Mechanical and hygrothermal aging study on quaternary polyamide 6/maleated styrene-ethylene-butylene-styrene/clay/short glass fiber hybrid composites

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Abstract: Elastomer toughened PA6 hybrids reinforced with short glass fiber and organoclay were fabricated by melt mixing and injection molding. The structure, mechanical and hygrothermal aging behaviors of such hybrids were investigated. XRD patterns showed the absence of clay diffraction peaks in low angle region. TEM observation showed that the organoclay platelets are fully exfoliated in the PA6 matrix of hybrids. Mechanical tests demonstrated that the incorporation of organoclay into PA6/SEBS-g-MA/SGF composite lead to a significant enhancement in the elastic modulus of hybrids. However, the clay additions reduced the tensile ductility and fracture toughness of hybrids. The tensile stiffness and strength of the clay reinforced hybrids deteriorated but the tensile ductility enhanced markedly upon exposure to hygrothermal aging.

Introduction

Polyamide (PA) composites reinforced with short glass fibers (SGFs) find attractive applications in automotive, building, transportation and chemical sectors. The SGF additions to PAs improve tensile stiffness, strength and thermal stability at the expenses of tensile elongation and impact toughness. Therefore, elastomers such as maleated styrene-ethylene-butylene-styrene (SEBS-g-MA) and maleated ethylene-propylene random copolymer (EPR-g-MA) are selected as toughening agents for improving tensile ductility and impact strength of PA/SGF composites [1-3].

The PA/SGF/SEBS-g-MA micocomposites can be mass-produced through existing melt-compounding techniques such as extrusion and injection molding. The load bearing capacity of short fiber composites depends greatly on the length of fibers embedded within PA6 matrix. The length of fibers is reduced drastically during melt-compounding process due to fiber collision with machinery surface and fiber interaction with viscous polymer. Further, PA/SGF/SEBS-g-MA microcomposites may contain up to 30 wt% SGF, thus increasing melt viscosity of polymer and causing serious wear to the extruder/injection molder.

Recently, there is a high level of interest in using clay particles with nanometer scale to reinforce composite materials. Layered silicates are attractive fillers to reinforce polymers due to their relatively low cost, high strength and stiffness. The incorporation of low clay loadings (e.g., 1-4 wt%) to PA6 generally leads to remarkable enhancement in tensile strength and stiffness. This is due to the exfoliation of clay platelets within PA6 matrix. Furthermore, lower filler loadings facilitate composite processing and reduce the product weight. However, strain-
related properties such as ductility and toughness of PAs degrade markedly as a result of clay additions [4]. To improve the toughness of brittle PA6/clay nanocomposites, elastomer must be added to the composite materials.

More recently, Zhou et al. investigated the effect of organoclay additions on the morphological behavior of PA6 reinforced with short carbon fibers (CFs) [5]. They reported that the organoclay additions reduce the fiber breakage of PA6/CF composites during melt-compounding. Wu et al. demonstrated that the silicate clay enhances the tensile strength and stiffness as well as heat distortion temperature of PA6/CF composites but reduces the impact strength markedly [6]. Accordingly, we attempted to incorporate commercial organoclay (Cloisite 30B) into PA/SGF/SEBS-g-MA composite and studied the microstructure, fracture behavior and hygrothermal aging characteristic of resulting quaternary hybrids. Hygrothermal aging was included because PA6 absorbed moisture readily from the environment, leading to deterioration in tensile strength and stiffness.

Results and discussion

Structural and Morphological Examinations

Figure 1 shows the XRD patterns of pristine organoclay and hybrids investigated. Cloisite 30B displays a characteristic (001) diffracting peak at ~ 4.9°, corresponding to an interplanar distance of 1.79 nm. However, XRD traces of hybrids show the absence of diffraction peaks of organoclay at 2θ ~ 4.9°, indicating exfoliation of silicate layers within PA6 matrix. Wide-angle X-ray diffraction patterns of PA6 and its composites are shown in Fig. 2. By adding organoclay into PA6/SEBS-g-MA/SGF composite, the diffraction peak (2θ = 21°) of γ-form PA6 appears [7]. In other words, the clay addition favors formation of the γ crystalline form but suppresses α-form of PA6. The molecules in α-form are fully extended into zig-zag conformation and grouped into essentially planar, H-bonded sheets [8]. The γ-form derives from a parallel chain arrangement with hydrogen bonding in which amide groups are twisted out of the zig-zag plane of methylene groups.

![Fig. 1. XRD patterns of Cloisite 30B, PA6/SEBS-g-MA/SGF composites with and without Cloisite 30B.](image-url)
**Fig. 2.** WAXD patterns of pure PA6, PAS20G10 composite and clay reinforced hybrids.

**Fig. 3.** TEM micrographs of 2PAS20G10 specimen. (a) Cloisite 30B dispersed in PA matrix; (b) SEBS-g-MA phase dispersed in PA matrix.

To verify the formation of an exfoliated structure in hybrids, TEM was used to examine the morphology of silicate platelets dispersed in PA6 matrix. Figs. 3(a)-(b)
show representative TEM micrographs of the 2PAS20G10 specimen. It can be seen from Fig. 3(a) that the silicate layers are dispersed homogeneously in PA6 matrix and exfoliated into individual nanoscale platelets. The exfoliation of silicate platelets arises from reactive functional groups of PA6 (carboxyl and amine end groups) react with the hydroxyl group of Cloisite 30B [9-13] during compounding. TEM micrograph further reveals that SEBS-g-MA elastomer particles are homogeneously distributed in PA6 matrix as elongated domains (Fig. 3(b)).

Fig. 4. SEM micrographs showing impact-fractured surfaces of (a) PAS20G10, (b) 1PAS20G10 and (c) 3PAS20G10.
Figures 4(a)-(c) are SEM micrographs showing fracture surfaces of the PA6/SEBS-g-MA/SGF composite and its clay reinforced hybrids. For the PAS20G10 composite, its fiber surfaces are covered with matrix material, indicating good interfacial adhesion between SGF and matrix consisting of PA6 and maleated SEBS. Generally, weak physical interaction develops between PA6 and SGF due to their polar structures. However, MA functional group of SEBS-g-MA phase interacts with hydroxyl functional group of SGF during melt compounding via the following reaction:

In contrast, the fiber surfaces of 1PAS20G10 hybrid are covered with a small amount of matrix material. When the clay content is increased to 5.1 wt%, the fiber surfaces of 3PAS20G10 hybrid are very clean. This implies that the organoclay weakens the interfacial adhesion between SGF and matrix.

**Mechanical behavior**

The tensile and impact properties of PA6/SEBS-g-MA/SGF composite and its clay reinforced hybrids are listed in Table 1. The Young’s modulus of hybrids increases considerably with increasing clay content. The stiffness of 3PAS20G10 hybrid is 55% higher than that of PAS20G10 composite. However, the tensile elongation and impact strength of hybrids decrease markedly with increasing clay content as expected. The mechanical properties of quaternary hybrids are rather complicated and depend greatly from the contribution of each phase components. The strength of short fiber reinforced composites derives mainly from effective load transfer from the matrix to fibers during mechanical loading. Good interfacial adhesion between SGFs and matrix ensures effective load transfer mechanism. Despite the fact that clay platelets exfoliate completely in polymer matrix, the reinforcing effect of clay platelets is compensated by weaker fiber-matrix interfacial bonding. In other words, the increase in tensile strength caused by the clay exfoliation is offset by the decrease in composite strength due to weaker fiber-matrix bonding. Accordingly, the clay additions only lead to a slight increase in tensile strength of hybrids.

**Tab. 1. Mechanical properties of PAS20G10 composite and its nanocomposites.**

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Young’s Modulus (GPa)</th>
<th>Tensile strength at break (MPa)</th>
<th>Elongation at break (%)</th>
<th>Izod Notched Impact energy (kJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAS20G10</td>
<td>1.41±0.12</td>
<td>34.6±0.1</td>
<td>193.9±47.5</td>
<td>6.7±0.5</td>
</tr>
<tr>
<td>1PAS20G10</td>
<td>1.70±0.02</td>
<td>34.8±0.1</td>
<td>72.4±8.8</td>
<td>5.7±0.5</td>
</tr>
<tr>
<td>2PAS20G10</td>
<td>1.89±0.06</td>
<td>35.3±0.4</td>
<td>29.4±2.7</td>
<td>4.1±0.2</td>
</tr>
<tr>
<td>3PAS20G10</td>
<td>2.18±0.04</td>
<td>35.5±0.2</td>
<td>11.6±0.1</td>
<td>2.3±0.2</td>
</tr>
</tbody>
</table>

In this study, essential work of fracture (EWF) was used to determine the fracture toughness of composite materials. This approach was originally developed by
Broberg [14], and widely used to determine the fracture toughness of elastomer toughened polymer microcomposites and nanocomposites due to its simplicity [2, 4]. The approach assumes that the total energy ($W_f$) required to fracture a notched specimen can be separated into two components: essential work of fracture ($W_e$), being the work required to create new surfaces in inner fracture surface zone and is surface related, and non-essential work ($W_p$). The latter relates to the energy dissipated in outer plastic zone and is volume related. Hence, the total fracture work ($W_f$) can be written as:

$$W_f = W_e + W_p$$  \hspace{1cm} (1) \\
$$W_f = w_e L t + \beta w_p L^2 t$$  \hspace{1cm} (2) \\
$$w_f = \frac{W_f}{L t} = w_e + \beta w_p L$$  \hspace{1cm} (3) \\

where $w_f$ is the specific total fracture work, $w_e$ and $w_p$ are the specific essential fracture work and specific plastic work, respectively; $L$ is the ligament length, $t$ is sample thickness, and $\beta$ is a shape factor of the plastic zone. An important prerequisite of EWF approach is that crack propagates only after the ligament has fully yielded and the plastic zone is scaled with the square of the ligament length.

Fig. 5. Load-displacement curves of (a) PAS20G10 and (b) 3PAS20G10 specimens having various ligament lengths.

Figures 5(a)-(b) shows typical load-displacement curves for PAS20G10 and 3PAS20G10 composites. Apparently, these materials display completely stable crack propagation for various ligament lengths. The variation of $w_f$ versus $L$ for these specimens is shown in Fig. 6. The $w_e$ and $w_p$ values can be determined from the intercept and slope of regression lines. For comparison purpose, the fracture behavior of PA6/SEBS-g-MA 80/20 blend was also studied. The results are listed in Table 2. Apparently, addition of 10 wt% SGF to the PA6/SEBS-g-MA blend enhances $w_e$ but reduces $\beta w_p$. Thus, SGF toughens the PA6/SEBS-g-MA blend effectively [2]. The PAS20G10 composite exhibits much higher fracture toughness than that of PA6/SEBS-g-MA 80/20 blend, and commonly termed as super-tough composite [15]. From Table 2, the incorporation of Cloisite 30B into PAS20G10 composite reduces both $w_e$ and $\beta w_p$. This indicates that the matrix plasticity is constrained by the exfoliated clay platelets.
Fig. 6. Plots of the specific total work of fracture, $w_t$, against ligament length for PAS20, PAS20G10 and hybrid nanocomposites.

Tab. 2. EWF parameters for PAS20 blend and composites investigated. $R$ is correlation coefficient.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>$w_e$ (kJ/m$^2$)</th>
<th>$\beta w_p$ (MJ/m$^3$)</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAS20</td>
<td>17.49</td>
<td>8.85</td>
<td>0.85</td>
</tr>
<tr>
<td>PAS20G10</td>
<td>22.05</td>
<td>4.98</td>
<td>0.91</td>
</tr>
<tr>
<td>1PAS20G10</td>
<td>15.22</td>
<td>1.87</td>
<td>0.31</td>
</tr>
<tr>
<td>2PAS20G10</td>
<td>8.88</td>
<td>1.16</td>
<td>0.48</td>
</tr>
<tr>
<td>3PAS20G10</td>
<td>4.51</td>
<td>0.48</td>
<td>0.39</td>
</tr>
</tbody>
</table>

Hygrothermal aging

Polyamides exhibit high water absorption because of the amide functionality [16]. The absorption of water results in a dimensional change and a lowering of the glass transition temperature ($T_g$). However, the tensile elongation and impact strength of polyamides increase considerably since the amorphous phase is softened by the plasticizing effect of the absorbed water molecules [17, 18]. For fiber-reinforced polymer composites, the absorbed water results in more detrimental effects on the mechanical properties since water interacts with polymer matrices (plasticization) and attacks the fiber-matrix interfaces [19, 20]. Moisture penetration into composite materials takes place via diffusion of water molecules into the matrix, and capillary flow along the fiber-matrix interface, followed by diffusion from the interface into the matrix. Recently, several researchers studied the effect of clay addition on water absorption of PA/clay nanocomposites [21-28]. Their results indicated that strong interaction between exfoliated silicate layers and PA6 matrix reduces the water absorption as a result of barrier effect.

The combined effects of moisture and temperature exposure on the mechanical properties (hygrothermal aging) of PA6-based composites at 60 and 90 °C are summarized in Table 3. It is obvious that hygrothermal aging (HA) deteriorates the
tensile strength and Young’s modulus while the elongation at break increases. This can be attributed to the plasticization of PA6 matrix. Compared to the PAS20G10 composite, organoclay addition further degrades the tensile strength of hybrids as revealed by lower percentage retention of strength. As mentioned above, organoclay addition weakens the bonding between the SGF and matrix, thereby facilitating water attack at this region. Figs. 7(a)-(c) show the effect of HA treatment of the tangent loss ($T_g$) of PA6 and its composites. Apparently, the glass transition of PA6 shifts from 71.1 °C in the as-molded condition to -1.71 °C after HA treatment at 60 °C. The SGF and organoclay additions further reduces the $T_g$ of PA6 matrix of the composites investigated (Table 3).

Tab. 3. Effect of hygrothermal aging on mechanical properties of PA6 and its composites investigated.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Tensile Properties</th>
<th>AR</th>
<th>HA at 60 °C</th>
<th>HA at 90 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA6</td>
<td>Young’s Modulus (MPa)</td>
<td>2343</td>
<td>410.6 (17.5%)</td>
<td>367.7 (15.7%)</td>
</tr>
<tr>
<td></td>
<td>Tensile Strength (MPa)</td>
<td>68.0</td>
<td>28.7 (42.2%)</td>
<td>28.7 (42.2%)</td>
</tr>
<tr>
<td></td>
<td>Elongation at break (%)</td>
<td>52.8</td>
<td>128.2</td>
<td>216</td>
</tr>
<tr>
<td>PAS20</td>
<td>Young’s Modulus (MPa)</td>
<td>1568</td>
<td>367.9 (23.5%)</td>
<td>336.0 (21.4%)</td>
</tr>
<tr>
<td></td>
<td>Tensile Strength (MPa)</td>
<td>41.8</td>
<td>26.3 (62.9%)</td>
<td>23.5 (56.2%)</td>
</tr>
<tr>
<td></td>
<td>Elongation at break (%)</td>
<td>60.2</td>
<td>455.3</td>
<td>252.7</td>
</tr>
<tr>
<td>PAS20G10</td>
<td>Young’s Modulus (MPa)</td>
<td>1881</td>
<td>444.3 (23.6%)</td>
<td>385.5 (20.5%)</td>
</tr>
<tr>
<td></td>
<td>Tensile Strength (MPa)</td>
<td>41.6</td>
<td>23.1 (55.5%)</td>
<td>23.15 (55.6%)</td>
</tr>
<tr>
<td></td>
<td>Elongation at break (%)</td>
<td>46.2</td>
<td>280.7</td>
<td>221.3</td>
</tr>
<tr>
<td>1PAS20G10</td>
<td>Young’s Modulus (MPa)</td>
<td>2118</td>
<td>507.3 (24.0%)</td>
<td>463.1 (21.9%)</td>
</tr>
<tr>
<td></td>
<td>Tensile Strength (MPa)</td>
<td>41.5</td>
<td>19.7 (47.5%)</td>
<td>20.9 (50.4%)</td>
</tr>
<tr>
<td></td>
<td>Elongation at break (%)</td>
<td>32.3</td>
<td>114.7</td>
<td>78.2</td>
</tr>
<tr>
<td>2PAS20G10</td>
<td>Young’s Modulus (MPa)</td>
<td>2258</td>
<td>553.2 (24.5%)</td>
<td>483.2 (21.4%)</td>
</tr>
<tr>
<td></td>
<td>Tensile Strength (MPa)</td>
<td>41.8</td>
<td>19.0 (45.5%)</td>
<td>21.1 (50.5%)</td>
</tr>
<tr>
<td></td>
<td>Elongation at break (%)</td>
<td>19.3</td>
<td>76.7</td>
<td>62.7</td>
</tr>
<tr>
<td>3PAS20G10</td>
<td>Young’s Modulus (MPa)</td>
<td>2482</td>
<td>580.3 (23.4%)</td>
<td>498.2 (20.1%)</td>
</tr>
<tr>
<td></td>
<td>Tensile Strength (MPa)</td>
<td>41.9</td>
<td>18.9 (45.1%)</td>
<td>19.7 (47.0%)</td>
</tr>
<tr>
<td></td>
<td>Elongation at break (%)</td>
<td>7.5</td>
<td>41.2</td>
<td>26.7</td>
</tr>
</tbody>
</table>

AR: As molded condition. The values in parentheses are the percentage retention of the mechanical properties in HA condition.
Conclusions
Quaternary PA6/SEBS-g-MA/clay/short glass fiber hybrid composites were fabricated by melt mixing and injection molding. The structure, mechanical and hygrothermal aging behaviors of such hybrids were studied. XRD and TEM examinations showed that the organoclay platelets are fully exfoliated in PA6 matrix of the hybrids. Mechanical measurements indicated that the incorporation of organoclay into
PA6/SEBS-g-MA/SGF composite lead to a significant enhancement in the elastic modulus of hybrids. However, the clay additions reduced the tensile ductility and fracture toughness of the hybrids. Finally, the tensile stiffness and strength of the PA6/SEBS-g-MA/SGF composite and clay reinforced hybrids deteriorated but the tensile elongation enhanced markedly upon exposure to hygrothermal aging. The glass transition temperature of the PA6 matrix of composites shifted to low temperatures due to the water absorption.

**Experimental part**

**Materials**

PA6 (Durethan B30S) and SEBS-g-MA grafted with 1.84 wt% of MA (Kraton FG 1901X) were purchased from Shell Co. and Bayer Co.(Hong Kong), respectively. Short glass fiber (SGF, 144A-14C) with a length of ~ 4mm and a diameter of ~ 10µm was obtained from Owens Corning. The organoclay used was Cloisite 30B supplied by Southern Clay Products (USA). All materials were dried at 100 °C for 48 h prior to melt processing.

**Preparation of hybrids**

The matrix material of hybrids was PA6/SEBS-g-MA/SGF 80/20/10 (wt%) composite designated as PAS20G10. Clay loadings of 1.6, 3.3 and 5.1 wt % were incorporated into PAS20G10 composite, forming quaternary hybrids designated as 1PAS20G10, 2PAS20G10 and 3PAS20G10. These hybrids were prepared by initial melt mixing of Cloisite 30 with PA6 at 30 rpm, followed by granulized into pellets. These pellets were then mixed with SEBS-g-MA and SGF at 35 rpm in a twin-screw Brabender extruder. The blending temperature was set at 235 °C. The extrudates were pelletized and dried again before injection molding. Such hybrid pellets were directly injection-molded into plaques. The mold temperature was maintained at 40 °C, and the barrel zone temperature profiles were set at 245 °C, 240 °C and 235 °C.

**Microstructural examination**

X-ray diffraction (XRD) measurements were performed with a diffractometer (Siemens D500) equipped with Ni-filtered CuKα radiation having a wavelength of 0.154 nm. The diffractometer was operated at 40 kV. The scanning rates employed were 1°/min for 2θ =1-10° and 2°/min for 2θ =1-50°.

The specimens for transmission electron microscopy (TEM) observation were cut from injection molded plaques using a Leica Ultracut-S ultramicrotome. The films were retrieved onto copper grids and then placed into the specimen chamber of TEM (Philips CM-20).

**Mechanical Measurements**

Dog-bone tensile specimens were cut from injection molded plaques. Tensile tests were performed at room temperature using an Instron 5567 tensile tester at a crosshead speed of 10 mm/min (ASTM D638). The notched Izod impact strength was determined with a CEAST impact tester (ASTM D256). Five specimens of each material were used for mechanical tests and the average values were collected. The fractured surfaces of impact specimens were examined in a scanning electron
microscope (Jeol JSM 835). The fracture surfaces of the samples were coated with a thin gold layer prior to SEM observation.

Single-edge notched three-point-bend (SEN-3PB) specimens were used for fracture toughness characterization. SEN-3PB specimens with a dimension of 70 mm × 12.5 mm × 3.2 mm were cut from injection molded plaques in which the longitudinal direction of specimens was paralleled to the melt flow direction. They were loaded in compression using an Instron 5567 at room temperature under a rate of 1 mm/min. Sharp notches with different ligament lengths \( (L) \) were made by a fresh razor blade after the formation of saw cut slot. The exact \( L \) value was measured with a travelling microscope (Topcon profile projector VP-300, Topcon Optical Lt., Japan). The load vs. displacement plots for the specimens were recorded and analyzed.

Dynamic mechanical measurement

The glass transition temperature of specimens investigated was performed using a dynamic mechanical analyzer (Model 2980) at a fixed frequency of 1 Hz and at an oscillation amplitude of 10 mm. The samples with dimensions of 60 mm × 13 mm × 3.2 mm were examined at temperatures ranged from \(-100 \) to \(140 \) °C with a heating rate of \(5 \) °C /min under nitrogen.

Hygrothermal aging

Dog-bone tensile specimens were dried in an oven at \(70 \) °C for \(48 \) h, and denoted as AM in this article. Other specimens were immersed in water at \(60 \) °C for \(240 \) h and \(90 \) °C for \(60 \) h respectively. After immersion, the specimens were removed from water, dried and then subjected to tensile tests.

References