Reactive compatibilization as a proper tool to improve PA6 toughness

Carlos Bruno Barreto Luna 1, Danilo Diniz Siqueira 1, Eduardo da Silva Barbosa Ferreira 1, Edcleide Maria Araújo 1 and Renate Maria Ramos Wellen 2

1 Academic Unit of Materials Engineering, Federal University of Campina Grande, Av. Aprígio Veloso, 882—Bodocongó, 58429-900, Campina Grande—Paraíba, Brazil
2 Department of Materials Engineering, Federal University of Paraíba, Cidade Universitária, 58051-900, João Pessoa, PB, Brazil
E-mail: brunobarretodemaufcg@hotmail.com

Keywords: polyamide 6, EPDM-MA, reactive extrusion, polymer blends

Abstract
Polyamide 6 (PA6) is a widely applied thermoplastic, however, drawbacks as low notch impact strength and high moisture absorption hinder its commercialization. Seeking improvements for PA6, this work investigated blends based on PA6/maleic anhydride grafted ethylene propylene diene copolymer (EPDM-MA) with 1% maleic anhydride (MA). In the first step, blends were processed using a co-rotational twin-screw extruder, afterwards, pellets were injection moulded. Torque rheometry, impact strength, tensile strength, thermal deflection temperature (HDT), differential scanning calorimetry (DSC), contact angle and scanning electron microscopy (SEM) were performed and the main properties were defined. Torque of PA6/EPDM-MA blends increased compared to neat PA6. Only subtle decreases were verified in the tensile strength, elastic modulus and HDT parameters. Nevertheless, significant increases were observed for the elongation at break and the impact strength. EPDM-MA addition to PA6 did not affect its melting and crystallization parameters. Contact angle of all blends increased when compared to PA6, suggesting higher hydrophobic character of PA6/EPDM-MA blends. Improved results were collected for EPDM-MA 10%, reaching increases of 850% and 213% in impact strength and elongation at break. From SEM images, particles were observed with diameters ranging from 0.1 to 2 μm, which were well dispersed and properly distributed in the PA6 matrix; additionally, for the blends with 10%; 12.5% and 15% EPDM-MA, higher level of plastic deformation was reached corroborating with the significant increase in the impact strength and elongation at break.

Introduction
Polymeric blends are physical mixtures of two or more polymers with some specifically improved properties [1, 2]. There is great commercial interest to develop blends due to the possibility of low cost potential applications which is an alternative to the synthesis of new polymers [3, 4]. Generally, blends are produced in order to improve brittle polymers, i.e., getting better impact strength [5, 6]. Upon toughening polymers become able to absorb higher deformational energy levels prior to fracture [7]. In this context, blends are proper alternatives to improve performance of commercial plastics such as PA6 [8, 9].

PA6 is semi crystalline polymer being chemically, mechanically and thermally resistant, able to support high abrasion mechanisms; it presents low melt viscosity. Currently it is an engineering polymer widely applied in the automotive, aircraft, electronic and electro technical, clothing and healthcare industries. However, PA6 becomes fragile in contact with stress concentrators such as notches and solid fillers. Additionally it presents high moisture absorption, dimensional instability along with brittleness at sub-ambient temperatures, forbidding its use where these requirements are applied [10–14]. To overcome these weaknesses, academic and technical researchers have implemented the toughening procedure between PA and elastomeric materials, for
improving performance and widening the application fields [15–18]. According to the literature [19–23] the most commonly impact modifier for PA6 is the styrene–butadiene–acrylonitrile (ABS) copolymer, which usually improves PA6 notch impact strength, as its polybutadiene-based elastomeric phase has potential for increasing blend toughness as well as decreasing its high moisture absorption. Nevertheless, compatibilizer agents based on maleic anhydride or imidized acrylics need to be added to maximize performance and settle down morphology [24].

Oliveira et al [25] investigated PA6/ABS blends using styrene maleic anhydride (SMA) copolymer with 7% maleic anhydride as compatibilizer regarding the effect of three mixing sequences on the morphology and properties. The results showed that the morphology and mechanical properties of ternary blends were quite different and depend on the mixing sequence. Impact strength was significantly affected, whereas the blend processed by simultaneous mixing of all components (PA6/ABS/SMA) in a single extrusion showed the highest impact. On the other hand, when ABS and SMA were firstly mixed and PA6 was added in a second step, the impact strength was lower than that of neat PA6 and PA6/ABS not compatibilized blend. Chemical reaction evidences between maleic anhydride groups of SMA copolymer and PA6’s amine end groups were verified, as also an increase in HDT of all blends. Slight reduction of the elastic modulus of the blends was found.

Sui et al [26] analysed compatibilized blends of PA6/ABS with SEBS-g-(MA-co-St) and ABS-g-(MA-co-St). Significant reduction in ABS particle size with typical core–shell morphology was observed, which provided better mechanical properties, with 36% increase in tensile strength and 1300% in impact strength compared to PA6/ABS.

PA6/ABS blends processed through reactive extrusion via ε-caprolactam ring anionic polymerization were analysed by Zhao et al [27]. The morphology and mechanical properties of the blends indicated ABS played critical role, improving the compatibility. Sub micrometric ABS domains were obtained, and optimizing the ABS content, super toughening was achieved for PA6, with evidence of significant improvement in impact, suggesting in situ reactive extrusion may be useful for increased performance of PA6/ABS blends.

Araújo et al [28] added acrylonitrile butadiene styrene (ABS) as impact modifier for PA6; additionally, using methyl methacrylate—glycidyl methacrylate (MMA-GMA) and methyl maleic anhydride methacrylate (MMA-MA) copolymers as compatibilizer agents. The morphology and impact strength of these blends were evaluated considering the blends composition. Compatible blends with MMA-MA copolymer presented impact strength up to 800 J m⁻¹ and well-dispersed ABS domains, where contents ±5% of MA in the compatibilizers seem to be sufficient to improve impact and ABS dispersion.

ABS is susceptible to UV radiation when in contact with oxygen, which hinders its outdoor applications. Photo oxidative degradation of ABS has been attributed to the high carbon–carbon double bonds present in butadiene phase, promoting highly reactive free radicals, peroxides and hydro peroxides, responsible for inducing oxidation on polystyrene of acrylonitrile macrophase [29]. As EPDM elastomer displays high impact strength, low glass transition temperature (Tg), excellent thermal and ultraviolet stability, together these properties promote it as an ideal additive for PA6 improvement. Nevertheless, despite great achievements, only few studies have been reported on the development of PA6/EPDM–MA blends [30–32]. Based on the aforementioned, this work aimed to evaluate EPDM–MA as PA6 potential impact modifier. Focused at this, reactivity, impact strength, tensile properties, thermal deflection temperature (HDT), thermal properties, contact angle and morphology were investigated.

Methodology

Materials

Polyamide 6 (PA6), coded B300°, density 1.13 g cm⁻³ and melt flow rate (MFR) 2.9 g/10 min (235 °C/2.16 kg) was provided as pellets by Polyform. Maleic anhydride grafted ethylene propylene diene (EPDM-MA), coded Royaltuf 498°, with 1.0% maleic anhydride, density 0.87 g cm⁻³ and mooney viscosity at 125 °C [33], as pellet was supplied by Addivant, this EPDM-MA was obtained from the copolymerization of ethylene-propylene monomers and unconjugated diene which is present in the copolymer at lesser content but it is absent in the main macromolecular chain. Chemical structures of these materials are presented in table 1.

Methods

Blend processing

Prior to processing, PA6 was vacuum oven dried at 80 °C for 24 h. Table 2 shows blends’ contents used in this work.

Blends were dry mixed and afterwards processed in a Coperion Werner-Pfleiderer model ZSK (D = 18 mm and L/D = 40) modular co-rotating twin screw extruder settled at 230 °C in all zones, screw rotation of
200 rpm and feed rate of 2 kg h⁻¹; the screw profile was configured with distributive and dispersive mixing elements, as shown in figure 1. Blends were granulated and vacuum oven dried for 24 h at 80 °C. Neat PA6 was processed and dried under the same conditions for comparison purposes.

Granulated material was injection moulded using an Arburg Model Allrounder 207 C Golden Edition injector to mould impact, tensile and HDT specimens according to ASTM D256, ASTM D638 and ASTM D648, respectively. The injection parameters are presented in table 3.

After injection, specimens were stored in a desiccator until characterization.
**Characterizations**

Rheological plots were computed in a Thermo Scientific Haake PolyLab QC mixer, with roller rotors, at 230 °C, rotors rate of 60 rpm, under air atmosphere for 10 min.

Izod impact strength measurements were performed on ASTM D256 notched specimens in a Ceast Resil 5.5 J device operating with 4.0 J hammer at room temperature (∼25 °C). Presented results are an average of seven specimens.

Tensile test was performed on injected specimens according to ASTM D638 using an EMIC DL 2000 universal testing machine with elongation rate of 50 mm min⁻¹ and load cell of 20 kN at room temperature (∼23 °C). Presented results are an average of seven specimens.

Heat deflection temperature (HDT) was evaluated according to ASTM D648, in a Ceast model HDT 6 VICAT equipment, with voltage of 1.82 MPa and heating rate of 120 °C h⁻¹. HDT was determined after sample deflection 0.25 mm. Presented results are an average of three specimens.

Contact angle analysis was performed through sessile drop method, using a portable contact angle, Phoenix-i model from Surface Electro Optics—SEO. The drop was dripped on an impact specimen using a micrometer dozer; images were captured and analysed using the equipment software.

Thermogravimetry (TG) analyses carried out in a TA Instruments SDT Q600 simultaneous TG/DSC device employing samples with 5 mg, heated from room temperature (∼25 °C) to 600 °C, the heating rate was 10 °C min⁻¹ and nitrogen flow rate of 100 ml min⁻¹.

Differential scanning calorimetry (DSC) scans were computed using a TA Instruments DSC-Q20. Experiments were executed from room temperature (∼25 °C) to 260 °C, under heating rate of 10 °C min⁻¹, afterwards samples were kept for 3 min at 260 °C, and cooled down to room temperature. A nitrogen flow rate of 50 ml min⁻¹ was used, and tested samples were 5 mg weighted.

Scanning electron microscopy (SEM) images were captured on the fractured surface from impact test. A scanning electron microscope, Shimadzu SSX-550 Superscan, at voltage of 30 kV under high vacuum was used. Fractured surfaces were gold coated. SEM analyses were conducted after dispersed phase (EPDM-MA) extraction in xylene for 24 h, afterwards samples were vacuum oven dried at 60 °C for 24 h.

**Results and discussion**

**Torque rheometry**

Torque rheometry was employed to evaluate blends reactivity and processability. Increases in torque values can be interpreted as chain extension, crosslinking and interactions between chemical groups of macromolecules. Degradation reaction evidences can be identified as torque decreasing along with time [34].

Figure 2 shows torque plots as function of processing time for PA6, EPDM-MA and PA6/EPDM-MA blends with 5; 7.5; 10; 12.5; 15; 30 and 40% EPDM-MA, as indicated.
practically constant. This behaviour suggested viscosity stability for the applied process parameters, i.e., 60 rpm
and 230 °C. Stabilizing torque has processing significance, i.e., the point at which the material should be
extruded or injected [35].

Upon EPDM-MA addition to PA6, slight increase in torque and consequently viscosity increase of PA6/
EPDM-MA is observed. Into investigated range of EPDM-MA contents, i.e., 5; 7.5; 10; 12.5 and 15%; no
significant differences in viscosity were verified for 5 and 7.5% contents compared to neat PA6; only from 10%
EPDM-MA on, pronounced torque increase was displayed.

In order to understand effects of higher EPDM-MA contents, blends with 30 and 40% of reactive copolymer
(EPDM-MA) were produced. EPDM-MA content increasing in PA6/EPDM-MA was followed by significant
torque increase, being for EPDM-MA 40% more pronounced. Viscosity increase in PA6/EPDM-MA blends
may be linked to two factors: low melt flow rate (MFR) of EPDM-MA, or chemical interactions development
between MA from EPDM and PA6 end groups. Torque increase is believed to be proportional to EPDM-MA
amount, as it increases functional groups that can react with PA6. Literature [35, 36] has shown reactive MA
groups from EPDM-MA copolymer react with PA6 amino terminal groups, forming an imide group and thus
resulting in in situ copolymer located at the interface.

Figure 3 illustrates a hypothetical scheme for PA6/EPDM-MA blending. During reaction between PA6
amino terminal groups and MA from EPDM-MA, water is produced as by-product, which is undesirable, once
water can drive to PA6 hydrolytic degradation by chain scission, reducing molecular weight [37]. However,
figure 2 shows that PA6/EPDM-MA torque remained constant, suggesting degradation absence.

Impact strength

Impact strength is one of the most important parameters to select a particular polymer for engineering
applications and often it is used as decisive factor for this purpose [38].

Figure 4 presents impact strength of PA6 and PA6/EPDM-MA blends with 5; 7.5; 10; 12.5 and 15% EPDM-
MA, respectively. PA6 displayed the lowest value, which is due to its brittle character when notched. Addition of
5 and 7.5% EPDM-MA provided considerable increase in impact related to neat PA6, reaching gains of 101.0
and 186.5%, respectively. EPDM-MA addition to PA6 matrix is able to act as an impact modifier, thus
promoting greater energy dissipation mechanisms. This behaviour is linked to the morphology as further on
presented in figure 10, in which particles are well dispersed along with PA6 matrix, therefore, improving toughening. Gathered results can be assumed interesting from the technological point of view, since PA6/EPDM-MA blends (5 and 7.5%) can be considered toughened at room temperature.

Addition of EPDM-MA 10% to PA6 provided significant increase in impact related to neat PA6, reaching an 850% higher value; being translated in synergic state. Barra et al. [39] produced PA6/EPDM compatibilized with EPDM-MA in an extruder, specimens were compression moulded. It was found the highest impact obtained for PA6/EPDM-MA blend (80/20%) was 167 J m$^{-1}$, this result is much lower than these found in the present work with PA6/EPDM-MA (10%), indicating the processing route has great influences on the final mechanical performance. To maximize PA6/EPDM-MA blend properties, twin-screw extruder with distributive and dispersive blending elements, as well as performed injection moulding parameters must be used. In this present work screw configuration favoured impact strength, due to generated morphology, as will be shown later.

Change and inversion behaviours were verified in blends with 12.5 and 15% EPDM-MA, where there was impact reduction compared to EPDM-MA blend 10%. Therefore, there is an optimal reactive copolymer content for PA6/EPDM-MA toughening, after which impact starts decreasing. From the collected data, addition of EPDM-MA 10% to PA6 is enough to produce toughened blend. Indeed, it is unnecessary adding higher amounts of EPDM-MA as it will saturate PA6/EPDM-MA the system with MA, in which case there will not have enough PA6 amine end groups for reaction [10, 40]. Similar finding was verified by Kudva et al. [41] during development of PA6/PE blends compatibilized with PE-g-MA; these indicated high levels of MA are also unnecessary to get toughened and refined particulate compounds.

In general, the mechanical properties of PA6/EPDM-MA blends are interesting for automotive and electronic applications since the impact strength of blends with 10; 12.5 and 15% EPDM-MA approaches to super toughening blends, indicating synergism state.

Impact behaviour of PA6/EPDM-MA blends, regardless EPDM-MA content, suggests reactive copolymer provided interaction with PA6, rendering strong interface, which is fundamental for proper stress transfer between phases [42, 43]. At the same time, dispersion degree and domain size of EPDM-MA in PA6 matrix had significant influence in impact strength [44]. Figure 5 shows the average diameter of dispersed phase in PA6/EPDM-MA blends.

Distinct behaviour in the average particle size of EPDM-MA is verified in figure 5, in this case, influencing impact strength results. Blends with 5 and 7.5% EPDM-MA showed particles that are more refined. On the other hand, when higher contents of EPDM-MA (≥10%) were added, particles tended to get larger. Apparently, EPDM-MA 10% is the ideal content for particle size ranging from 0.816 to 1.172 μm, which optimizes impact. Indeed, when higher levels of EPDM-MA, i.e., 12.5 and 15%, were used, particles became lower, as consequence, impact strength was reduced, as shown in figure 4. This indicates, within a certain range, dispersed phase at reduced size is important for impact strength as it increases interfacial area and improves stress transfer mechanism. Literature [45, 46] has shown that super tough PA6 blends were obtained with rubber particles in sizes ranging from 0.1 to 2 μm, this finding suggests the size range reached for PA6/EPDM-MA blends was ideal, providing high impact performance.
Table 4. Elastic modulus, tensile strength and elongation at break of PA6 and PA6/EPDM-MA blends.

| Compound         | Elastic modulus (MPa) | Tensile strength (MPa) | Elongation at break (%) |
|------------------|-----------------------|------------------------|-------------------------|
| PA6              | 1048.9 ± 48           | 55.0 ± 2               | 78.3 ± 4                |
| PA6/EPDM-MA (5%) | 760.2 ± 23            | 44.6 ± 1               | 126.7 ± 12              |
| PA6/EPDM-MA (7.5%) | 738.0 ± 16           | 43.1 ± 2               | 135.6 ± 10              |
| PA6/EPDM-MA (10%) | 701.5 ± 20            | 42.5 ± 1               | 245.1 ± 15              |
| PA6/EPDM-MA (12.5%) | 695.7 ± 24         | 40.7 ± 0.8             | 214.4 ± 17              |
| PA6/EPDM-MA (15%) | 706.1 ± 18            | 38.0 ± 1               | 228.32 ± 48             |

**Tensile strength**

Table 4 shows gathered data with tensile test for PA6 and PA6/EPDM-MA blends with 5; 7.5; 10; 12.5 and 15% EPDM-MA, respectively, EPDM-MA addition to PA6 matrix led, within tested range of reactive copolymer contents, to decrease its elastic modulus, suggesting blends with greater flexibility. Adding 5% EPDM-MA provided 27.5% reduction in elastic modulus compared to neat PA6, while 15% EPDM-MA reduced the elastic modulus by 32.6%. This decrease can be attributed to the elastomeric component, with low elastic modulus. Regarding PA6/EPDM-MA blends, for EPDM-MA content ranging from 10 to 15%, it was observed blends within experimental margin of error, thus with comparable stiffness.

Regardless the EPDM-MA content used, there was no drastic reduction in the elastic modulus of PA6/EPDM-MA blends related to PA6, which it is important from the technological point of view, since the major limitation of PA6 for applications is its low impact upon stress concentrator addition. Nevertheless, PA6/EPDM-MA blends with low content of EPDM-MA presenting proper balance of stiffness and impact strength can be obtained.

Table 4 shows tensile strength data of the blends, which can be translated as the material answer when mechanically required, an important parameter to define blends’ specific applications. PA6/EPDM-MA blends have lower tensile strength than neat PA6 due to the elastomeric component. As EPDM-MA content increases, tensile strength decreases, suggesting origin of deformable blends at lower stresses. However, blends with 5; 7.5 and 10% EPDM-MA are within the experimental error and in this case, comparable tensile strength was obtained. Reduced PA6/EPDM-MA tensile strength implies greater energy dissipation. This finding corroborates impact strength results, i.e., higher level of energy dissipation for PA6/EPDM-MA blends related to PA6.

Regarding elongation at break of PA6/EPDM-MA blends, significant increase compared to PA6 was verified, suggesting high-toughened blends. These data corroborate assumptions that interactions occur between PA6 and EPDM-MA, as proposed in figure 3. Blends with EPDM-MA 10 and 15% showed substantial increase in elongation at break, as shown in figure 6.

It appears that from 10% EPDM-MA on there is property optimization, with significant gains in elongation at break and, consequently, in tensile strength. It is reasonable to suggest 10% EPDM-MA is a critical concentration in which there is sufficient amount of maleic anhydride to react with PA6 end groups. As consequence, the synergic effect was observed in elongation at break upon addition of 10% EPDM-MA to PA6. Indeed, it is believed the reaction between EPDM-MA and PA6 increases the entanglement likelihood, thus providing greater resistance to molecular disentanglement, increasing elongation data. At concentrations higher than 10% EPDM-MA, elongation decreases suggesting there is excess of maleic anhydride reactive groups in compositions with 12.5 and 15%, which end up deteriorating this property. Overall, the PA6/EPDM-MA blend (10%) has the highest level of ductility, an important result for improved applications. Additionally, blends’ behaviour is associated to morphological characteristic, which will show proper EPDM-MA particles distribution in these blends, which undoubtedly is a determinant factor for higher elongation and toughness characters.

**Thermal deflection temperature (HDT)**

Simulation of polymers’ application at above ambient temperatures can be obtained through HDT experiments, which is very relevant for material selection [47].

Figure 7 shows acquired HDT for PA6 and PA6/EPDM-MA blends, it can be seen that EPDM-MA subtly reduces PA6 thermo-mechanical strength, since all PA6/EPDM-MA blends have lower HDT than neat PA6. HDT is influenced by the rubber content increase, since this property depends significantly on the continuous phase, which is crucial for material stiffness [48]. Therefore, blends’ HDT decrease can be attributed to EPDM-
Figure 6. Elongation evolution from specimens under tensile test: (a) PA6; (b) PA6/EPDM-MA (5%); (c) PA6/EPDM-MA (7.5%); (d) PA6/EPDM-MA (10%); (e) PA6/EPDM-MA (12.5%); (f) PA6/EPDM-MA (15%).

Figure 7. HDT of PA6 and PA6/EPDM-MA blends at indicated EPDM-MA content.
MA, due to its rubbery character being higher flexible and driving to HDT losses. This finding is in agreement with elastic modulus data presented above.

One limitation of PA6 for technological applications is its low impact strength when featuring stress concentrator. Although EPDM-MA did not provide increased thermo-mechanical strength, its addition did not drastically reduce PA6 HDT, and at the same time considerably increased impact, summing up, development of PA6/EPDM-MA blends make an important technological contribution. HDT of PA6/EPDM-MA blends are quite relevant as they provide the quality of injection moulded products. After injecting the product is only considered safe to be removed from the mould when it is near or below the HDT value, meaning the deformation will be kept within acceptable limits after removing.

**Differential scanning calorimetry (DSC)**

DSC parameters acquired during fusion and melt crystallization events are provided in table 5 and scans are displayed in figure 8. EPDM-MA showed low crystallinity, since it has two different meres in the main chain, packaging is difficult and therefore it is predominantly amorphous. Although EPDM-MA has two semi-crystalline meres its crystallization is complex. Melting and crystallization peaks are associated with the ethylene phase, suggesting it is the major phase in the main chain.

PA6 scans presented two melting peaks defined as $T_{m3}$ and $T_{m2}$, which measured parameters are presented in table 5, these peaks may be attributed to the two distinct crystalline forms, called $\alpha$ and $\gamma$ [50], which have $T_m$ at approximately 222.1 °C and 214 °C, respectively. Blends’ melting temperatures were quite similar to that of neat PA6. However, as presented in figure 8(a) all blends have a third melting peak ($T_{m1}$), regardless of EPDM-MA content, whereas, most likely, addition of reactive copolymer modified PA6 macromolecular ordination mechanism.

Another hypothesis may be based on the fusion-recrystallization-fusion phenomena, where the first melting peak originally associated to less stable $\gamma$ form afterwards is transformed into $\alpha$; thus promoting development of $T_{m3}$, i.e., PA6’s main endothermic peak [51]. Therefore, it is suggested EPDM-MA addition affected structural organization of PA6 crystals [52], in parallel reduction in blends’ $\Delta H_m$ related to PA6 is verified, indicative of lower crystallinity.

Blends crystallization temperatures ($T_c$) (figure 8(b)) practically did not change related to the PA6 one. On the other hand, although not significant, blends’ degree of crystallinity ($X_c$) decreased, corroborating with elastic modulus and impact strength. PA6 crystallization was hindered through EPDM-MA addition. Packaging and crystal formation are believed to be hampered by incorporation of amorphous (EPDM-MA) and, as consequence smaller and imperfect crystals are produced [53], as verified upon $T_{m1}$ peak. Indeed, PA6/EPDM-MA blends presented the lowest melting enthalpy ($\Delta H_m$), due to less energy consuming to melt the crystalline phase.

HDT also depends on degree of crystallinity [54], whereas $X_c$ reduction in PA6/EPDM-MA agrees with HDT data above presented.

| Compounds        | $T_{m1}$ (°C) | $T_{m2}$ (°C) | $T_{m3}$ (°C) | $T_c$ (°C) | $\Delta H_m$ (J/g) | $X_c$ (%) |
|------------------|--------------|--------------|--------------|------------|-------------------|-----------|
| PA6              | —            | 214.0        | 222.1        | 188.5      | 56.4              | 30.0      |
| PA/EPDM-MA (3%)  | 205.9        | 213.0        | 221.1        | 188.0      | 53.2              | 29.8      |
| PA/EPDM-MA (7.5%)| 205.0        | 214.2        | 222.4        | 187.5      | 48.8              | 28.1      |
| PA/EPDM-MA (10%) | 204.7        | 214.3        | 222.2        | 186.3      | 42.1              | 24.9      |
| PA/EPDM-MA (12.5%)| 206.7       | 213.7        | 221.2        | 186.7      | 48.3              | 29.4      |
| PA/EPDM-MA (15%) | 204.0        | 213.9        | 222.0        | 186.7      | 45.6              | 28.5      |
| EPDM-MA          | —            | 123.8        | —            | 94.4       | 7.8               | 4.8       |

$X_c = \frac{\Delta H_m}{\Delta H_m^{100\%}}$, where $\Delta H_m^{100\%} = \Delta H_m$ at 100% of crystallinity, 188 J g$^{-1}$ [18]. The melting enthalpy for 100% crystalline PE was assumed as 293 J g$^{-1}$ [49].
Figure 9 displays TG plots of PA6, EPDM-MA and PA6/EPDM-MA blends. EPDM-MA showed high thermal stability, with started decomposition above 380 °C. It can be observed EPDM-MA addition only subtly changed thermal stability of PA6, i.e., blends behave similarly. This finding reinforces HDT results, which were similar for PA6 and blends. Apparently, adding low concentrations of EPDM-MA had positive effect on PA6/EPDM-MA blends.

**Figure 8.** DSC scans of PA6, EPDM-MA and PA6/EPDM-MA blends: (a) endothermic melting peaks, and (b) exothermic crystallization peaks.

**Thermogravimetry (TG)**

Figure 9 displays TG plots of PA6, EPDM-MA and PA6/EPDM-MA blends. EPDM-MA showed high thermal stability, with started decomposition above 380 °C. It can be observed EPDM-MA addition only subtly changed thermal stability of PA6, i.e., blends behave similarly. This finding reinforces HDT results, which were similar for PA6 and blends. Apparently, adding low concentrations of EPDM-MA had positive effect on PA6/EPDM-MA blends.
blends, favouring to keep PA6 thermal stability, which can be assumed as synergic interaction between components. In TG plots, from room temperature to approximately 120 °C, for all tested samples the weight loss was 1.2%, due to residual moisture. In general, a single decomposition step at approximately 370 °C is verified for PA6 and PA6/EPDM-MA blends due to macromolecular chains degradation. Data acquired from thermogravimetry ensure proper thermal stability of tested compounds at applied processing temperatures.

Contact angle

Through contact angle analysis the surface character, i.e., hydrophilic or hydrophobic, can be assessed measuring interaction energy between surface and dropped liquid [55]. Specimens with contact angle $\theta < 90^\circ$, are assumed having liquid affinity and therefore called hydrophilic. On the other hand, when the contact angle is $\theta > 90^\circ$ specimens should have hydrophobic surface [56].

Figure 10 presents surface contact angle results of PA6, EPDM-MA and PA6/EPDM-MA blends, which have hydrophilic character, since the contact angle ($\theta$) < 90°. PA6 has the highest hydrophilic character (47.3°), indicating it has water affinity. In fact, PA6 has hydrogen bonds between carbonyls and hydrogen from amide group, providing hygroscopic character. These bonds make water permeation easier, diffusing between chains and being located on hydrogen bond. On the other hand, EPDM-MA presented the lowest water affinity (75.7°), most due to the nonpolar ethylene propylene diene character. The contact angle of the blends was intermediate between to those of PA6 and EPDM-MA.

For the blends the contact angle was higher than that for PA6, it was assumed EPDM-MA decreased PA6 hydrophilic character. Most likely, as EPDM-MA has ethylene propylene diene (EPDM) as non-polar group, once it was dispersed into PA6 matrix, along with the surface, it headed to reduced water interaction, i.e., increased blends contact angle.

Upon EPDM-MA addition and in the range from 5 to 12.5%, no significant differences in contact angle were verified. However, for higher content, i.e., EPDM-MA 15% blend surface became more hydrophilic, such behaviour can be attributed to the increased maleic anhydride amount conducting to greater water interaction.

Contact angle results are greatly important, since PA6 presents as thresholding factor high water interaction, nevertheless, adding low EPDM-MA contents, PA6 hydrophilic character is reduced.

Scanning electron microscopy (SEM)

SEM images of PA6 and PA6/EPDM-MA blends are presented in figure 11, in figure 11(a) PA6 surface with regular appearance of ductile fracture is seen. SEM images of PA6/EPDM-MA blends reveal typical morphological surface of immiscible blends with separated phase. It is worth mentioning that complete miscibility between PA6 and EPDM-MA is not welcome, once it would drive to unfeasible toughness mechanisms. Increased addition of EPDM-MA produced distinct surfaces, as shown in figures 11(b)–(f). In blends with 5 and 7.5% EPDM-MA more homogeneous and smooth looking morphology was verified.
compared to richer EPDM-MA compounds (10; 12.5 and 15%). This finding corroborates impact data, where blends with EPDM-MA at 5 and 7.5% presented lower impact performance.

Figures 11(b), (c) shows well-dispersed EPDM-MA in PA6 matrix, forming very small domains, represented by extracted solvent voids. EPDM-MA dispersed domains range from 0.1 to 2 μm, which are considered ideal to reach good impact properties [45, 46]. PA6/EPDM-MA compounds show efficient morphology, since well dispersed EDPM-MA and small particles are reached due to decreased interfacial tension between phases. Observed morphology of blends containing 5 and 7.5% EPDM-MA corroborates impact strength results, which were higher than neat PA6.

Blends with 10; 12.5 and 15% of EPDM-MA clearly presented evidence of more ductile fracture mechanism, with intense plastic deformation, as shown in figures 11(d)–(f). Voids are verified from solvent-extracted EPDM-MA particles surrounded by highly deformed structure, suggesting strong interaction of PA6 and EPDM-MA, providing increased mechanical properties, especially impact strength, tensile strength and elongation at break. Apparently, the blend with EDPM-MA 10% showed morphology with the highest plastic
deformation, indicating to be the most toughened blend, with 850% gain in impact strength related to PA6, evidencing greater synergism. At the same time, the morphological aspect of the blend with 10% EPDM-MA reinforces the hypothesis at this concentration properties are optimized as well as the morphology is stabilized. In this case, above 10% saturation, dispersed phase exists. In addition, when adding 10% EPDM-MA compatibility increase of PA6/EPDM-MA blend is reached, which is reflected as improved impact strength, ductility and HDT. When 12.5% EPDM-MA was added reduction of plastic deformation was observed on fractured surface related to EPDM-MA 10% blends, plastic deformation recovering is visualized for 15% compared to EPDM-MA 12.5%. However, this recovering is at lower extension if compared to the EPDM-MA 10% blend. Plastic deformation level directly influences impact and elongation at break improvements, since these properties increased proportionally, as shown in figures 4 and 6, respectively. From morphological analyses, it is suggested that greater interactions take place between PA6/EPDM-MA with EPDM-MA 10%, defining it as the ideal.

Increased elongation at break and impact strength are related to toughening processes such as micro fibrillation and micro flow under shear [57]. However, in multiphase systems such as PA6/EPDM-MA, these mechanisms can act simultaneously as complex interactions. Indeed, high impact performance and generated morphology of PA6/EPDM-MA with 10; 12.5 and 15% EDPM-MA suggest combination of these mechanisms.

Figure 11. SEM images of fractured surface for: (a) PA6; (b) PA6/EPDM-MA (5%); (c) PA6/EPDM-MA (7.5%); (d) PA6/EPDM-MA (10%); (e) PA6/EPDM-MA (12.5%); and (f) PA6/EPDM-MA (15%), respectively. Extraction in xylene was performed.
In these cases, shear bands represent barriers to microfibrillation propagation and catastrophic crack origin, as consequent reduction of the microfissures propagation rate [58]. Therefore, maximizing the synergic effect, obtaining high impact as seen in figure 4.

Conclusions

In this work, effects of maleic anhydride grafted ethylene propylene diene reactive copolymer (EPDM-MA) on torque rheometry, mechanical, thermal, thermo-mechanical properties and morphology of PA6/EPDM-MA blends were investigated in detail. PA6/EPDM-MA blends can be considered toughened due to favourable molecular interactions between phase components. Main results indicated, although EPDM-MA addition provided slight reduction in tensile strength and elastic modulus, significant increases in elongation at break and impact strength were reached. At the same time, no significant reduction was verified in thermo mechanical stability. EPDM-MA addition provided increased contact angle, driving to minimize PA6 hygroscopic character. Although EPDM-MA is an amorphous copolymer, it did not drastically change PA6 stability. EPDM-MA addition provided increased contact angle, driving to minimize PA6 hygroscopic character. In this case, favouring high performance blend under impact, indicative PA6/EPDM-MA (10%) has great technological potential and commercial viability.

Acknowledgments

Authors thank to Addivant for supplying EPDM-MA; MCTIC/CNPq, and CAPES/PNPD for financial support. Professor Edcleide Maria Araújo and Professor Renate Maria Ramos Wellen are CNPq fellows.

ORCID iDs

Carlos Bruno Barreto Luna @ https://orcid.org/0000-0002-2441-7439
Danilo Diniz Siqueira @ https://orcid.org/0000-0002-3533-513X
Eduardo da Silva Barbosa Ferreira @ https://orcid.org/0000-0002-2670-2794
Edcleide Maria Araújo @ https://orcid.org/0000-0003-4906-864X
Renate Maria Ramos Wellen @ https://orcid.org/0000-0002-3565-7366

References

[1] Agrawal P, Araújo E M and Mélo T J A 2008 Reometria de torque, propriedades mecânicas e morfologia de blendas compatibilizadas de PA6/PEAD Polímeros: Ciência e Tecnologia 18 152–7
[2] Utracki L A 1995 History of commercial polymer alloys and blends Polym. Eng. Sci. 35 2–17
[3] Luna C B B, Silva D F, Basílio S K T, Araújo E M, Silva A L and Bezerra A F C 2015 Desenvolvimento de blendas poliméricas visando a tenacificação dos polímeros: uma revisão Seminá Ciências Exatas e Tecnológicas 3667–80
[4] Utracki L A 1982 Economics of polymer blends Polym. Eng. Sci. 22 1166–75
[5] Libio I L, Grassi V G, Dal Pizzol M F and Nachtigall S M B 2012 Toughened polystyrene with improved photoresistance: Effects of the compatibilizers J. Appl. Polym. Sci. 126 179–85
[6] Silva D F, Luna C B B, Araújo E M and Silva A L 2016 Blendas poliméricas: conceitos, obtenção e aplicações Revista de Engenharia e Tecnologia 8 58–77 https://www.revistas2.uepg.br/index.php/ret/article/view/11663/209209209639
[7] Lazzeri A and Bucknall C B 1993 Dilatational bands in rubber-toughened polymers J. Mater. Sci. 28 6799–808
[8] Bezerra E B, Leite A M D, Araújo E M and Mélo T J A 2014 Obtenção e caracterização de membranas obtidas a partir de blendas poliméricas de poliamida 6 Polímeros: Ciência e Tecnologia 24 381–7
[9] Luna C B B, Silva D F and Araújo E M 2014 Estudo do comportamento de blendas de poliamida 6/resíduo de borracha da indústria de calçados Revista UniVap 20 98–110
[10] Araújo E M, Júnior E H and Carvalho A J F 2003 Compatibilização de blendas de poliamida 6/ABS usando os copolímeros acrílicos reativos MMA-GMA e MMA-MA. Parte 1: comportamento reológico e propriedades mecânicas das blendas Polímeros: Ciência e Tecnologia 13 205–11
[11] Botan R, Pinheiro I F, Ferreira F V and Luna L M F 2018 Correlation between water absorption and mechanical properties of polyamide 6 filled with layered double hydroxides (LDH) Mater. Res. Express 5 065004
[12] Mattos H S C, Brandão J F S, Amorim F C, Araújo P V S and Reis J M L 2019 A unified expression to estimate the stress-strain curve of polyamides at different temperatures Mater. Res. Express 6 015304
[13] Filho E A S, Medeiros K M, Araújo E M, Ferreira R S B, Oliveira S S L and Medeiros V N 2019 Membranes of polyamide 6/clay/salt for water/oil separation Mater. Res. Express 6 105313
[14] Luna C B B, Silva D F and Araújo E M 2014 Análise do comportamento termomecânico, térmico e mecânico de blendas 6/resíduos de borracha Revista de Engenharia e Tecnologia 6 160–9 https://www.revistas2.uepg.br/index.php/ret/article/view/11532/209209209508
[15] Oshinski A J, Keskkula H and Paul D R 1996 The role of matrix molecular weight in rubber toughened nylon 6 blends: 1 Morphology. Polymer 37 4891–907
[16] Bassani A, Hage J E and Pessan L A 2002 Propriedades mecânicas de blended de nylon-6/ Acrylonitrile-EPDM-Styrene (AES) compatibilizadas com copolímero acrílico reativo (MMA-MA) Polímeros: Ciência e Tecnologia 12 102–8
[17] Lu M, Keskiula H and Paul D R 1995 Toughening of nylon 6 with grafted rubber impact modifiers J. Appl. Polym. Sci. 58 1175–88
[18] Carvalho A P A and Siqueira A S 2016 Effect of compatibilization in situ on PA/SEBS blends Polímeros: Ciência e Tecnologia 26 123–8
[19] Majumdar B, Keskiula H and Paul D R 1994 Deformation mechanisms in nylon 6/ABS blends J. Polym. Sci., Part B: Polym. Phys. 32 2127–33
[20] Majumdar B, Keskiula H and Paul D R 1994 Mechanical properties and morphology of nylon-6/acylonitrile-butadiene-styrene blends compatibilized with in situ oxidized polyacrylamide Polymer 35 5463–57
[21] Majumdar B, Keskiula H and Paul D R 1994 Effect of the nature of the polyamide on the properties and morphology of compatibilized nylon/ acrylonitrile-butadiene-styrene blends Polymer 35 5468–77
[22] Majumdar B, Keskiula H, Paul D R and Harvey N G 1994 Control of the morphology of polyamide/styrene-acylonitrile copolymer blends via reactive compatibilization Polymer 35 4263–79
[23] Majumdar B, Keskiula H and Paul D R 1994 Morphology and mechanical properties of nylon-6/ABS blends compatibilized by styrene/maleic anhydride copolymer Polymer 35 3164–72
[24] Correa CA, Yamakawa R S, Razzino C A and Júnior E H 2007 Tenacidade à fratura de blends PA6/ABS avaliada através do método EWF (Trabalho Essencial de Fratura)—parte A: avaliação do efeito do compatibilizante Polímeros: Ciência e Tecnologia 17 36–45
[25] Oliveira A D, Lurochka N M and Pessan L A 2011 Efeito da sequência de mistura nas propriedades de blends de PA6/ABS compatibilizadas com o copolímero SMA Polímeros: Ciência e Tecnologia 21 27–33
[26] Sui X and Xie X M 2019 Creating super-tough and strong PA6/ABS blends using multi-phase compatibilizers Chin. Chem. Lett. 30 149–52
[27] Zhao D, Yan D, Zhang N and Yang G 2019 Preparation of super-toughened PA6 with submicron-sized ABS by in situ reactive extrusion method Lett. Mat. 251 18–22
[28] Araújo E M, Júnior E H and Carvalho A F 2003 Acrylonitrile–butadiene–styrene toughened nylon 6: The influences of compatibilizer on morphology and impact properties J. Appl. Polym. Sci. 87 842–7
[29] Santos R S, Botelho G and Machado A V 2010 Avaliação da fotodegradação de ABS exposto a condições naturais Ciência & Tecnologia dos Materiais 22 87–90 http://www.scielo.mp.pr.gov.br/pdf/cstm/v22n1-2/v22n1-2at99.pdf
[30] Dou R, Wang W, Zhou Y, Gong L, Yin B, Yang M B and Xie B H 2016 Cristalização behaviour of HDPE in PA6/EPDM-g-MA/HDPE ternary blend with different phase morphology Plast. Rubber Comp. 45 207–15
[31] Yang W, Tang X G, Xie B H, Zhu Y P, Yang M B and Hou M 2009 Heterogeneous dispersion of the compatibilizer in the injection molding of polyamide 6/ polypropylene blends J. Appl. Polym. Sci. 113 239–305
[32] Li L P, Yin B, Zhou Y, Gong L, Yang M B, Xie B H and Chen C 2012 Characterization of PA6/EPDM-g-MA/HDPE ternary blend: The role of core–shell structure Polymer 53 3043–51
[33] Oliveira A D, Castro L D C, Jung M K and Pessan L A 2015 Influência da modificação da argila montmorillonita nas propriedades mecânicas, termo-mecânicas e morfológicas de nanocompósitos de blends de poliamida 6/Acrylonitrile-estireno Polímeros: Ciência e Tecnologia 25 219–28
[34] Bezerra E B, França D C, Morais D D S, Ferreira E S B, Araújo E M and Wellen R M R 2017 Comportamento reológico do Bio-PE e do PCL na presença do PegAA e PegMA Matéria (Rio de Janeiro) 22 e11798
[35] Bretas R E S and D’Avila M A D (ed) Rheology of polymer melts. 2ª (São Carlos: EduScar) 2010
[36] Jiang C, Filippi S and Maggino P 2003 Reactive compatibilizer precursors for LDPE/PA6 blends. I: maleic anhydride grafted polybutadiene Polymer 44 2144–9
[37] Bassani A, Júnior E H and Pessan L A 2005 Evolução da morfologia de fases de blends PA6/ AES em extrusora de dupla roscas e moldagem por injecção Polímeros: Ciência e Tecnologia 15 176–85
[38] Guo Z, Fang Z and Tong L 2007 Application of percolation model on the brittle to ductile transition for polystyrene and polyolefin elastomer blends Polymer Express Polymer Letters 1 37–43
[39] Barra G M O, Roeder J, Soldi V, Pires A T N and Agnelli J A M 2003 Blends of poliamida 6/ elastômero: propriedades e influência da adição de agente compatibilizante Polímeros: Ciência e Tecnologia 13 94–101
[40] Araújo E M, Júnior E H and Carvalho A F 2003 Morphological, mechanical and rheological properties of nylon 6/acylonitrile-butadiene-styrene blends compatibilized with MMA/MA copolymers J. Mater. Sci. 38 3515–20
[41] Kudva R A, Keskiula H and Paul P R 1999 Morphology and mechanical properties of compatibilized nylon 6/polystyrene blends Polymer 40 6003–21
[42] Agrawal P, Rodrigues A W B, Araújo E M and Melo T J A 2009 Blends of PA6/PE: avaliação da reatividade de diferentes compatibilizantes com a PA6 por reometria de torque Revista Eletrônica de Materiais e Processos 3 4 01–10 http://www2.ufcg.edu.br/revista-remap/index.php/REMAP/article/download/153/131
[43] Agrawal P, Rodrigues A W B, Araújo E M and Melo T J A 2010 Influence of reactive compatibilizers on the rheometrical and mechanical properties of PA6/LDPE and PA6/HDPE blends J. Mater. Sci. 45 496–502
[44] Rocetto L B, Zeni M and Brandalise R N 2016 Utilização de elastômeros como modificadores de impacto em poliamidas Scientia Cum Industria 4 135–47
[45] Yu Z, Ou Y, Qi Z and Hu G 1998 Toughening of nylon 6 with a maleated core–shell impact modifier J. Polym. Sci., Part B: Polym. Phys. 36 1987–94
[46] Okada O, Keskiula H and Paul D R 2000 Fracture toughness of nylon 6 blends with maleated ethylene/propylene rubbers Polymer 41 8061–74
[47] Luna C B, Siqueira D D, Araújo E M and Wellen R M R 2019 Tailoring PS/PP/recycled blends compatibilized with SEBS. Evaluation of rheological, mechanical, thermomechanical and morphological characters Mater. Res. Express 6 075316, 2019
[48] Grassi V G, Forte M M C and Pizzol M F D 2001 Aspectos morfológicos e relação estrutura propriedades de poliestereno de alto impacto Polímeros: Ciência e Tecnologia 11 158–68
[49] Castro D O, Frollini E, Mariní J and Filho A R 2013 Preparation and characterization of biocomposites based on curaua fibers, high-density biopolyethylene (HDPEPE) and liquid hydroxylated Polybutadiene (LHPB) Polímeros 23 63–73
[50] Bhardwaj I S, Kumar V, Mathur A B and Das A 1990 Characterization of multicomponent polymer system nylon 6/ABS blends J. Therm. Anal. 36 2339–47
[51] Chiu F C, Laí S M, Chen Y L and Lee T H 2005 Investigation on the poliamide 6/organoclay nanocomposites with or without a maleated polyolefin elastomer as a toughener Polymer 46 11609–9
[52] Oliveira M F L, Oliveira M G and Leite M Ç A M 2011 Nanocompósitos de poliamida 6 e argila organofílica: estudo da cristalinaidade e propriedades mecânicas Polímeros: Ciência e Tecnologia 21 78–82
Castro L D C, Oliveira A D, Kersch M, Altstädt V and Pessan L A 2016 Effects of mixing protocol on morphology and properties of PA6/ABS blends compatibilized with MMA-MA J. Appl. Polym. Sci. 133 43612

Takemori M T 1979 Towards an understanding of the heat distortion temperature of thermoplastics Polym. Eng. Sci. 19 1104–9

Bezerra E B, França D C, Morais D D S, Silva I D S, Siqueira D D, Araújo E M and Wellen R M R 2019 Compatibility and characterization of Bio-PE/PCL blends Polímeros: Ciência e Tecnologia 29 e2019022

Hebbar R S, Isloor A M and Ismail A F 2017 Contact angle measurements. Membrane Characterization 1 219–55

Mazidi M M and Aghjeh M K R 2015 Synergistic toughening effects of dispersed components in PP/PA6/EPDM ternary blends; quantitative analysis of the fracture toughness via the essential work of fracture (EWF) methodology RSC Adv. 58 47183–98

Rabello M S 2000 Aditivação de polímeros. (São Paulo: Artliber Editora) https://www.artliber.com.br/amostra/aditivacao_de_termoplasticos.pdf