, surface treatment with QAC, sodium hexametaphosphate (SHMP), sodium hydroxide (NaOH), and PP-*g*-Ma was carried out. Better dispersion of kaolin fillers with smaller-sized kaolin agglomerates were obtained by surface treatment. The most effective dispersing agent for kaolin was QAC. It increased the impact strength by 47%. The melt flow index of the mixture and the crystallinity of polypropylene were also increased.

Melting and degradation behavior of PP did not change with the surface treatment of natural zeolites with silane coupling agents [13]. Basalp and Tihminlioglu [13] investigated the thermal characterization of PP composites having a natural zeolite and silane coupling agent–treated zeolite. The coupling agents were 3-aminopropyltriethoxysilane (AMPTES), methyltriethoxysilane (MTES), and 3-mercaptopropyltrimethoxysilane (MPTMS). It was found that silane treatment and 2–6 mass% zeolite addition have no significant effect on the melting and degradation temperatures of the composites. The crystallization temperatures of the composites were increased owing to the nucleating effect of zeolite. These modifications were found to increase the crystallinity and crystallization temperature of the composites due to the nucleating effect of the zeolite.

No adhesion between PEG-coated natural zeolite and PP was observed [14]. Ozmihi *et al.* [14] investigated the preparation and characterization of PP and natural zeolite composites. Natural zeolite mined in Gördes, Turkey was fractionated to particle size below 2 μm and surface modified by polyethylene glycol 4000 (PEG 4000). Films were prepared by the extrusion of PP and surface-modified zeolite. The transmitted optical micrographs of modified natural zeolite and pure natural zeolite had 6 and 600 μm agglomerates. PEG 4000 reduced the size of the agglomerates of zeolite particles. These zeolite-filled composites had densities between 0.73 and 0.83 g cm<sup>-3</sup> and had void fractions of 0.07–0.20. The yield stresses of 2–4% zeolite-containing films were around 26–27 N mm<sup>-2</sup> and were lower than that of PP, which indicated no adhesion between PP and zeolite.

Composites from unmodified and modified natural zeolites both had improved yield strengths [15]. Kodal and Demirhan [15] investigated the mechanical and physical properties of PP filled by natural zeolite. For this purpose, a natural zeolite was modified using two different silane coupling agents (3-aminopropyltriethoxysilane (AMTES), and 3-glycidoxypropyltrimethoxysilane, GPTMS). The hardness and density of both unmodified and modified zeolite-filled PP composites were higher compared with neat PP. Composites having AMPTES-modified zeolite showed improved yield strength, impact strength, and stiffness.



Both dry and wet tensile strengths were improved by silane coupling agent treatment of natural zeolite particles [16]. Metin *et al.* [16] investigated the effect of interfacial interactions on the mechanical properties of PP–natural zeolite composites under dry and wet conditions. Natural zeolite was modified by surface treatment with a nonionic surface modifier; 3 wt% PEG and three different types of silane coupling agents, AMPTES, MTES, and MPTMS, at four different concentrations (0.5–2 wt%). PP composites containing (2–6 wt%) zeolite were prepared by an extrusion technique. Silane treatment indicated significant improvements in the mechanical properties of the composites. According to the dry and wet tensile test results, the maximum improvement in the mechanical properties was obtained for the PP composites containing 1 wt% AMPTES-treated zeolite. SEM studies also revealed better dispersion of silane-treated filler particles in the PP matrix.

In intumescent flame retardants having ammonium polyphosphates (APPs), pentaerythritol, and natural zeolites, the silane treatment increased the elongation at break of the PP composites [17]. Demir *et al.* [17] investigated intumescent flame retardant system for PP. An intumescent system, consisting of APP as an acid source and blowing agent, pentaerythritol (PER) as a carbonific agent, and natural zeolite (clinoptilolite) as a synergistic agent, was used in their study to enhance the flame retardancy of polypropylene (FR-PP). Zeolite was incorporated into the flame-retardant formulation at four different concentrations (1, 2, 5, and 10 wt%) to investigate synergism with the flame-retardant materials. Filler content was fixed at 30 wt% of the total amount of flame-retardant PP composites. Zeolite and APP were treated with two different coupling agents namely, 3-(trimethoxysilyl)-1-propanethiol (MS) and (3-aminopropyl)-triethoxysilane (AS) for investigation of the influence of surface treatment on the mechanical properties and flame-retardant performance of composites. PP-*g*-Ma was used for making polypropylene hydrophilic. Flammability of FR–PP composites was measured by the determination of limiting oxygen index (LOI). The LOI values reached a maximum value of 41% for mercapto silane-treated APP:PER (2:1) PP composite containing 5 wt% zeolite. The tensile strength of composites was increased by the addition of PP-*g*-Ma and elongation at break of composites was increased with silane treatments. Surface treatments with coupling agents did not enhance the interface between the polypropylene matrix and inorganic fillers, hence the tensile strength properties of composites was not improved. PP-*g*-Ma addition enhanced the tensile strength of composites by 12–28% compared to untreated ones.

The impact strength of the composites was increased by using oxidized polyethylene emulsion in modifying ATP in ATP–PP composites [18]. Li *et al.* [18] investigated the PP–ATP nanocomposites with enhanced mechanical properties that were prepared by melt blending. ATP was pretreated by oxidized polyethylene emulsion, and then dispersed in PP melt by strong shear stress. The nanocomposites prepared from treated ATP lead to higher mechanical properties than those of PP–untreated ATP nanocomposites and pure PP. The impact strength of the composites was increased by 44–83%, the tensile strength

was increased by 6–11%, the flexural strength was increased by 33–45% and the flexural modulus was increased by 90–106%. ATP was dispersed homogeneously in the PP matrix and mainly existed in the form of an anomocytic crystal bundle. The diameter of treated ATP units was in the range of 20–40 nm that was much less than that of untreated ATP which was in the range of 50–80 nm. The size of PP crystallites was decreased with the addition of ATP. The addition of ATP can increase the crystallization temperature and crystallinity of PP/ATP. It is proved that the addition of ATP also acts as crystal nucleator. The enhancement of the mechanical properties is mainly due to the uniform dispersion of ATP and strong interfacial force of PP/ATP.

Montmorillonite exfoliated with quaternary ammonium compounds and compatibilizers affected the oxygen permeabilities of composites [19]. Mittal [19] prepared nanocomposites of polypropylene with montmorillonite modified with dimethyldioctadecylammonium ions and investigated the effect of compatibilizers (PP-*g*-Ma1, PP-*g*-Ma2, and PP-*b*-PPG) on the mechanical and permeation properties. Compatibilizers were selected on the basis of their chemical nature, molecular weight, amount of grafting, and location of the polar groups. Compatibilizers increased the exfoliation of clay platelets. The modulus of the composites increased as compared with the values without compatibilizers. The oxygen permeation through the composite films either increased or remained unaffected due to two opposing effects. Permeability increases with possible interfacial free volume enhancement due to incompatibility of surface modification and the compatibilizer and it decreases with the increased path tortuosity due to exfoliation of clay by the compatibilizer. The higher extent of exfoliation improved the yield and break stress of the nanocomposites. The thermal behavior and crystallinity of the composites were not affected by the compatibilizer.

Furfuryl palmitate coated with fly ash improved the impact strength of the composites [20]. Sengupta *et al.* [20] investigated the preparation of fly ash particle/recycled PP composites. They coated the FA particles with furfuryl palmitate (FP) in different wt% such as 1, 2, 3, and 5. The surface of the fly ash became smoother after the coating process. The highest enhancement in properties was observed in 2 wt% FP (FP2)-coated fly ash-filled composites, where the flexural strength, breaking energy, and modulus increased by 6.4, 64, and 1.4% respectively, with a shift of glass transition temperature to a higher temperature. The highest impact strength was observed in 1 wt% FP-coated fly ash-filled composites.

#### 4.5

##### Mg(OH)<sub>2</sub> and Eggshell Modification

The changes that occurred on modification of Mg(OH)<sub>2</sub> and eggshell are shown in Table 4.4.

Magnesium hydroxide is used as flame-retardant filler in PP composites. Chiang and Hu [21] used acrylic acid (Aac) for interfacial enhancement of

**Table 4.4** Effects of surface modifiers and compatibilizers on properties of PP–Mg(OH)<sub>2</sub> and PP–eggshell composites.

Filler type	Surface modifier	Compatibilizer	Property change	References
Mg(OH) <sub>2</sub>	Acrylic acid	Benzoyl peroxide-coated particles	Tensile strength Young's modulus Impact resistance Increases	[21]
Chicken eggshell (95% CaCO <sub>3</sub> )	Isophthalic acid	—	Higher tensile modulus Impact strength Flexural	[22]

PP–Mg(OH)<sub>2</sub> composites. Acrylic acid and benzoyl peroxide-coated PP particles and Mg(OH)<sub>2</sub> were extruded at 200 °C in a twin-screw extruder. The tensile strength of the composites was analyzed using an equation developed by Pukanszky (Eq. 4.1) from which both matrix tensile strength  $\sigma_0$  and interfacial adhesion strength were found to be increased.

$$\sigma_{yc}/\sigma_{ym} = \frac{1 - \phi_f}{1 + 2.5\phi_f} e^{(B\phi_f)} \quad (4.1)$$

where  $\phi_f$  is the volume fraction of filler, and  $\sigma_{yc}$  and  $\sigma_{ym}$  are the tensile yield strengths of the composite and matrix respectively. While the yield point increased from 37.79 to 43.51 MPa, the  $B$ -value increased from 1.668 to 2.035 when 4% Aac was added to the feed. The enhancement of  $\sigma_{yc}$  is due to the intermolecular cross-linking of PP by Aac grafting. This cross-linking caused increases in tensile strength, Young's modulus, impact resistance, and thermal resistance, but decreased the elongation at break of the composites. The increase in  $B$ -value indicated better interfacial adhesion. No change in flame retardancy was observed by matrix graft modification.

Chicken eggshell can be used as filler in PP composites. Kumar *et al.* [22] reported the mechanical, thermal, and morphological properties of PP–chicken eggshell (ES) composites. They washed, dried, and ground eggshells to obtain 3.0  $\mu\text{m}$  sized powder with 95.2% CaCO<sub>3</sub>. They investigated mechanical properties such as tensile strength, tensile modulus, izod impact strength, flexural modulus of PP composites with normal (unmodified) eggshell and chemically treated ES (modified eggshell (MES) with isophthalic acid). Isophthalic acid, which was used for chemical treatment of ES, has both hydrophilic and hydrophobic sides. The hydrophilic side of isophthalic acid was compatible with the filler, whereas its hydrophobic side was compatible with the polymer. The hydrophilic side reacted with the surface of the inorganic filler to form bonds, which ultimately made the polymer more stiff resulting in a higher tensile modulus. PP–calcium carbonate (CaCO<sub>3</sub>) composites at the same filler loadings were also prepared and used as reference. The results showed that PP composites with chemically MES had better mechanical properties compared to the unmodified ES and CaCO<sub>3</sub> composites.

An increase of about 3–18% in tensile modulus, 4–44% in izod impact strength, and 1.5–26% in flexural modulus at different filler loadings was observed in MES composites as compared to unmodified ES composites. SEM micrographs of fractured tensile specimens confirmed better interfacial adhesion of MES with polymer matrix resulting in lower voids and plastic deformation resulting in improved mechanical properties of the composites. Transmission electron microscope (TEM) micrographs showed acicular needle-shaped morphology for modified ES and have contributed to better dispersion which was the prime reason for enhancement of all the mechanical properties. At higher filler loading, the modulus of the MES composite was found to be higher by 5% as compared to commercial  $\text{CaCO}_3$  composites.

## 4.6

### Cellulose

*Luffa cylindrica* fibers [23], sisal fiber(SF) [24–26], flax fibers [27, 28], aspen fiber [29], cellulose [30], thermomechanical pulp (TMP) [31], cellulosic microfiber [32], hemp fibers [33], wood flour (WF)[34–36], and cellulose powder from milling spelt were used in the preparation of cellulose-based PP matrix composites. The surface modification methods and their effects are reported briefly in Table 4.5. Silane coupling agents [23, 29], alkali treatment [24, 29, 35], isocyanates [25, 30, 32], organic acids [27], heat treatment [26], acetylation [29], carboxylic anhydrides [30], vinyl sulfone [30], chloro triazine [30], octanoyl chloride [34], corona treatment [33], enzymatic treatment [37], and  $\gamma$ -irradiation were used in the modification of the cellulose-based fillers. Detailed studies on the modification of cellulose and their effect on properties of composites are described in the following.

*L. cylindrica* fibers can be modified with silane coupling agents [23]. Demir *et al.* [23] investigated the effect of fiber surface treatments on the tensile and water sorption properties of PP–luffa fiber (LF) composites. The interfacial interactions between the PP matrix and LF were increased by using three different types of coupling agents, AS, MS, and PP-*g*-Ma. Atomic force microscope (AFM) studies also showed that the surface roughness of LFs decreased with the employment of silane coupling agents. The PP composites containing 2–15 wt% of LF were prepared in a torque rheometer. The tensile strength and Young's modulus were increased with employment of the coupling agents; this was accompanied by a decrease in water absorption with treatment, due to the better adhesion between the fiber and the matrix. Maximum improvement in the mechanical properties was obtained for the MS-treated LF composites. The interfacial interactions improved the filler compatibility, mechanical properties, and water resistance of the composites. The improvement in the interfacial interaction was also confirmed by the Pukanszky model (Eq. 4.1). Good agreement was obtained between experimental data and the model prediction. Morphological studies demonstrated that better adhesion between the fiber and the matrix was achieved especially for the MS- and AS-treated LF composites. Composites with the untreated LF fiber and treated LF

Table 4.5 Effects of surface modifiers and compatibilizers on the properties of PP-cellulose composites.

Filler type	Surface modifier	Compatibilizer	Property change	References
Luffa cylindrica fibers	3-(Aminopropyl)-triethoxysilane (AS), 3-(trimethoxysilyl)-1-propanethiol (MS)	PP-g-Ma	Increase in Young's Modulus Decrease in water absorption Strong fiber matrix interaction with MS	[23]
Sisal fiber	Interfacial crystalline morphologies		Significant interfacial enhancement due to formation of crystalline interface	[24]
Sisal fiber	Sodium hydroxide Isocyanates Benzoyl chloride Urethane derivative of propylene glycol and cardanol Permanganate Alkalinization Heat treatment	PP-g-Ma	Improved adhesion between fiber and matrix PP-g-Ma gives the best result	[25]
Sisal fiber		PP-g-Ma	Improved mechanical properties Decomposition temperature	[26]
Nonwoven flax batting	Acrylic acid 4-Pentanoic acid 2,4-Pentadienoic acid 2-Methyl-4-pentanoic acid		Water resistance Tensile strength Flexural strength Impact strength	[27]
Flax fibers	Functionalization of PP and polypropylene-ethylene propylene diene terpolymer matrices with maleic anhydride		Reduced interfacial stress concentration Accelerated crystallization	[28]
Aspen fiber	Alkali treatment Acetylation Silane treatment	PP-g-Ma	Better adhesion of fiber and matrix Better tensile properties	[29]

(continued overleaf)

Table 4.5 (Continued)

Filler type	Surface modifier	Compatibilizer	Property change	References
Cellulose fibers	Carboxylic anhydrides Isocyanates Vinyl sulfone Chlorotriazine Phenol formaldehyde	PP-g-Ma	Decrease in water regain in isocyanate treatment	[30]
Thermo mechanical pulp	Urea formaldehyde 1,6-Diisocyanate cyclohexane	PP-g-Ma	Increase in tensile strength with 1% resin Reduced polarity and hydrophilicity	[31] [32]
Highly crystalline microfibrer Hemp fibers	Corona treatment		Improved interfacial adhesion Enhanced mechanical anchorage and interfacial adhesion	[33]
Wood flour	Octanoyl chloride		Increased water resistance Lower flexural strength and modulus	[34]
Wood flour	Alkalkization Esterification $\gamma$ -Irradiation		Transcrystallinity	[35]
Wood flour	—	PP-g-Ma	Improved water resistance Flexural strength Flexural modulus	[36]
Cellulose powder from milling spelt	Enzymatic treatment	—	Odor removal during processing increased thermal stability	[37]

fiber with AS, MS, and PP-*g*-Ma had *B*-values  $-2.93$ ,  $0.43$ ,  $0.81$ , and  $-1.57$ , respectively. The *B*-values increased with the treatment of the fiber, and the MS-treated composites had the highest *B*-value indicating the strongest interaction between the polymer and the fiber compared to others.

Formation of a crystalline interface can improve the bonding between cellulose fibers and PP [24]. Han *et al.* [24] investigated interfacial adhesion between natural SF and isotactic polypropylene (iPP) composites. Three kinds of interfacial crystalline morphologies, spherulites, medium nuclei density transcrystallinity (MD-TC) and high nuclei density transcrystallinity (HD-TC), were obtained in the single fiber-reinforced composites. A combination of single-fiber fragmentation testing and optical microscope observation was used to demonstrate the development of IFSS. A close correlation between IFSS and morphological characteristics of interfacial crystallization was well elucidated. The increases in IFSS were very different for spherulitic, MD-TC, and HD-TC morphologies. The highest IFSS obtained was 28 MPa, after the formation of HD-TC, which was about 62% of the tensile strength of neat iPP (45 MPa). Significant interfacial enhancement due to the formation of a crystalline interface was observed.

Different modification of SFs had different effects on the properties of SF-PP composites [25]. Joseph *et al.* [25] used SFs for the reinforcement of polypropylene matrix. Cellulose fibers were treated with sodium hydroxide, isocyanates, maleic anhydride-modified polypropylene (PP-*g*-Ma), benzyl chloride, and by using permanganate. Surface fibrillation was found to occur during alkali treatment, which improved interfacial adhesion between the fiber and PP matrix. The grafting of the fibers by PP-*g*-Ma enhanced the tensile strength of the resulting composite. The hydrophilic nature of cellulose was reduced by treatment with the urethane derivative of polypropylene glycol and cardanol. Benzoylation of the fiber improves the adhesion of the fiber to the PP matrix. The benzoylated fiber was analyzed by IR spectroscopy. Experimental results indicated a better compatibility between benzoylated fiber and PP. The permanganate-induced grafting of PP on to SFs was obtained by treating with permanganate at low concentrations. PP-*g*-Ma treatment gave superior mechanical properties compared to other modifications.

The water resistance of composites can be improved by modification of the fibers and using PP-*g*-Ma [26]. Kaewkuk *et al.* [26] prepared SF/PP composites at fiber content of 10, 20, and 30 wt% and investigated their mechanical, thermal, morphological, and water absorption properties. The effects of fiber treatment (alkalization and heat treatment) and adding a compatibilizer (PP-*g*-Ma) on the properties of the PP composites were comparatively studied. The fiber treatment and adding PP-*g*-Ma led to an improvement of mechanical properties, cellulose decomposition temperature, and water resistance of the PP composites.

Fibers treated with organic acids affected the properties of cellulose-PP composites [27]. Erasmus and Anandjiwala [27] improved the interfacial adhesion between the polypropylene matrix and the nonwoven flax batting by chemical treatment of the fibers with acrylic acid, 4-pentanoic acid, 2,4-pentadienoic acid, and 2-methyl-4-pentanoic acid. The composites were processed by compression

molding using a film stack method. The mechanical properties of these modified composites, such as tensile, flexural, and impact strength were dependent on the kind and amount of chemical treatment.

MA treatment of fibers and PP increased the adhesion between flax fibers and PP [28]. Manchado *et al.* [28] improved the compatibility between flax fibers and PP and polypropylene-ethylene propylene diene terpolymer (PP-EPDM) blends by the functionalization of both matrices with MA. Incorporation of small amounts of functionalized polymer considerably improved the adhesion at the fiber–matrix interface. A significant increase in the composite strength was observed by using PP-*g*-Ma and EPDM-*g*-Ma as the fibers were perfectly embedded in the matrix compared to the composites prepared with the pure homopolymers. It was assumed that the functionalization of the matrix reduced interfacial stress concentrations and prevented the fiber–fiber interactions, which were responsible for premature composite failure. Flax fiber and rubber both acted as effective nucleation agents and accelerated PP crystallization. Moreover, these results are particularly relevant when the grafted matrices are added to the composite.

Chemically treated aspen fibers can be used in PP composites [29]. John and Anandjiwala [29] reviewed the recent developments in chemical modification and characterization of natural fiber-reinforced composites. Alkali treatment, acetylation, and silane treatment were the important modification methods of cellulose-based natural fibers. They reported that the PP-*g*-Ma coupling agent improved the adhesion between aspen fiber and polypropylene and the tensile properties of the composites were improved.

Functionalization of cellulosic fibers had important effect in water vapor adsorption of composites [30]. Joly *et al.* [30] modified different cellulosic fibers with various chemical functions, carboxylic anhydrides, isocyanates, vinylsulfone, and chlorotriazine systems. All these compatibilizing agents carry an alkyl chain or a PP chain. Determination of the water sorption isotherm for the treated fibers shows an important decrease in water regain in the case of isocyanate treatments in swelling medium. The interfacial shear stress obtained by the microbond test increases by 70% for cellulosic fibers treated with maleated PP.

Thermoset adhesives can be used for fiber-to-fiber adhesion in PP composites [31]. Lee *et al.* [31] improved the interfacial adhesion properties at the interface of the TMP fiber and iPP using thermoset adhesives such as phenol formaldehyde (PF) and urea formaldehyde (UF). Fiber-to-fiber adhesion using thermoset adhesives before the molten iPP would flow into the fiber web was also investigated. An increased TMP fiber failure was observed with increased thermoset quantity at the interface. The tensile strength was increased almost twofold higher than the strength of control samples by using 1% resin. Additional adhesive contents of 3 and 5% showed gradual strength enhancement. However, the enhanced strength was statistically insignificant. UF resin showed slightly better strength performance over PF resin; this was attributed to higher solid contents and additional pigments in the UF resin.



Diisocyanates and PP-*g*-Ma reduced the hydrophilicity of cellulose fibers [32]. Qiu *et al.* [32] prepared composites of a highly crystalline cellulosic microfibrils with PP as well as with PP-*g*-Ma by using 1,6-diisocyanatohexane (DIC) as a compatibilizing agent. The tensile strength and Young's modulus of the composites were improved considerably by using DIC. The polarity and hydrophilicity of cellulose fiber were reduced by DIC treatment of the fibers through the reaction of the free superficial OH groups of cellulose and the NCO group of diisocyanate. However, chemically bound PP-*g*-Ma chains on cellulose fiber were present in PP-*g*-Ma-based composites. Through the imidization reaction of NCO group and anhydride group of PP-*g*-Ma, many more PP-*g*-Ma chains were linked on the cellulose fiber due to the many more obtainable reactive sites of cellulose. Tensile properties of the composite can be maximized by optimizing the DIC content. The interfacial adhesion between the cellulose fibers and PP or PP-*g*-Ma matrix was improved in DIC-coupled composites. Furthermore, DIC affects the thermal dynamic mechanical properties, as well as melting and crystallization behavior of the composites.

Etching cellulose fibers by corona treatment increased the contact surface between the fiber and PP [33]. Ragoubi *et al.* [33] investigated the mechanical properties of composites from untreated and corona-treated hemp fibers and polypropylene prepared by extrusion–compression molding. For treated as well as untreated fiber, a fiber content of 20% led to maximal values in the tensile strength and Young's modulus. When either the fibers or the matrix was treated, there was a significant increase in tensile strength. The modification of hemp fibers rather than polypropylene allowed for greater improvement of the composites' properties with an enhancement of 30% in the Young's modulus. The etching effect generated by corona discharge treatment (CDT) and evidenced by microscopy was mostly responsible for the enhanced mechanical anchorage and interfacial adhesion between the compounds. This effect permitted a large surface contact with the PP matrix and favored insertion of PP in the bulk of fibers so that composites failed mostly by local shear yielding of the matrix around the fiber, rather than tensile failure or de-bonding of the fillers.

Modification of fiber surface with short-chain alkyl groups improved the water resistance but did not affect the mechanical properties [34]. Zhang *et al.* [34] made WF–PP composites by extrusion and hot press compression molding. WF esterified with octanoyl chloride was used in WF/PP composites to improve the composites' water resistance. Maleated polypropylene (PP-*g*-Ma) was also studied and compared with esterification by acid chlorides. Esterification by octanoyl chloride reduced the composite water uptake as hydrophobic interactions were enhanced. However, flexural strengths and flexural moduli decreased as the C(8) chain was still not long enough to form effective entanglements with the PP matrix. On the other hand, PP-*g*-Ma (MW = 47 000) polymer chains can entangle with the matrix polypropylene molecules. Therefore, when PP-*g*-Ma's MA functions esterified WF surface hydroxyls, improved water resistance and composite flexural properties were achieved. It was shown that the modifier chain length was of

critical importance and more important than the surface density of hydrophobic groups for improving WF–PP interfacial adhesion and composite mechanical performance.

Mercerization of cellulose and treatment with anhydrides changed the transcrystallinity of composites [35]. Borysiak [35] investigated the effects of alkalization, esterification, and  $\gamma$ -irradiation of wood on the transcrystalline morphology of wood/polypropylene composites. The occurrence of transcrystallization in wood–polypropylene composites was strongly dependent on the type of chemical modification of lignocellulosic materials. A detailed analysis of the results obtained proved that the transcrystallization was strongly influenced by the conditions of the mercerization process of wood and the kind of anhydrides. Moreover, it was found that the amount of cellulose in wood plays a key role in the development of transcrystallinity. The absence of cellulose in wood seems to be unfavorable for the growth of transcrystallinity. It has been established that the mechanical properties of wood composites depend on the proper choice of a modifier and are obtained after optimization of the process of modification.

PP-*g*-Ma was used as compatibilizer in WF–PP composites [36]. Pal *et al.* [36] investigated PP-*g*-Ma and WF reinforcement and their effects on the dynamic, mechanical, morphological, and rheological properties of waste PP composites. PP-*g*-Ma was used as a compatibilizer to improve the physical interaction between the filler and matrix. The composites were prepared by using a twin-screw extruder followed by injection molding. Thermal stability and mechanical properties of the compatibilized system increased as compared to their values for the uncompatibilized system. The enhanced properties of the PP-*g*-Ma-reinforced composite were attributed to the improved interfacial adhesion between the WF and the matrix. The composites were buried in soil for biodegradability. Nearly 60% and 30% loss was found for mechanical properties and weight, respectively for 90 days buried PP-*g*-Ma reinforced composite.

Enzyme treatment of grain husks removed the odor in grain husk/PP composites [37]. Bledzki *et al.* [37] investigated odor removal by enzyme treatment of cellulose fibers from milling spelt (*Triticum spelta*), rice husks (*Oryza sativa*) and rye brans (*Secale cereale*). It was aimed to evaluate microfibers from grain by-products as a substitute for WF in wood–thermoplastic composites. Grain husks are an abundant and cheap source of annual, renewable raw material, which may also contain, besides lignocellulose, substantial amounts of starch, proteins, and fats. These grain residues may negatively affect the mechanical properties of their composites, and generate an odor when decomposition occurs at higher temperatures during plastics processing. Such odors may also be present in the end product. A simple and effective enzymatic treatment was proposed for odor removal. This environmental-friendly process removed protein, starch, and fats in a selective manner. Lower amount of odor emission during plastics processing as well as in the final, injection-molded parts (25–65% decrease) were observed. The mechanical properties of composites were either preserved or slightly improved.

## 4.7

### Carbon

Single-walled carbon nanotubes (SWNTs) [38], multiwalled carbon nanotube (MWCNT) [39], oxidized CNTs [40], C-nanofibers [41], and graphene oxide [42–44] were used as C-based fillers in PP matrix composites. Ethylene diamine [38], hexamethylene diamine [42], long-chain alkyl amines [43], *p*-phenylene diamine and cyanuric chloride [44], lauryl peroxide [39], polypropylene-graft-glycidyl methacrylate [40], and peroxide initiator [41] were used in modification of C-based composites. The surface modification methods and their effects on the properties of composites with C-based fillers are summarized in Table 4.6. The details of the modification methods and their effects on properties are explained in the following.

Single-walled C-nanotubes grafted with polypropylene increased the electrical conductivity of their PP composites [38]. Liu *et al.* [38] presented a strategy for fabricating PP/polypropylene-regrafted-single-walled carbon nanotube (PP-re-*g*-SWNT) composites with a high loading of SWNTs (20 wt%). PP/PP-grafted SWNT composites with PP containing 1 wt% MA (PP-*g*-Ma) and amine-functionalized SWNTs were prepared. The PP-*g*-SWNTs were further grafted a second time with ethanediamine treatment. The polymer-regrafted SWNTs filled with PP showed improved mechanical performance compared with the pure PP and PP reinforced with traditionally functionalized CNTs. The improvement was due to the covalent bonding of polymer chains to SWNTs, where strong chemical bonds and a conjugated network between the nanotubes and polymers were established. Moreover, the regrafted SWNTs had obvious effects on the PP crystallinity and elevated electrical conductivity from  $10^{-10}$  to  $10^{-2} \text{ S m}^{-1}$ .

MWCNTs were alkyl functionalized by organic peroxides [39]. Koval'chuk *et al.* [39] functionalized MWCNTs by addition of undecyl ( $\text{C}_{11}$ ) radicals generated by thermal decomposition of lauroyl peroxide. iPP and syndiotactic polypropylene (sPP) nanocomposites containing both purified and alkyl-functionalized MWCNTs were synthesized via *in situ* polymerization method. The synthesized materials demonstrated improved filler dispersion and mechanical characteristics as a result of nanotube chemical functionalization. The MWCNT functionalization led to markedly improved nanocomposite plasticity and noticeable enhancement of sPP tensile modulus. The authors concluded that the problem of creating strong interfaces between nonpolar polyolefin matrices and CNTs still remained unsolved and they suggested as the most promising strategy was the incorporation of polar functional groups in PP macromolecules (e.g., by propylene/methyl methacrylate block copolymerization) that would apparently induce stronger interfacial interactions between the polymer chains and filler particles.

Polypropylene-grafted oxidized C-nanotubes were used to increase the melt strength in the chemical blowing process [40]. Chen *et al.* [40] utilized a

Table 4.6 Effects of surface modifiers and compatibilizers on the properties of PP-carbon composites.

Carbon type	Surface modifier	Compatibilizer	Property change	References
Single walled C-nanotube	Ethylene diamine treatment for amine functionalization	PP-g-Ma	Improved mechanical performance	[38]
Multiwalled C-nanotube	Undecyl(C <sub>11</sub> ) radicals from lauroyl peroxide		Elevated electrical conductivity Improved filler dispersion	[39]
Oxidized C-nanotube	Polypropylene-graft-glycidyl methacrylate		Improved nanocomposite plasticity Reinforcing interfacial adhesion	[40]
C-nanofiber	Oxidation with peroxide initiator		Increase in melt strength and elastic modulus in chemical blowing of foam	[41]
Graphene oxide	Hexamethylene diamine	PP-g-Ma	Increase in Young modulus Peroxide induced degradation of PP chains Improved crystallization characteristics	[42]
Graphene oxide	Long chain alkyl amine with 6, 10, 16, 18 C atoms	PP-g-Ma	Mechanical and electrical properties enhanced Improved crystallization characteristics	[43]
Graphene oxide	Modified with <i>p</i> -phenylene diamine and cyanuric chloride and then grafted with PP-g-Ma		No change in graphitic structures Increased tensile modulus Tensile strength Lowered percolation threshold Good dispersion Exfoliated and intercalated nanostructure Strong interfacial adhesion Increased thermal stability Increased thermal conductivity Lowered elongation at break	[44]

nucleophilic substitution reaction between the epoxy group in polypropylene-graft-glycidyl methacrylate and carboxyl groups in oxidized carbon nanotubes (O-CNTs), to fabricate PP-*g*-CNT for reinforcing the interfacial adhesion between CNTs and the PP matrix. The foaming ability of PP composites by chemical blowing agent DDL-01 was enhanced by the increase of the melt strength and elastic modulus. The average cell diameter of PP foams decreased from 289.2  $\mu\text{m}$  (PP-*g*-Ma) to 96.7  $\mu\text{m}$  (PP-*g*-CNT foams with 2.0 wt% O-CNT) and the distribution of cell size also became more uniform.

Polypropylene and CNTs were cross-linked with peroxides to increase the Young's modulus of their PP composites [41]. Oyervides *et al.* [41] enhanced the interfacial interactions between isotactic poly(propylene) and carbon nanofibers by a free radical coupling reaction. Nanofibers were oxidized by the peroxide initiator before their incorporation to an isotactic poly(propylene) matrix. An increase of up to 17% in the Young's modulus of the composites was obtained by pretreating the fibers with only 3 ppm of peroxide. The mechanical performance of the modified composites was dependent on two combined opposite effects, increased chemical interaction at the interface and peroxide-induced isotactic poly(propylene) degradation.

The crystallization characteristics and electrical conductivity of PP were improved by chemical modification of graphene oxide [42]. Ryu and Shanmugharaj [42] grafted hexamethylene diamine chemically to the graphene oxide (GO) surface via two type of reactions, namely, (i) an amidation reaction between the amine groups and carboxylic acid sites of GO and (ii) nucleophilic substitution reactions between the amine and epoxy groups on surface. These chemically modified graphene oxides (AGO) with varying loading amount were incorporated in polypropylene matrix in the presence of PP-*g*-Ma compatibilizer through melt processing technique. X-ray diffraction (XRD) and differential scanning calorimetric (DSC) studies revealed that the loading of AGO resulted in an improvement in the crystallization characteristics of polypropylene. Owing to the strong interfacial interactions between AGO and the polymer, significant enhancement in mechanical and electrical properties was observed, when compared to pristine GO-filled polypropylene composites.

Graphene oxide modified by long-chain alkyl amines lowered the percolation threshold of their PP composites [43]. Ryu and Shanmugharaj [43] investigated surface modification of GO by grafting long-chain alkylamines with alkyl chains having 6, 10, 16, 18 C atoms. Two types of reactions, (i) amidation reactions between amine groups and carboxylic acid sites of GO and (ii) reactions between amine and epoxy groups on the surface were used for grafting. The grafting of long-chain alkylamines did not affect the graphitic structures of GO. These chemically modified GOs with varying loading amounts were incorporated in a PP matrix in the presence of PP-*g*-Ma compatibilizer by melt processing. The loading of alkylamine-modified GO resulted in significant improvement in crystallization characteristics with significant variation in orientation parameters of crystalline phases on increasing the chain length of the grafted alkylamines. Owing to the strong interfacial interactions between alkylamine-grafted GO and

polymer, significant enhancement in mechanical and electrical properties was observed when compared to pristine, GO-filled PP composites. Increasing the percentage of weight of pristine GO or long-chain, alkylamine-modified GO resulted in significant improvement in tensile properties such as modulus and tensile strength of PP nanocomposites. Alkylamine-modified GO composites had higher tensile modulus and tensile strength. The electrical percolation threshold values were lowered from 0.77 wt% down to 0.63% when modified GO was used.

Graphene oxide was exfoliated using cyanuric chloride as the modifier [44]. Yuan *et al.* [44] reported a novel approach to fabricate covalently functionalized graphene oxide (fGO)/PP nanocomposites. Graphene oxide was modified with *p*-phenylenediamine and cyanuric chloride and then grafted with PP-*g*-Ma. The modifier, cyanuric chloride increased the number of amine functional group on the surface of GO and promoted the grafting reaction. The fGO achieves good dispersion with exfoliated and intercalated nanostructure and strong interfacial adhesion in PP. A significant enhancement of thermal stability of the nanocomposites was obtained at low fGO loading, such as a 133 °C increase in initial decomposition temperature and a 94 °C increase in the temperature at maximum rate of weight loss in the nanocomposite with 1 wt% of fGO. The great enhancement of thermal stability in the nanocomposites were attributed to the restriction of polymer motion, physical barrier effect on emission of degradation products, charring property of triazine compound, radical-scavenging properties of graphene, and improvement of thermal conductivity in the nanocomposites. The high content of fGO (1 wt%) could act as a  $\beta$ -nucleating agent for PP crystallization. The addition of only 0.5 wt% fGO increased the storage modulus and heat deflection temperature (HDT) of PP by 15.4% and 11 °C, respectively. However, the elongation at break of nanocomposites was decreased and the value of tensile strength showed no change with increasing loading of fGO, which was in contrary to those of the nanocomposites as expected. The reduction of mobility of lamellae by fGO is the main reason for the decrease in ductility. The orientation of polymer chains and lamellae with respect to the direction of action of the force during deformation were inhibited in the presence of fGO.

#### 4.8

#### Conclusion

The surface modification of fillers affects the properties of the polypropylene matrix composites in different aspects depending on the types of the filler and the modifications. The polypropylene phase was also functionalized by treating PP with MA or amines. The properties most affected are the tensile strength, Young modulus, and elongation at break of the composites. If crosslinking occurs between the filler and functionalized PP, the tensile strength increases and elongation at break decreases owing to decrease in mobility. The corona treatment of some fillers creates bumps and wells on the surface improving the adhesion of filler and matrix. PP crystallite formation at the interface also increases the

adhesion between filler and matrix. Even dispersion of fillers without agglomerate formation could be achieved by making the surface of the fillers hydrophobic. However the tensile strength is lowered if there is no adhesion or crosslinking between the filler and the polypropylene. Coating of filler particles with alkyl chains make them hydrophobic and water uptake from liquid phase and vapor phase is lowered. If pp macromolecules which are longer than the entanglement molecular weight are grown on the fillers the adhesion to PP matrix will be good and tensile strength will increase. The crystallization temperature and crystallization rate of PP phase change with surface modification. Higher thermal and electrical conductivity of composites can be obtained by surface modification of conductive fillers. The melt strength can be increased by surface modification of fillers and PP foams with smaller and even cells can be obtained. Enzymatic treatment of lignocellulosic fillers lowers the odor release during composite preparation and use.

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