Effect of Organoclay and SEBS-g-MA Contents on Constituting Balance between Stiffness vs. Toughness in PP/SEBS-g-MA/Organoclay Nanocomposites

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Abstract: The effect of Maleated Styrene/Ethylene-Butylene/Styrene (SEBS-g-MA) and organoclay contents on the constituting balance between stiffness/strength versus toughness/ductility by melt blending with Polypropylene (PP) in an internal mixer has been investigated. In this direction, 9 different formulations varying in montmorillonite (MMT) and SEBS-g-MA contents were made. X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to evaluate the effects of the Org-MMT and SEBS-g-MA additions on the structure of nanocomposites. XRD traces showed that the characteristic (001) peak of the nanocomposites shifted to the lower angle region. On the other hand, XRD and TEM results showed simultaneous existence exfoliated and intercalated structure in produced nanocomposites. The tensile properties and impact strength of these toughened nanocomposites are discussed in terms of the MMT and rubber contents and morphology. Adding of nanoclay enhanced and improved the stiffness properties (modulus and strength) of produced nanocomposites but reduced their toughness properties (impact strength). On the other hand, adding of SEBS-g-MA reduced stiffness properties but increase toughness properties. Hardness results analyzed and SEM micrograph considered in this project. As a main result, we gain access a best, optimum composition that which, there is a clear trade-off between stiffness/strength versus toughness/ductility, in this work.

Key-Words: Nanocomposites; Toughening; Morphology; SEBS-g-MA; Polypropylene.

1 Introduction

In recent years, polymer nanocomposites reinforced with low volume content of layered silicates have attracted much academic and industrial interest since they exhibit unique physical and mechanical properties. Addition of silicate clays to polymers generally leads to enhanced stiffness and strength but also to very low ductility and toughness \cite{1-4}. The low ductility and inferior toughness performance of nanocomposites limit its application as structural material for engineering applications. To improve the structural integrity to prepare tougher materials, addition of elastomer particles is needed to restore the ductility and impact toughness of polymer-clay nanocomposites \cite{5}. Polypropylene (PP) is a semi-crystalline polymeric material with very interesting mechanical (stiffness and toughness) and thermal properties. It has also easy processability and versatility of applications. However, its application as an engineering thermoplastic is somewhat limited because of its relatively poor impact resistance, especially at low temperature or high impact rate. Another limitation of PP is its poor adhesion to the surface of other phases such as rubber or polar material because of the nonpolar nature of PP. To improve impact toughness of PP, it is common to incorporate with elastomers such as poly (stylene-ethylene-butylene-styrene) (SEBS), ethylene-propylene rubber (EPR) and ethylene-propylene-diene monomer (EPDM); but its stiffness and strength are reduced simultaneously. On the other hand, addition of organoclay (org-MMT) to this polymer, mostly improve the stiffness properties such as modulus, strength, hardness and abrasion resistance; but it usually reduce its impact strength \cite{6-8}.

In this paper 9 different nanocomposites formulations based on PP/SEBS-g-MA/Cloisite 15A were prepared using melt compounding. These formulations are varying in MMT and SEBS-g-MA contents. The results of intercalated/exfoliated structure (morphologic studies) and mechanical tests such as tensile, impact, hardness and etc were reported and discussed. As a main result, we gain access a best, optimum composition that which, there is a clear trade-off between stiffness/strength versus toughness/ductility.

2 Experimental
2-1 Materials
The materials used in this study were PP, SEBS-g-MA, Nanoclay and Irganox1010. The PP used in this study was injection grade with a melt flow index (MFI) of 7.0g/10min (at 180oC and 2.16kg load) produced by Iran national petrochemical Co (NPC) with the commercial name of PI0800. Styrene-ethylene-butylene-styrene triblock copolymer grafted with 1.84%wt of maleic anhydride (SEBS-g-MA) was supplied by Shell Cemical Co under the trade name of Kraton FG 1901X. It has been reported that the ratio of styrene to ethylene/butylene in the triblock copolymer was 28/72 by wt% and its MFI value of 22g/10min (at 230oC and 5kg load). The glass transition of the SEBS-g-MA is -42oC. The Commercial organic modified montmorillonite (O-MMT) clay used was Cloisite 15A supplied by Sothern Clay Product Inc. A natural montmorillonite modified with dimethyl dehydrogenated tallow quaternary ammonium having a cation exchange capacity (CEC) of 125mequiv/100g and a specific gravity 1.66 of an average particle diameter of 8µm. The Irganox1010 was supplied by Ciba Specialty Chemicals. Its density is 1.15g/cm3 and the melting temperature is between 110-125oC. This material is added to prevent of thermal degradation of PP during melt compounding.

2-2 Preparation of nanocomposites
In order to prepare PP/SEBS-g-MA/montmorillonite nanocomposite samples, the SEBS-g-MA, PP and Irganox1010 were premixed initially and then melt mixed in a Haake HBI system 90 internal mixers for 12 min at 180oC and rotor speed of 75rpm, during which the imposed torque reached an equilibrium value. After 2-3 min compounding in internal mixer, the organomodified nanoclay (Cloisite15A) was added before compounding process was finished. The composition of the prepared samples has been presented in Table 1. In all formulations, we added 0.5%wt Irganox1010; because of prevent PP from thermal degradation. In fact, high difference between PP and SEBS-g-MA causes that reaching to homogenous blends especially in short time and low temperature, is hard and when the temperature and shear rate increase so enough, PP degradation is occurred; therefore, used of Irganox1010 is necessary. To compare, one basis sample was prepared in same condition with other samples due to have same stress and thermal memory. After 24hr due to remove trapped stresses, the melt was transformed to a laboratory press (Toyoseiki Mini Test Press M-PS) and compression molded into tensile, impact and hardness test specimens according to ASTM-D 638, ASTM-D 256 and ASTM-D 2240-75, respectively. The pressing temperature was 200oC, pressure 27Mpa, pressing time 6 min. afterwards, the plates were cooled to 130oC with cooling water and then cooled to ambient temperature.

<table>
<thead>
<tr>
<th>Sample Codes</th>
<th>PP(wt%)</th>
<th>SEBS-g-MA(wt%)</th>
<th>Cloisite15A(phr)</th>
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<td>0</td>
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</tr>
<tr>
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<tr>
<td>PSC25-5</td>
<td>75</td>
<td>25</td>
<td>5</td>
</tr>
</tbody>
</table>

Table1. Composition of the prepared samples

2-3 Test methods
Tensile properties were measured by Gotech Servo Control Universal Testing Machine at 23±2oC and at crosshead speed of 10mm/min, according to ASTM-D 638. At least 5 specimens were tested for each sample and the average values were calculated. Notched izod impact strength test was according to ASTM-D 256 by Ceast Resil 5.5 J apparatus at 23±2oC and 50% humidity. For each sample, 6 measurements were carried out and the average values were calculated. Hardness test was according to ASTM-D 2240-75 by Zwick-Roell hardness tester in form of shore D at 23±2oC and 50% humidity. For each sample, 5 measurements were carried out and the average values were calculated. Before the mechanical tests, all samples were kept at room temperature for at least 24hr.

The nanocomposites morphology was characterized by means of scanning electron microscopy (SEM), X-ray diffraction measurement (XRD) and transmission electron microscopy (TEM). The fractured surfaces of impact test specimens were examined by a Cambridge Instruments S360 Analytical SEM. All samples were coated with a thin gold layer in a BIO RAD E5200 auto sputter coater. XRD and TEM were employed to evaluate the dispersion and extent of increase in the basal spacing of nanoclay in the nanocomposites. A Phillips X-Pert WAXS diffractometerunit operating at 40kV and 40mA was used to carry out the experiments at room temperature. The interlayer distance of Cloisite 15A in nanocomposite was calculated from the 001 peak by using Bragg equation. The x-ray source was Cu-Kα radiation with a wavelength of 0.154nm. The diffractograms were scanned in the 2θ range 1.2-10° at a rate of 0.02°s-1. TEM observations were obtained by a Phillips CM200 SEM/TEM apparatus at an acceleration voltage of 200kV, Ultrathin cut (80nm) from the nanocomposites samples were carried out with a C-Reichert OMU3 ultramicrotome under cryogenic conditions.
3 Results and Discussion

3-1 X-ray diffraction analysis

The X-ray diffraction patterns of Cloisite 15A and nanocomposites have been shown in figure 1. The figures indicate for 1% (a), 3% (b) and 5% (c) of nanoclay category of nanocomposites. A peak appeared at an angle of $2\theta=2.64^\circ$ in the XRD pattern of Cloisite 15A which is attributed to the $d_{001}$ basal spacing of 3.34nm. As it can be seen, this peak shifted to lower angles in all categories of nanocomposites, indicating an increase in the distance between the layers of cloisite 15A and indicates that PP and SEBS-g-MA chains have intercalated into the galleries of cloisite 15A. This peak

![XRD patterns of Cloisite 15A and PP/SEBS-g-MA/Cloisite 15A nanocomposites. (a) 1%, (b) 3% and (c) 5% of Cloisite 15A.](image)

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in PSC15-5 and PSC25-5 located at $2\theta=2.38^\circ$ and $2\theta=2.36^\circ$ corresponding to basal spacing of 3.71nm and 3.74nm, respectively. In addition, it is clear that the intensity of $d_{001}$ peak decreases with increasing SEBS-g-MA content due to its low molecular weight and compatibilizing function. As the non-polar PP macromolecule chains can hardly intercalate into the gallery of Org-MMT, the polar function group MA grafted to the SEBS backbone is beneficial for the intercalation polymer chains into the gallery of Org-MMT. It is considered that the interaction via hydrogen bonding between the hydroxyl group of the silicate and MA group grafted to SEBS would assist nanodispersion of the organoclay in polyolefin matrix [9, 10]. However, as it can be observed from figure2, $d_{001}$ diffraction peak has approximately been disappeared in the XRD pattern of the some compositions, which indicate that degree of exfoliated structure increases in such nanocomposites. As a main result from XRD patterns, it can be said, in a sense of morphology, we observe simultaneous existence exfoliated and intercalated structure in best produced nanocomposites. TEM images confirm this claim, in the follow.

3-2 TEM images

Figure 4 shows the TEM images of PSC25-3 nanocomposite, which has best structure from XRD pattern due to higher degree of exfoliation and best mechanical results, as we’ll see. The dark regions and lines represent the intersection of individual (B) and agglomerated (A) silicate layer while the gray base corresponds to the polymer matrix phase. This implies the formation of mixed intercalation and exfoliated structures.

3-3 SEM images

The morphology of the binary and ternary blends was studied with SEM. Some of the mechanical properties are closely associated with the superstructure of polymer blends. Figure 3 shows SEM images from binary (a) blends and ternary nanocomposites (b). It can be seen from SEM images, there is an interface compatibility and better adhesion between PP and SEBS-g-MA. Chemical structure of PP is similar with ethylene-butylene (EB) midblocks from SEBS-g-MA chain. On the other hand, the maleic anhydride groups, grafted with backbone of SEBS-g-MA, have good compatibility with PP molecular chains. These causes an enhancement in mechanical properties especially impact resistance in binary blends via multiple crazing and cavitations toughening mechanisms. The dispersed SEBS-g-MA phase in small average particle size observed in these micrographs that aids for stress transfer across the interface to matrix.
3-4 Tensile properties

Figure 4 (a&b) shows the effect of SEBS-g-MA on the tensile modulus and tensile strength of PP/SEBS-g-MA/Cloisite15A blends. It can be seen that the incorporation of Org-MMT into PP/SEBS-g-MA matrix significantly increased its tensile modulus and tensile strength due to interaction between nanoclay and polymer matrix.

It can also be observed that the addition of SEBS-g-MA into the blend slightly decreased the tensile modulus and tensile strength due to elastomeric nature of SEBS-g-MA. Because of constituting balance between stiffness/strength versus toughness/ductility, the highest value was obtained from tensile test, necessarily, isn’t better nanocomposite, but as we saw by XRD and TEM results, the better structure in the nanocomposites that is believed to be reasonable for the high (not highest) tensile modulus and strength, is PSC25-3. There is good dispersion and high degree of exfoliation (semi-exfoliate) of silicate layers in this case. A high aspect ratio of clay particles which are dispersed more finely coupled with a good interfacial interaction with the polymer matrix will facilitate a good stress transfer to the silicate layers; this consequently leads to improvement of tensile strength [11].

The elongation at break was drastically decreased in the presence of nanoclay (figure 5). This may be due to the restraints on mobility of the polymer chains caused by the intercalated/exfoliated nanoclays [12]. It is clear that the incorporation of SEBS-g-MA increased the elongation at break due to adhesion between PP and SEBS-g-MA.
3-5 Impact strength

Figure 6 indicates the effect of SEBS-g-MA and nanoclay on the impact strength of binary blends and nanocomposites. It can be seen the addition of nanoclay decreases impact strength, like about elongation at break. The reduction in impact strength could be attributed to the immobilization of the macromolecular chains by the clay particles which limited their ability to adapt to the deformation and make the material more brittle. In addition, each silicate layer or aggregates was the site of stress concentration and could act a micro crack initiator [11]. On the contrary, incorporation of SEBS-g-MA significantly improve the impact strength due to improved interfacial adhesion between PP and EB midblock of SEBS-g-MA molecular chain and hydrogen bonding between the hydroxyl group of the silicate and MA group grafted to SEBS, as we said previously.

4 Conclusion

PP/SEBS-g-MA/Cloisite15A nanocomposites were prepared via melt compounding using an internal mixer and followed by compression molding. X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to evaluate the effects of the Org-MMT and SEBS-g-MA additions on the structure of nanocomposites. XRD traces showed that the characteristic (001) peak of the nanocomposites shifted to the lower angle region. On the other hand, XRD and TEM results showed simultaneous existence exfoliated and intercalated structure in produced nanocomposites.
The tensile properties and impact strength of these toughened nanocomposites are discussed in terms of the MMT and rubber contents and morphology. Adding of nanoclay enhanced and improved the stiffness properties (modulus and strength) of produced nanocomposites but reduced their toughness properties (impact strength). On the other hand, adding of SEBS-g-MA reduced stiffness properties but increased toughness properties. Hardness results analyzed and SEM micrograph considered in this project. As a main result, we gain access to a best, optimum composition that which, there is a clear trade-off between stiffness/strength versus toughness/ductility, in this work.

References: