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INTERFACIAL ROLE OF COMPATIBILIZERS TO IMPROVE MECHANICAL PROPERTIES OF SILICA- POLYPROPYLENE COMPOSITES

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Polymers have tremendous applications from household to high technology applications. The polymers are easy to produce, light, and flexible. However, mechanical properties of polymers, in some industries, is a point of its weakness. Therefore, a mineral, as a bulk filler, was used to overcome this limitation and to reduce the cost of polymer composites and their manufacturing. In this study, the silica flour was introduced into the polypropylene (PP) matrix to enhance its mechanical properties. In addition, the styrene-ethylene/butylene-styrene (SEBS) triblock copolymer and its grafted maleic anhydride (SEBS-g-MA) were used as silica/ PP compatibilizers. The results showed an improvement in mechanical properties after the addition of silica to the PP matrix. However, silica addition led to drop in strain measures. On the other hand, the addition of the compatibilizer enhances the interfacial bonding and smoothen the transfer of the stresses between filler particles and the polymeric matrix.

keywords: polymers, silica, polypropylene, mechanical properties, fillers

1. INTRODUCTION

Minerals represent the most important filling materials. Their advantages are twofold; firstly, as functional filler because the mineral addition is incorporated to achieve a specific performance attribute to the end-product. While in the second case the mineral represents merely a bulk filler or an extender for the costly polymer base matrix (Trivedi et al., 1994; Lee, 2000; DeArmitt, 2000; Nielsen, 1974; Lindsey et al., 1974; Haddout, 1992; Chuang et al., 1985; Leidner et al., 1974).

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Silica is one of the most extensively and cheapest mineral commodity used as a filler [Lofthouse 1979]. Silica application ranges from using as an extender to a functional filler. In plastics, it is used to increase abrasion, heat, corrosion and scratch resistance, to improve compressive, flexural strength, and dielectric properties. However, the compatibility of the silica flour with polymeric matrices is constrained by its siliceous surface properties and its high degree of hydrophilicity (Bryk, 1991; Scherbakoff, 1993; Payne, 1985; Zhang et al., 1993; Shang et al., 1994; Leempoel, 1997; Sahnoune et al., 1997; Kauly et al., 1997; Lyman, 1991; Krysztafkiewicz et al., 1992; Malewski et al., 2010).

Different compatibilizers were used to improve the adhesion between the filler and the matrix and accordingly enhance the mechanical properties of the end-product (Kolarik et al., 1990; Osch et al., 1994). Styrene-Ethylene/Butylene-Styrene (SEBS) and its grafted maleic anhydride (SEBS-g-MA) have already been used as efficient interfacial agents in PE/PS blends (Karrad et al., 1997; Sahnoune et al., 1997).

In this paper, the addition of silica flour to the PP matrix with and without SEBS and SEBS-g-MA compatibilizers was investigated in terms of the mechanical properties of silica/PP composites. Furthermore, the compatibilizing mechanism was proposed.

2. EXPERIMENTAL

2.1. MATERIALS

A representative white silica sand sample was used. Polypropylene (KM 6100, abbreviated PP) of density 0.91g/cm^3 as the base matrix was used in this study. Two thermoplastic elastomers (TPE) were used. The first was triblock copolymer [poly(styrene)-poly(ethylene, butylene)-poly(styrene)], (SEBS). The second was its corresponding grafted 2 wt. % maleic anhydride (SEBS-g-MA). Both the two triblock copolymers were of density 0.90g/cm^3 .

2.2. METHODS

2.2.1. PREPARATION AND CHARACTERIZATION OF SILICA FLOUR

The original sample was chemically analysed. The sample was subjected to dry beneficiation process. At first, sieving was carried out to reject both +0.6mm and -0.1mm fractions which contain the free particles of heavy oxides and most of the soft clayey material, respectively. The -0.6 + 0.1mm sand sample was directed to dry high intensity magnetic separation using "Magnaroll" magnetic separator to remove magnetic impurities. The cleaned sample was ground in a porcelain Fritsch ball mill to produce silica flour. The sand sample was also characterized by microscopic examination under visible as well as polarized light.

2.2.2. BLENDING AND COMPOUNDING

Different batches of compositions were prepared. Polypropylene alone (as the base matrix), polypropylene with 3% by volume silica flour, and batches with surface compatibilizers (SEBS and SEBS-g-MA) addition to silica/PP blend in two dosages: 2.5% and 5% by volume. Each batch was thoroughly mixed for 15 min in a plastic tumbling mixer and dried at 110°C for 2 hr. The blends were subjected to compounding using a Collin twin screw extruder at 200°C. The materials were fed by a horizontal metering screw hopper with 2 kg/hr feeding rate. A Collin granulator was connected to cut the compounded film samples into short specimens of 1 cm in length.

2.2.3. PREPARATION OF SPECIMEN FOR MECHANICAL TESTING

Milacron K-TEC 40 injection moulder was used for preparation of 60 mm x 10 mm x 4 mm rectangular bars for mechanical testing. Meanwhile, 10 mm x 6 mm x 2 mm rectangular bars were moulded for Izod impact strength measures. At least six readings were taken for each test and the average measure was reported. Tests were performed at ambient temperature (25°C) and humidity.

3. RESULTS AND DISCUSSION

3.1. SILICA FLOUR PREPARATION AND CHARACTERIZATION

Microscopic examination of the white sand sample showed the presence of ferrogated reddish-brown inclusions above 0.6 mm, where traces of color particulates of Fe₂O₃, Cr₂O₃, and TiO₂, below 0.1 mm. Rejection of both +0.6mm and -0.1mm fractions removed most of these undesirables. Dry high intensity magnetic separator was used to reject iron oxides in -0.6+0.1 mm. Chemical analysis of sand sample before and after cleaning was given in Table 1. It showed the high grade of prepared sample. D₉₈ and D₅₀, μm of the ground sample as well as its main physical measures were depicted also in Table 1.

3.2. MECHANICAL PROPERTIES

3.2.1. EFFECT OF FILLER ADDITION

Figure 1 shows the mechanical properties of the silica/PP blend after adding 3% silica to PP matrix. It is obvious that the silica filler improves the yield and impact strengths, and negatively affects the tensile strength. In case of tensile stress the elongation of PP without silica is higher than in the presence of silica. This behaviour can be attributed to the rigidity of the silica particle because of its higher resistance to plastic deformation (Järvelä et al., 2001).

Table 1. Chemical and physical characterization of Ground Silica Sample

Chemical analysis		Physical properties	
Oxide	Wt. %	Property	Measure
SiO ₂	99.85	Refractive Index	1.55
MgO	-	Specific Gravity	2.65
Al ₂ O ₃	0.020	Hardness	7.0
CaO	0.026	Oil Absorption, %	35
Fe ₂ O ₃	0.016	Surface Area, m ² /g	4.75
Na ₂ O	-	Dry Brightness, %	88
TiO ₂	0.017	<i>D</i> ₉₈ <i>D</i> ₅₀ , μm	20 10

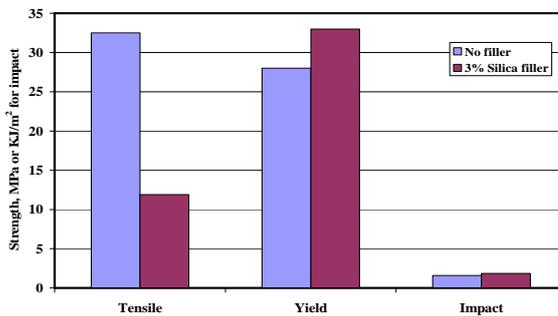


Fig. 1. Effect of the silica addition on the blend strength

3.2.2. TENSILE STRENGTH

SEBS, (styrene-ethylene-butylene-styrene) triblock copolymer, is mainly a nonpolar polymer and is extensively used as a compatibilizer (Legge et al., 1987). It is not compatible with a polar substance unless it has been modified. The well-known modification is grafting with MA.

Figure 2 shows the effect of compatibilizer on tensile strength of silica/PP composite. It was noticed that the addition of styrene-ethylene/butylene-styrene block and its grafted maleic anhydride as silica/PP surface compatibilizers was positively affects the tensile strength of the blend as shown in Figure 2.

One the other hand, increasing the SEBS-g-MA concentration from 2.5% to 5%

increases the number of MA groups responsible for the bonding with hydroxyl groups on the Silica surfaces and consequently increase the blend strength.

The abovementioned results indicated that both compatibilizers SEBS and SEBS-g-MA enhanced the interfacial compatibility of silica-PP composites. The higher tensile strengths are attributed to the formation of an interfacial adhesion layer in presence of compatibilizers. This layer facilitates the stress transfer between the matrix and the filler interface (Nielsen 1966; Pukanszky, 1990). The presence of suitable layer thickness with a good interfacial adhesion provide many advantages such as a filler wetting, enhance the contact between the filler and matrix at their interface, bear and transfer of the applied load from/to polymeric matrix during deformation under applied stresses (Dekkers 1985).

This finding agrees with what is reported in the literature (Du et al., 2002). However, it is worth to mention that the improvement was observed up to 5% after which a decrease in tensile strength was observed due to the lower tensile strength of the SEBS-g-MA.

3.2.3. YIELD STRENGTH

Figure 2 shows the effect of compatibilizer on yield strength of silica/PP composite. It was noticed that the silica/PP composite showed the highest yield strength. While the addition of both surface compatibilizers to the silica/PP system was inversely affected the yield strength (Fig. 2). The higher the concentration of the compatibilizer is the lower the yield strength. The higher yield strength at lower concentration of SEBS and SEBS-g-MA may be explained by the molecules flexibility, their freedom, and higher probability of taking a proper orientation in the force field. While the reduction in the yield strength at compatibilizers higher concentrations can be attributed to the molecules coiling and lose its effect at the interfacial region. Furthermore, it may render the interfacial region stiffer (less flexible), therefore, lower in the yield strength.

The same trend of both grafted and ungrafted SEBS indicates the absence of sufficient number of polar sites on the silica surface that can participate in the adhesion layer between silica and SEBS-g-MA.

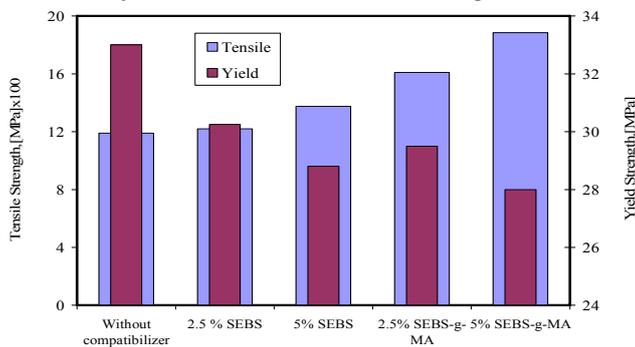


Fig. 2. Effect of the compatibilizer type and amount on the tensile and yield strengths of silica / PP composite

3.2.4. IZOD IMPACT STRENGTH

Figure 3 depicts the effect of compatibilizer on Izod impact strength of silica/PP composite. It was noticed that the addition of either compatibilizers improves the impact strength. A gradual increase in impact strength from 1.85 kJ/m^2 without compatibilizer to 2.7 kJ/m^2 in case of adding a compatibilizer (5% SEBS-g-MA).

The impact strength can be enhanced either by good adhesion between the filler and the matrix or the formation of the elastic interlayer between the filler and the matrix or both reasons together. In our case, the encapsulation of silica inside the SEBS enhances the impact strength due to the good adherence of the silica to the matrix, elasticity of the interfacial layer which leads to minimization of cracks initiation. On the other hand, the good adhesion between silica and PP can prevent coiling of the compatibilizer molecules and the formation of agglomerates.

The superior performance of SEBS-g-MA impact modifiers may be attributed to the interaction of the polar groups in the grafted MA with the silica surface resulting in better interfacial adhesion and substantially formation of small dispersed particles. It was recorded that the inclusion of small well-dispersed particles has a very positive influence on the impact strength of PP matrices (Valji, 1999; Hawley, 2000; Fellahi et al., 1993; Gaskell, 1997).

3.2.5. STRAIN

The effect of type and amount of compatibilizer on strain of silica/PP blends was shown in Fig. 3. It was noticed that both compatibilizers positively affected the strain. Yet some studies followed the influence of processing behavior of the mineral/polymer inside the extruder on the strain. This was carried out by controlling sample stretching during the process (Fourty, 1997). It was concluded that the increase in the orientation of the blend during melting i.e. the extrusion stage, could improve the strain. Moreover it was supposed that a better mineral filler orientation in injection molded parts could improve not only the strain, but also its impact strength (Fourty, 1997).

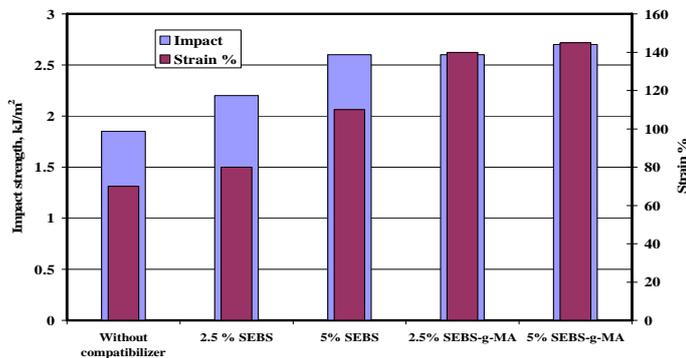


Fig. 3. Effect of the compatibilizer type and amount on the izod impact strength and strain of silica / PP composite

Also, it is obvious from the strain results (Fig. 3) that the formation of adhesive layer and the elasticity of the interface layer leads to the elongation of the composite in percentages higher than the original matrix alone. In case of the ungrafted SEBS the encapsulation of silica within coiled SEBS molecules is the reason behind the formation of a layer with a reasonable elasticity. In case of SEBS-g-MA, the superior performance was referred to the formation of adhesive layer in addition to presence of MA polar groups which enhance the elasticity.

3.3. SUGGESTED COMPATIBILIZATION MECHANISMS

Addition of filler particles, as rigid particles, into polymeric matrix represents spots of stress concentration and induces local micromechanical deformation processes. From one hand, presence of filler particles is advantageous for increasing plastic deformation and impact resistance, but on the other hand, deterioration in the properties of the composite may be occurred. Stress distribution around the filler particle can be modified by encapsulating the filler particles by a compatibilizer layer especially when functionalized compatibilizer was used.

The simultaneous introduction of both filler and compatibilizer is beneficial. It was reported that the PP has a poor impact strength at low temperatures, which is frequently improved by the introduction of elastomers (Karger-Kocsis et al., 1984, Trivedi, N. C., Hagemeyer, R.W., 1994, and Valji, S.E., 1999). However, it may affect other mechanical properties such as elastic modulus, which cannot be accepted in certain applications. Therefore, filler is added to compensate this effect.

Figure 4 represents a schematic representation of the mode of filler and compatibilizer distribution in the matrix in case of the SEBS and SEBS-g-MA which reflects the change in the composite behaviour to applied stresses.

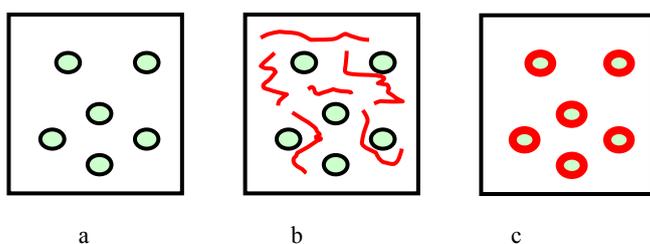


Fig.4. Schematic distribution of the compatibilizer around the filler particles, (a) no compatibilizer, (b) unmodified compatibilizer, and (c) modified compatibilizer

Since SEBS-g-MA has a polar nature and PP is non-polar, the adhesive interaction of the SEBS-g-MA with both filler particles and the polymeric matrix may be described by three mechanisms: (1) the inter-diffusion and entanglement of the poly(ethylene-butylene) segments within the polypropylene matrix that may lead to a good physical anchoring of ungrafted SEBS and the SEBS-g-MA into the PP matrix. (2) presence of ionic interaction between the SEBS-g-MA and the filler surface. First reason may explain a good performance of ungrafted SEBS while both reasons may

3. The effect of surface modifiers e.g. SEBS and SEBS-g-MA was studied at two different additions (e.g. 2.5 and 5%). The results showed that the structure of the surface modifier plays a significant role in forming an adhesion layer between the filler particles and the polymeric matrix. It was found that the SEBS-g-MA performs better due to the presence of MA functional groups that can bond the modifier molecule to the silica surface and at the same time the rest of the molecule as a hydrocarbon chain can bond the modifier molecule to the polymeric matrix. This bonding behaviour helps in the stress transfer between the filler and matrix and consequently the improvement in the mechanical properties.
4. Finally, the working mechanism of the compatibilizer was suggested according to the effect of the compatibilizer on the mechanical properties of the final blend as well as the structure of compatibilizer and filler particles surface.

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Polimery znajdują szerokie zastosowanie od przedmiotów użytku domowego do aplikacji technologicznych. Polimery są łatwe w produkcji, lekkie i elastyczne. Jednakże, mechaniczne właściwości polimerów są niewystarczające w pewnych przemysłowych zastosowaniach. Dla tego, sproszkowane materiały są wprowadzane jako wypełnienie. Pozwala to na pokonanie wspomnianych ograniczeń i zredukowania kosztów wytwarzania rzeczy z plastiku. W przedstawionych badaniach, mączka kwarcowa była dodawana do propylenu dla podwyższenia jego mechanicznej wytrzymałości. Dodatkowo, trój-blokowy polimer (styren-etylen/butylen-styren i anhydryt maleinowy (SEBS-g-MA) były użyte jako odczynniki łączące krzemionkę z PP.

Otrzymane wyniki wskazują na poprawę właściwości mechanicznych po dodaniu krzemionki do matrycy polimerowej (PP). Jednakże, nadmierne dodanie krzemionki prowadzi do zmniejszenia naprężenia. Odwrotne działanie mają odczynniki łączące. Powodują one intensyfikację wiązań ich zwiększenie oraz niweluje naprężenia między cząstkami wypełniacza a matrycą polimerową.

słowa kluczowe: polimery, krzemionka, polipropylen, właściwości mechaniczne, wypełniacze

