Preparation of Highly Rubber-toughened Nylons

Hossein Bordbar1,2, Ali Akbar Yousefi*1,3, and Ahmad Ramazani Saadatabadi2

(1) Iran Polymer and Petrochemical Institute, P.O. Box: 14965/159, Tehran, Iran
(2) Department of Chemical and Petroleum Engineering, Sharif University of Technology, P.O. Box: 11365-9465, Tehran, Iran
(3) Institute for Colorants, Paint and Coatings, P.O. Box: 16765/656, Tehran, Iran

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ABSTRACT

Nylon 6 and 66 were toughened with EPDM-g-MA and SEBS-g-MA and steady-state rheological behaviour of rubbers, nylons and their blends and mechanical properties of nylons and their rubber-toughened blends were investigated. The EPDM maleic grafting preparation was performed in the framework of this study where SEBS-g-MA was obtained from a commercial source. The results showed the ultra-toughened SEBS-g-MA blends, whereas EPDM blends under the same blending conditions did not show a significant improvement in toughness. In case of EPDM toughened blends an average of some micrometers was observed for the dispersed EPDM particles. Impact and tensile properties of the toughened blend with 20% of SEBS-g-MA rubber showed about 1540% improvement in impact and 240% in elongation-at-break of the blend as compared with those of neat nylon, whereas these properties only showed 30% reduction in Young’s modulus of the blends. Rheological measurements revealed the closeness of the viscosity of SEBS-g-MA and nylon 66, whereas the viscosities of EPDM rubber and nylons were found very far from each other under the blending conditions. Morphological observations using SEM technique revealed a co-continuous and a probable nano-scale-dispersed SEBS-g-MA in nylon matrix.

INTRODUCTION

Polyamides are commercially important polymers amongst crystalline engineering thermoplastics. This is mainly due to their high performance characteristics such as high melting points, good mechanical strength and ductility, as well as excellent resistance to solvents, fatigue and abrasion. Polyamides (nylons) are commonly synthesized from two distinguished routes:

1. Melt polymerization of the salts of diamines and dicarboxylic acids, nylon 66, nylon 46, and nylon 12.
2. Melt polymerization of ω-amino acids or lactam monomers, nylon 6, nylon 11, and nylon 12.
A common structural feature of nylons is their tendency towards formation of H-bonding. This characteristic favours strong intra- and inter-chain association. Their superior mechanical and physical properties stem from this segmental association and crystallization. The high performing nylons due to their ability to be injection moulded to the desired shapes are often replacing metals in automotive, consumer, electrical and power tool applications. The rigidity of the nylons in the segmental levels limits their applications. However, as demanding application grows up, there has been an increasing need to modify fracture behaviour of these polymers [1,2].

Crystalline thermoplastic polymeric materials such as low carbon monomer nylons are very sensitive to craze and crack propagation and so their toughness and impact resistance properties are relatively low. Nylon 6 and 66 are relatively low cost engineering thermoplastics that have been found so many applications including automotive industry. However, relatively low impact and bending resistance of these materials especially at low temperatures and high deformation rates, restrict applications of these materials. Rubber toughening can be considered as an economical and effective method to toughen and extend applications of nylon without any important increase in its price or decrease in its engineering properties [3]. Many rubbers such as EPR, EPDM (ethylene-propylene-diene monomers), NR (nitrile rubber), SBR (styrene-butadiene rubber), and SEBS (styrene-ethylene-butadiene-styrene tri-block copolymer) have been successfully used in toughening of thermoplastic materials [1-26]. However, most rubbers are not compatible with nylon and cannot be finely dispersed in it. However, most of non-modified rubbers coarsely disperse in the thermoplastic matrix with an average diameter about 50 microns. To remove this shortcoming, the rubber is to be modified to produce microscale particles. Grafting polar and reactive monomers such as maleic anhydride and carboxylic acid groups onto rubbers provide the necessary compatibility for rubbers with nylons [3-5].

The effect of adhesion of rubber to nylon and rubber particle size on the impact properties of ethylene/propylene rubber modified nylon 6 has been studied [4-6]. It was found that at a certain rubber content and rubber adhesion, there exists a critical rubber particle size at which the ductile-brittle transition happens. It was also found that as rubber concentration augments, the rubber particle size becomes coarser at this transition. Borggreve et al. studied EPDM toughened nylon 6 and found that position of brittle-ductile transition is independent on \(T_g\) of thermoplastic matrix. They also found that the transition temperature decreases with increasing rubber concentration and particle size reduction [7-9]. Oshinski et al. studied the effect of rubber, its modified forms and molecular weight of nylon on rubber particle size and its distribution [10-12]. They also reported that increases in content of maleic anhydride on SEBS and molecular weight of nylon leads to a decrease in particle size of the rubber. The SEBS copolymer is known as a well-characterized thermoplastic elastomer. The maleated form of this copolymer (SEBS-g-MA) is successfully used in toughening and compatibilization of different binary and ternary blends and composites of nylons and other similar polymers [13-26].

In this paper we report the effects of different functionalized rubbers on the rheology and mechanical properties of rubber-modified nylons. The morphology of the resulting blends is also presented. The superior properties of SEBS-g-MA toughened nylons are also highlighted. The novelty of this work remains in addition of SEBS-g-MA and finding the optimum processing conditions via rheological measurements to achieve a 16-fold improvement in impact properties of nylon.

**EXPERIMENTAL**

**Materials**

Nylon 66 (Akulon S223 E) and nylon 6 (Akulon F223 D) from DSM Co. and maleic anhydride grafted SEBS (Kraton™ FG1901X) from Shell Corporation and also four EPDM grades presented in Table 1, used as raw materials in this work. Dicumyl peroxide and maleic anhydride both from Merck Co. (Germany) were used.

**Procedures**

Grafting maleic anhydride on EPDMs was carried out in a Haake batch mixer (System 90) and compounding of rubber and nylons accomplished in an inter-
The optimum grafting conditions are as follows:

**Route A:** Maleic anhydride (2 wt%) was grafted onto EPDM in the presence of dicumyl peroxide as initiator (0.2 wt%) in a Haake batch mixer at 180°C and 40 rpm during 5 min in three steps. At first, rubber was heated and sheared in the internal mixer until torque became constant (about 2 min). Then, MA was introduced in the mixer and left to be mixed for the next 2 min till the torque became constant again. In the third step, dicumyl peroxide was added and shearing was continued for the next 1 min to complete the grafting reaction. Finally, mixing was stopped; the grafted rubber was removed and after cooling it was cut into small pieces.

**Route B:** To overcome the problem of viscosity increase during grafting route A, the peroxide initiator was premixed with rubber on a two-roll mill at 60°C. In this grafting route, the initiator is well mixed with rubber and rubber mastication happens as well. This process decreases the viscosity of rubber phase to an extent as low as that of nylon. Then the reaction was completed in the internal mixer as in route A.

Using viscosity data and also limitations of twin-screw extruder (co-rotating or counter-rotating intermeshing screws), temperature and screw rotation speed were adjusted in such a way that to have a shear rate at which the viscosity of both phases were as close as possible. For preparation of nylon 6/rubber blends, the screw rotation speed was fixed at 30 rpm (co-rotating twin extruder) and temperature profile of the extruder was 210, 225, 235, 238, and 235°C (die). The melt residence time in the extruder was 2 min. In preparation of nylon 66/rubber blends both co-rotating and counter-rotating extruders operated at 50 rpm. The temperature profile of the co-rotating extruder was 240, 250, 265, 275, and 280°C (die) with a 2 min melt residence time. In case of counter-rotating extruder the temperature profile was 230, 240, 250, 260, 265, and 260°C (die) with a 90 s melt residence time. To improve the mixing quality the blends were double passed in the co-rotating twin-screw extruder. In case of nylon/SEBS-g-MA blends, co-rotating extruder’s temperature profile was set at 230, 245, 260, 270, 275, and 275°C (die) and a melt residence time about 3 min was attained.

Tensile and impact test samples with and without notch were produced by an injection moulding machine. Apparent viscosity of melt materials was measured on a capillary viscometer (Instron 3211) (L/D=36 and L=53.24 mm). Tensile tests were carried out on an Instron 1113 according to ASTM-D638 and with rate of 4 mm/min. Charpy impact samples were impacted according to ASTM-D256 using a 20 kJ impact tester from Santam Co. (Iran). Blend morphologies were studied using a scanning electron microscope (Cambridge S360).

**RESULTS AND DISCUSSION**

**Nylon/EPDM-g-MA Blends**

To achieve the necessary compatibility between EPDM rubber and nylon 6 and 66 at first step, EPDM-g-MA was prepared according to our previous works [13,24]. The viscosity ratio of the two components to be mixed (by simple shearing) is a crucial criterion for achieving a good dispersion of minor-phase inclusions in the matrix. If the viscosity of the minor phase is four times larger than that of the matrix the critical capillary number $(C_{a,cr})$ cannot be attained, therefore, the shear stresses will never overcome the interfacial stresses and the particle size of the inclusions do
not decrease at all (no dispersive mixing will happen) [25,26]. In the other words, the maximum stress transfer between the phases during shear mixing of two different liquids was accomplished whenever the viscosity ratio of the liquids approaches unity:

$$\frac{\eta_{\text{dispersed phase}}}{\eta_{\text{matrix}}} \rightarrow 1$$

As a well known rule, a good dispersion of rubber inclusions in thermoplastic matrices is desired and always sought [1-12]. The ideal situation is where the rubber is finely dispersed and evenly distributed in the thermoplastic matrix. The highest rate of interaction and toughening efficiency is achieved whenever the components are mixed in a nano-scale or at a molecular level. Due to these facts that the polymers are high-viscosity materials and the shear rates and shear stresses applied by extruders during polymer blending are modest, the only remaining choices for achieving fine dispersions are rubber functionalization and viscosity matching. In the following paragraph the effect of viscosity matching on the rubber efficiency in toughened nylon is described.

Apparent viscosity of rubbers and nylons were measured under different conditions and tried to find mixing conditions under which the viscosity of the components are as close as possible. Figures 1 and 2 present the apparent viscosity of four EPDM grades against shear rate at 265°C and 285°C, respectively. In Figures 3 and 4 apparent viscosity of nylon 6 and 66
are presented, respectively. From Figures 1 to 4 it can be concluded that the viscosity of Polysar 345 is the closest one to the viscosity of nylons. Decreasing temperature and increasing shear rate bring the viscosity of nylons and EPDMs close together (Figures 1 to 5). Therefore, for mixing these polymers maximum screw-rotation speed and minimum temperature are favoured. However, the melting point of nylons and the necessary residence time for proper mixing limit the optimum conditions. The differences between the viscosity of Polysar-g-MA and both nylons at all experimental temperatures are very far from unity (Figures 6 and 7). As it is observed in these figures,

**Table 2.** Mechanical properties of nylon 66/EPDM-g-MA blends.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elongation-at-break</th>
<th>Young’s modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Impact strength (kJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N66</td>
<td>15</td>
<td>19.5</td>
<td>70.5</td>
<td>5.4</td>
</tr>
<tr>
<td>15%R-1 One pass mixing in co-rotating twin-screw extruder (Grafting route A)</td>
<td>8</td>
<td>14.5</td>
<td>44</td>
<td>7.2</td>
</tr>
<tr>
<td>effect</td>
<td>-47%</td>
<td>-25.6%</td>
<td>-37.5%</td>
<td>+33.3%</td>
</tr>
<tr>
<td>15%R-2 Double-pass mixing in co-rotating twin-screw extruder (Grafting route A)</td>
<td>8.5</td>
<td>14.5</td>
<td>43</td>
<td>7.5</td>
</tr>
<tr>
<td>effect</td>
<td>-43.3%</td>
<td>-25.6%</td>
<td>-39%</td>
<td>+38.9%</td>
</tr>
<tr>
<td>15%R-3 One pass mixing in counter-rotating twin-screw extruder (Grafting route A)</td>
<td>7</td>
<td>14.5</td>
<td>44</td>
<td>9.76</td>
</tr>
<tr>
<td>effect</td>
<td>-53.3%</td>
<td>-25.6%</td>
<td>-37.5%</td>
<td>80.7%</td>
</tr>
<tr>
<td>10%R-B One pass mixing in counter-rotating twin-screw extruder (Grafting route B)</td>
<td>15.5</td>
<td>17.7</td>
<td>50.5</td>
<td>9.3</td>
</tr>
<tr>
<td>effect</td>
<td>+3.3%</td>
<td>-9.2%</td>
<td>-28.4%</td>
<td>+72.2%</td>
</tr>
<tr>
<td>20%R-B effect</td>
<td>19.25</td>
<td>15</td>
<td>42</td>
<td>10.9</td>
</tr>
<tr>
<td>effect</td>
<td>+28.3%</td>
<td>-23.0%</td>
<td>-40.4%</td>
<td>+101.8%</td>
</tr>
</tbody>
</table>

- Decrease in property, ++ increase in property.
the viscosity ratio rises from 2 to larger 4 as temperature goes up. Consequently, a good dispersion of EPDM-g-MA in nylon cannot be obtained. Therefore, poor mechanical properties are expected for these blends.

Mixing nylon and EPDM-g-M together using our twin-screw extruder (L/D=15) under optimum conditions for three times only produces a mean particle size larger than 10 microns for the rubber inclusions. Figure 8 presents the SEM (magnification 200×) of nylon 6/EPDM-g-MA (85/55) blend (grafting route A). Mean particle size is larger than 10 microns and some particles with diameter larger than 50 microns are also observed.

To improve elongation and impact of EPDM modified nylon the average particle size of dispersed phase must be less than 1 micron [4,5]. The EPDM-g-MA from grafting route B was also blended with nylon. SEM Micrograph of modified nylon with this rubber presented in Figure 9 shows an average particle size distribution about 3 microns for dispersed phase, which is much less than previous one. However, it is still much larger than 1 micron, which is necessary in high efficiency rubber toughening and is clearly observable in mechanical properties of toughened nylons. Some other SEM micrographs of blends having different rubber contents and obtained under different mixing conditions show that the diameter of particles does not change so much and levels off around 3 microns. These results reveal that using
our EPDM-\(\text{g}\)-MA and machinery, an effective rubber toughening of nylons is not attainable and that rubber or mixing machines have to be changed (Table 2). Impact and tensile tests of different blends of EPDM-\(\text{g}\)-MA (grafting route A) show that the impact strength of these samples does not increase considerably even after twice mixing in the extruder. Table 2 shows that for all blends elongation-at-break, tensile strength, and modulus are reduced, whereas impact strength is slightly increased. Data presented for the double-pass mixed blends in Table 2 also show that double mixing cannot change these results considerably. Data of the blends (Table 2) prepared in counterrotating twin-screw extruder equipped with a blister ring show that although this type of screws improves blend properties, it does not provide an effective rubber toughening system as mentioned earlier. The trend of presented results does not change considerably with compositions of compound. Results for two blends prepared with 10 (10R) and 20 wt\% (20R) of EPDM-\(\text{g}\)-MA (grafting route B) are presented in Table 2. Comparing contents of Table 2 shows that elongation-at-break for this modified nylon is considerably increased; whereas its impact property is not completely satisfactory. It can be probably due to rubber particle size, which is still larger than the critical size [2-3] and also a lack of strong interactions between rubber and MA. These results show that considering the methods for decreasing particle size and improving toughness of compound were correct, but it should be improved. This subject is still under investigation.

**Figure 10.** Apparent viscosity of SEBS-\(\text{g}\)-MA versus shear rate at different temperatures.

**Figure 11.** Apparent viscosities and viscosity ratios of nylon 66 and SEBS-\(\text{g}\)-MA at: (a) 265°C, (b) 275°C, and (c) 285°C.

**Nylon/SEBS-\(\text{g}\)-MA Blend**

Apparent viscosity of SEBS-\(\text{g}\)-MA at different temperatures is presented in Figure 10. As it is observed, the flow curves of this copolymer are very different...
the flow curves of this copolymer are very different from those of EPDMs (Figures 1, 2 and 5). In the case of EPDMs a straight line is resulted, whereas for SEBS-g-MA a concave line with two different power-law indices is obtained at all three experimental temperatures. This behaviour is very similar to those of nylons (Figures 3 and 4). Apparent viscosity of SEBS-g-MA, that of nylon 66 and their ratios at 265°C and 275°C are presented in Figures 6a and 6b. Figure 11 shows that viscosity behaviour versus shear rate for SEBS-g-MA and nylon 66 at 265°C are similar and at 200 s⁻¹ are almost the same. Therefore, at this temperature a very good dispersion of this rubber in nylon 66 is attainable.

As mentioned, a SEBS-g-MA with rheological properties much similar to nylons was used. SEBS-g-MA was fed directly into the twin-extruder hopper. By starve-feeding, a residence time about 3 min in counter-rotation mode was attained. SEM Micrograph of the cryogenic fracture cross-section of this blend is presented in Figure 12. The figure shows that the rubber particle size is submicron. Almost a very fine continuous phase is observed for this blend, which reveals an excellent dispersion of phases and compatibility between two phases [4-5].

Table 3. Mechanical properties of nylon 66/SEBS-g-MA blend.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elongation-at-break</th>
<th>Young’s modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
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</tr>
</thead>
<tbody>
<tr>
<td>N66</td>
<td>15</td>
<td>19.5</td>
<td>70.5</td>
<td>5.4</td>
</tr>
<tr>
<td>20%R-S</td>
<td>51</td>
<td>14</td>
<td>40</td>
<td>88.5</td>
</tr>
<tr>
<td>Effect</td>
<td>+240%</td>
<td>-28.2%</td>
<td>-43.2%</td>
<td>1538.9%</td>
</tr>
</tbody>
</table>

- = decrease in property. += increase in property.

For preparation of rubber toughened nylon 66 with SEBS-g-MA, as already mentioned this rubber is directly incorporated in nylon in the twin-screw extruder’s feeder. Impact and tensile results for blends containing 20% rubber are shown in Table 3. Comparison of mechanical properties of this rubber-toughened nylon with those of virgin nylon shows 1540% and 240% increase in impact and tensile properties, respectively. These are very interesting results and show excellent toughening effect of SEBS-g-MA on nylon. Similarity of rheological behaviour (Figures 3 and 4) and also compatibility of these two polymers should be responsible for producing such interesting results, which are not attainable using EPDM-g-MA. The coincidence of flow curve of nylon 66 and to that of SEBS-g-MA at 275°C and existence of two power-law indices in the same shear rate range for both components result in the efficient toughening of nylon by this rubber.

CONCLUSION

Grafting four EPDM grades with MA in a batch mixer produces high viscosity rubbers that are not suitable for producing submicron particle during mixing in nylon matrix in a twin-screw extruder with a low L/D and short residence time under any conditions (route A). Premixing peroxide initiator with the rubber on a two-roll mill reduces the viscosity of rubber phase (route B) and improves interactions between rubber and the matrix. However, these grafting routes are not effective in toughening of nylons. Therefore, the mechanical properties of the blends are not effectively improved as compared to those of the neat nylon.
SEBS-g-MA flow curve coincides to that of nylon 66 at 275°C and a very efficient stress transfer happens in the molten state during shearing (mixing) the melts. Consequently, sub-micron rubber inclusions in nylon 66 are produced. SEM Micrograph of the resulting rubber toughened nylon revealed a continuous morphology for these toughened nylon. The mechanical properties of this blend are highly enhanced. 1540% improvement in impact strength and 240% increase in elongation-at-break were reported. These results highlight the exceptional usefulness of this grade of SEBS-g-MA in rubber toughening of nylons under the optimum blending conditions.

REFERENCES

19. Yousefi A.A., Ait-Kadi A., Effects of compatibilizer and post-extrusion stretching on properties


