Effect of Dynamic Crosslinking on Phase Morphology and Mechanical Properties of Polyamide 6,12/Ethylene Vinyl Acetate Copolymer Blends

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Abstract

The dynamic crosslinking of polyamide 6,12 and ethylene vinyl acetate (PA6,12/EVA) blends in the mixing chamber of a torque rheometer was investigated. EVA was selectively crosslinked within the PA6,12 phase through free radical reactions using dycumil peroxide. The degree of EVA crosslinking in the PA12,6/EVA materials was estimated based on the gel content (insoluble EVA fraction). The PA6,12/EVA phase morphology was investigated by scanning electron microscopy. The mechanical properties were investigated by determining the tensile strength and hardness. The half-life time ($t_{1/2}$) for homolytic scission of the dcumil peroxide (DCP) was 6s, and this time is longer than the dispersion time of the DCP in the blends. The addition of DCP resulted in increased torque values due to specific crosslinking in the EVA phase. For the pure EVA and its blends with PA6,12 the stabilized torque values increased proportionally with the amount of DCP in the system, due to a higher degree of crosslinking of the elastomeric phase. The gel content of the dynamically crosslinked blends increased with the amount of DCP incorporated until 4 phr. At 1 phr the gel content value was 2.6wt.%, while at 4 phr it was 17wt.%. For the polymer blend with 8 phr of DCP a lubricating effect contributed to reducing the gel content. The dynamically crosslinked blends, regardless of the amount of DCP added, showed a reduction in the mechanical properties, which is related to the morphological features of the system due to the low mechanical fragmentation during melt processing.

Keywords

TPV, polyamide 6,12, EVA, dynamic crosslink, DCP

I. INTRODUCTION

Thermoplastic vulcanizates (TPVs) are an emerging class of thermoplastic elastomers (TPEs) that provide the processing characteristics of thermoplastic polymers and the performance of conventional crosslinked elastomers. The mechanical, thermal and chemical properties of a TPV are dependent on the morphology developed during melt processing [1]. TPVs are produced by a dynamic process of vulcanization/crosslinking achieved through specific chemical reactions in the elastomeric phase using a crosslinking agent, resulting in the formation of new covalent bonds and an increase in the molecular weight and viscosity. The elastomeric phase in TPVs is fragmented by the action of mechanical forces during melt processing and dispersed in the thermoplastic phase (1-5 μm in diameter) [1]–[3]. The combination of behaviors similar to those of rubber and thermoplastic melts results in polymer system with a two-phase morphology: the soft phase, an elastomer, gives the rubber-like properties in the solid state, whereas the hard phase shows the properties of a thermoplastic polymer with a high glass transition temperature, which gives strength to the blend [4], [5]. At the temperature of utilization, the latter is the stiffer phase that acts as a physical crosslinker for the elastomer phase. At elevated temperatures (above the glass transition temperature or above the melting point), the hard phase softens and the TPE becomes processable [6], [7].

These materials have several advantages over the traditional vulcanized rubber elastomers, since functional performance similar to those of crosslinked elastomers means that they can be easily recycled as thermoplastics. The combination of these characteristics contributes to the abundant use of these materials, especially in the automotive sector. The production of TPV materials involves several phenomena which aid the processing including diffusion [8], phase inversion [9], phase compatibilization [10], semicrystalline component crystallization [11] and morphology stabilization [12]. Also, the processing conditions [12] as well as rheological and viscoelastic considerations related to the reactive melt blending process strongly affect the final properties [13]–[15]. Because of their unique characteristics, TPEs have very useful and attractive applications in a variety of markets, including the automotive, building and construction, and wires & cables industries [16].

Polyamide 6,12 (PA6,12) has excellent solvent and oil resistance, acid and alkali resistance, and excellent environmental stress cracking resistance at elevated temperatures [1], [17], [18]. This polymer exhibits good resistance abrasion and fatigue, and melt processability. The uses of polar elastomer in polymer blends with PA can improve the phase stability synergism in mechanical properties [17]. This is attributed to chemical interaction between the polar groups of the rubbers and the functional groups of polyamide (i.e., -NH_2, -COOH and -NH-CO-).

Ethylene vinyl acetate (EVA) copolymers are commonly used in the footwear and toy industries due to their chemical inertness, light weight,flexibility and toughness. EVA

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copolymer forms either a type of plastic or an elastomer, depending on its vinyl-acetate (VA) content. Crosslinked EVA copolymers are widely used in the rubber market. The general effects of crosslinking on the EVA properties are: stability at higher temperatures (thermal resistance), slightly better flame resistance, higher tensile strength, abrasion resistance, resistance to environmental stress cracking, and solvent resistance. Thermo-chemical crosslinking involving organic peroxides is widely used because of its controlled decomposition rate, minimal by products, and economical process [10], [19], [20].

TPVs prepared using polyamide 6 and ethylene vinyl acetate (EVA) show a tendency toward a decrease in the tensile strength and the tensile modulus with an increase in the EVA content. However, the Izod impact strength of PA6 increased in blends with higher EVA contents [8]. The formation of crosslinked EVA can be carried out using organic peroxides [9], however, the radicals formed have almost no effect on the properties of polyamides [2]. Thus, the use of the organic peroxide as a crosslinking agent is a viable approach to producing TPV PA6,12/EVA. The dynamic crosslinking of polyamide 12 and ethylene vinyl acetate (PA12/EVA) blends was carried out in a mixing chamber using dicumyl peroxide with a crosslinking agent. The 70/30 blend showed a disperse phase morphology with spherical shape (2.75μm) after the crosslinking process [2].

In this study, the dynamic crosslinking of PA6,12/EVA will be evaluated using dycumil peroxide (DCP) as a crosslinking agent in a batch mixer. The processability, degree of crosslinking of the EVA phase, morphology and mechanical properties were determined according to the amount of DCP in the blends.

II. MATERIALS AND METHODS

A. *Materials*

The copolymer ethylene-vinyl acetate (EVA) was supplied by “Braskem” Co. (HM728), contained 27.5 wt% of vinyl acetate, as determined by thermo gravimetric analysis (TGA), with an MFI of 6 g/10 min (190ºC/2.16kg) and a density of 0.95g.cm^{-3}. The polyamide 6,12 (PA6,12) was supplied by UBE Engineering Plastics S.A., with a density of 1.11 g.cm^{-3}. Dicumyl peroxide (DCP) (98% of purity), used as received and without any further purification, was supplied by Retilox Química Especial. All polymers were dried in a vacuum oven (50ºC) for 24 h before melt processing.

B. *Methods*

1) Processing: PA6,12/EVA (50/50 wt.%) blends were processed in the mixing chamber (75 cm^3) of a torque rheometer (Haake Rheomix 600p) using counter-rotating roller rotors. The materials were processed at 200ºC for 15 min at 120 rpm. Different amounts of DCP (0, 1, 4 and 8 phr in relation to EVA contents) contents were employed. The total amount of material was calculated in order to maintain the chamber 80% (by volume) filled. The materials were placed into the mixing chamber in the following sequence: PA6,12 and EVA were first melted for 5 min and then the DCP was added to the molten samples and mixing was applied for 15 min. For blends without DCP the same processing procedure was adopted. After the melt processing the samples were injection molded in a Haake mini injection II system to obtain and test specimens for mechanical testing and morphological investigation.

2) Gel content: The degrees of crosslinking in the dynamically vulcanized EVA and PA6,12/EVA materials were evaluating through the gel content (insoluble EVA fraction), applying a procedure based on the standard ASTM 2765. A 120-mesh wire cage containing approximately 0.3g of polymer was washed in a round-bottom flask containing boiling m-cresol for 8 h. After solvent extraction, all samples were dried at 60ºC for 48h.

3) Morphology: The SEM micrographs of the PA6,12/EVA blends were obtained using a Shimadzu SSX-550 electron microscope. The specimens were immersed in liquid nitrogen for 2 h and cryogenically fractured to observe a representative section of the materials, avoiding plastic deformation. Small samples (30x5x1mm^3) from the central core of the injection-molded bars were cryo-fractured. All samples were sputter-coated with gold before imaging.

4) Mechanical properties: Tensile tests were carried out according to ASTM D 638 using V-type specimens on an Emic Tensile Testing machine DL-2000, at a constant crosshead speed of 10 mm/min. Hardness Shore “D” was measured using Weltest durometer according to ASTM 412.

III. RESULTS AND DISCUSSION

When the polymer is introduced into the mixing chamber, the solid granules offer a certain resistance to the free rotation of the mixer rotors and therefore the torque increases. When this resistance is overcome, the torque required to rotate the rotors at the fixed speed decreases and reaches after a short time a steady-state regime [21], [22]. When the heat transfer is sufficient to completely melt the core of the particles, the torque decreases and reaches again a steady state condition.

The dispersion time (t_{disp}) of a component in a system can be obtained from a knowledge of the diffusion (D_{12}) coefficient of the species in the medium. The dispersion time for the EVA / DCP system can be determined using the following relationship [23], [24]:

$$t_{disp} = \sqrt[3]{\frac{64L^2}{D_{12}\gamma^2}} \tag{1}$$

where L is the characteristic thickness of the internal mixer, D_{12} is the diffusion coefficient of the DCP in the system and γ is the shear rate. The diffusion coefficient of the blend at the melt processing temperature (200ºC) was estimated according to the considerations of Msakni and coworkers [24]. The shear rate of the internal mixer was 96 s^{-1}, based on reports in the literature [25]. The dispersion time for the DCP in the system under the processing conditions used was $\sim$3s.

The crosslink agent was added after the steady state had been reached since, under these conditions, the morphology of the phases has become stable. At temperatures above 120ºC the homolysis reaction of the O-O bond of the DCP results in the formation of primary cumilox radicals and secondary methyl radicals [12]. The EVA copolymer has a large amount of tertiary carbons which facilitates the hydrogen abstraction via free radical reactions. Because of the lower stability, the abstraction of hydrogen occurs with greater ease in the case of tertiary carbons compared with primary and secondary carbons [5], [9], [10].

In homolytic scission and the radical formation step the half-life time ($t_{1/2}$) of the radical species is related to the temperature of the medium. The half-life time of DCP can be defined as the time required for half of the initial peroxide molecules to decompose and is estimated considering the relationship [26]:

$$t_{1/2} = \frac{0.693}{k_d} \tag{2}$$

where k_d is the dissociation constant with a temperature dependence described by an Arrhenius relationship:

$$k_d = Ae^{-\frac{E_a}{RT}} \tag{3}$$

where A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant and T is the absolute temperature. In this study, the following values were used as kinetic constants: A= $9.24x10^{15}$ and E_a= 152.7 kJ/mol [27].

Bianchi and coworkers [10] estimated the activation energy for the EVA crosslinking with DCP. The activation energy values for this reaction range from 91-107 kJ/mol. The authors showed that the variation in the activation energy for this reaction is dependent on the degree of crosslinking of the EVA copolymer. The crosslinking reaction increases the molecular weight of the polymer and hence the viscosity of the system, resulting in a higher activation energy. Thus, the use of a greater amount of peroxide would result in a higher activation energy for some degree of reaction [10]. After the step involving the formation of free radicals, the second reaction step consists of the abstraction of a hydrogen atom from the main chain of the polymer, this radical being transferred from the peroxide, generating a polymeric macroradical. In the third step, the polymeric macroradicals generated recombine and result in the formation of a new covalent bond (C-C) between the chains, resulting in an increase in the molecular weight and viscosity. The half-life time for homolytic scission of the DCP was ~6s, according application of equations 2 and 3. This time is longer than the dispersion time of the DCP in the blends, indicating that the radicals are generated in the mixture and homogenized well before the generation of the half species.

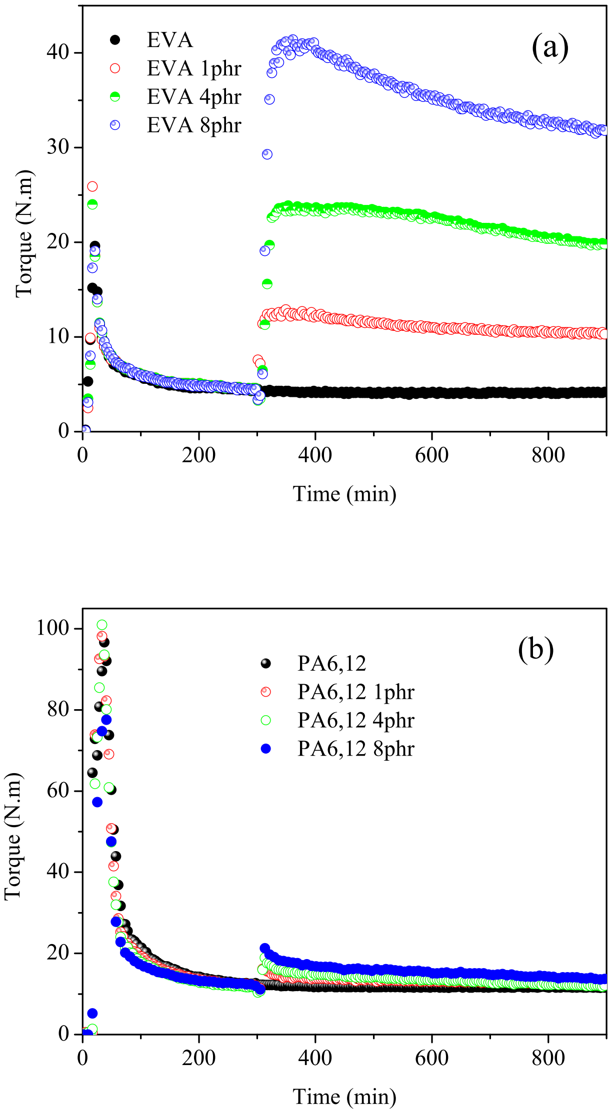

Fig. 1: (a) Torque *vs.* time curves for EVA materials with 0, 1, 4 and 8 phr of DCP and (b) torque *vs.* time curves for PA6,12 materials with 0, 1, 4 and 8 phr of DCP

The addition of larger amounts of DCP to the EVA resulted in increased torque, as shown in Figure 1 (a). This occurs because of the higher quantity of free radicals in the reaction medium, which increases the viscosity of the medium more rapidly. Figure 1 (b) shows the torque versus mixing time for PA6,12 with different DCP contents. The addition of DCP to PA6,12 did not change the stabilized torque values (12-15 min of processing). These results do not indicate the occurrence of crosslinking reactions or thermo-mechanical degradation in polyamide chains. Polyamides are characterized by carboxylic and amino end groups in addition to the amide groups. For polyamide with a higher ratio of carboxylic to amino end groups, making the polymer more sensitive to oxidation caused by free radical reactions, this phenomenon is catalyzed by carboxylic groups [28]. The amino groups have been found to stabilize the polyamide, possibly due to reactions with hydroperoxides or peroxyl radicals. It has also been suggested that the amino end groups react with carbonyl groups, causing the formation of azomethine groups and possible subsequent reactions which result in sequences of conjugated double bonds which may account for the observed yellowing [29]. Similar results were observed by Bondan and coworkers [2] for blends of PA12/EVA prepared in a torque rheometer. The addition of the DCP as a crosslinking agent showed higher selectivity toward the formation of crosslinks in the EVA phase that in the polyamide 12 phase. The pure polymers without DCP added showed stabilized torque values of around 4.0 and 11.5 Nm for EVA and PA6,12, respectively. The addition of different amounts of DCP to the system caused an increase in the stabilized torque of the EVA, with values of 20 and 32.2 N.m for samples containing 4 and 8 phr DCP, respectively.

Figure 2 shows the curves for the torque versus time for blends containing different amounts of DCP. The formation of macro radicals in the elastomeric phase resulted in the

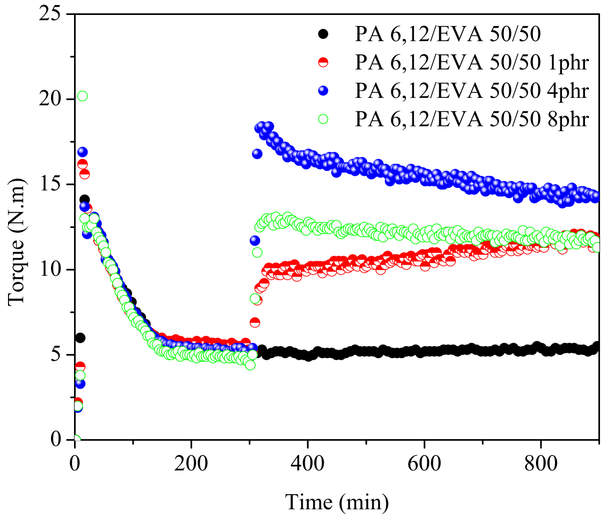

Fig. 2: Torque *vs.* time for PA6,12/EVA 50/50 blends with 0, 1, 4 and 8 phr of DCP

formation of new C-C bonds and an increase in the torque values, which provides an indirect measure of the viscosity of the system [1]–[3], [9]. The sample with 4 phr DCP had a higher torque value; however, for the sample with 8 phr DCP the torque value at the end of processing was lower when compared with the sample containing 4 phr DCP. This is because the DCP (in excess) acts as a lubricant system [9], [10]. The addition of DCP results in an increase in the mixing torque and the variation in the bulk temperature with mixing time was compared to that of PA12/EVA 50/50 with 0 phr of DCP. The use of DCP results in the formation of C-C linkages and an increase in the degree of crosslinking in EVA phase [9], [10], [20]. The increase in the degree of crosslinking results in the generation of viscous heat for blends with organic peroxide.

The degree of crosslinking of the dynamically crosslinked samples was estimated via the gel content. The PA6,12/EVA mixture without DCP is soluble in boiling m-cresol, due to the interaction between the polar groups of the solvent and polymers [11]. For this reason, the crosslinked fraction or gel content of the dynamically crosslinked samples can be determined, as shown in Table 1. The addition of DCP to the samples resulted in an increase in the gel content. In the case of PA6,12, the addition of DCP did not result in the formation of crosslinking. Similar results were observed for pure PA12 [2].

For the PA6,12-/EVA 50/50 blend without DCP, as expected, no crosslinked network was observed. The addition of larger amounts of DCP resulted in increased formation of gel structures, from 2.6wt.% for the sample with 1 phr of DCP to 17wt.% for the sample with 4 phr of DCP. A similar behavior was observed for the stabilized torque values (12-15 min of processing). For the sample containing 8 phr of DCP the gel content was 10.5wt.% This result is due to the excess of the DCP in this blend, which generates cumilox and methyl radicals that can recombine [12].

Blends of two polymers typically produce an immiscible system, thus presenting a morphology with two distinct phases. The morphology of the immiscible system is dependent on the composition of the blend, viscosity ratio, interfacial tension and viscoelastic characteristics of the polymers [13].

Figures 3 (a), (b), (c) and (d) shows the SEM micrographs for the samples of the 50/50 blend with different DCP contents (0, 1, 4 and 8 phr). The morphology of the PA6,12/EVA samples was found to be dependent on the DCP content. In Figure 3(a) the formation of a co-continuous phase morphology for the PA6,12/EVA sample without the addition of DCP can be observed. Figure 3(b) shows the partially fragmented EVA phase. After the addition of DCP, the formation of crosslinking in the EVA phase occurs, as described above. The action of mechanical forces during the processing resulted in the partial fragmentation of the EVA phase (Fig. 3 (c)). This result was also observed for the other samples. However, in the case of the sample containing 8 phr of the DCP (Fig. 3(d)), the EVA fragments were larger, due to the lubricating effect generated by the greater amount of peroxide [9], [10]. The lubricating action reduces the specific energy of the mixing, which, in turn, is not as effective in terms of the fragmentation.

The mechanical properties of polymer blends are strongly affected by the phase morphology. In polymer blends with a dispersed phase, it is common to observe a synergistic effect on the mechanical properties. The literature has shown that for mixtures with composition 50/50 is observed negative deviations of the mixing law for mechanical properties [14]. Similar observations are also noted for blends with high interfacial tension [30].

The morphology of TPVs of PA6,12/EVA show a coarse phase morphology, due to the partial fragmentation of the EVA during the dynamic melt processing. For this reason, there is a reduction in some of the mechanical properties with the addition of DCP contents higher than 1 phr.

IV. CONCLUSIONS

Dynamically crosslinked PA6,12/EVA blends were obtained through melt-mixing in a torque rheometer at temperatures and time-scales suitable for industrial polymer processing equipment. In these materials, the EVA phase was selectively crosslinked using free radical reactions.

The addition of different amounts of DCP to samples of PA6,12/EVA resulted in increased torque due to the formation of the crosslinked EVA phase. The phase morphology of the blends indicated that the PA6,12/EVA 50/50 materials showed co-continuous phase morphologies with high viscous and elastic EVA domains interconnected to PA6,12 regions. The dynamically crosslinked blends showed a coarse phase morphology, which does not result in significant increases in the tensile mechanical properties.

V. ACKNOWLEDGMENTS

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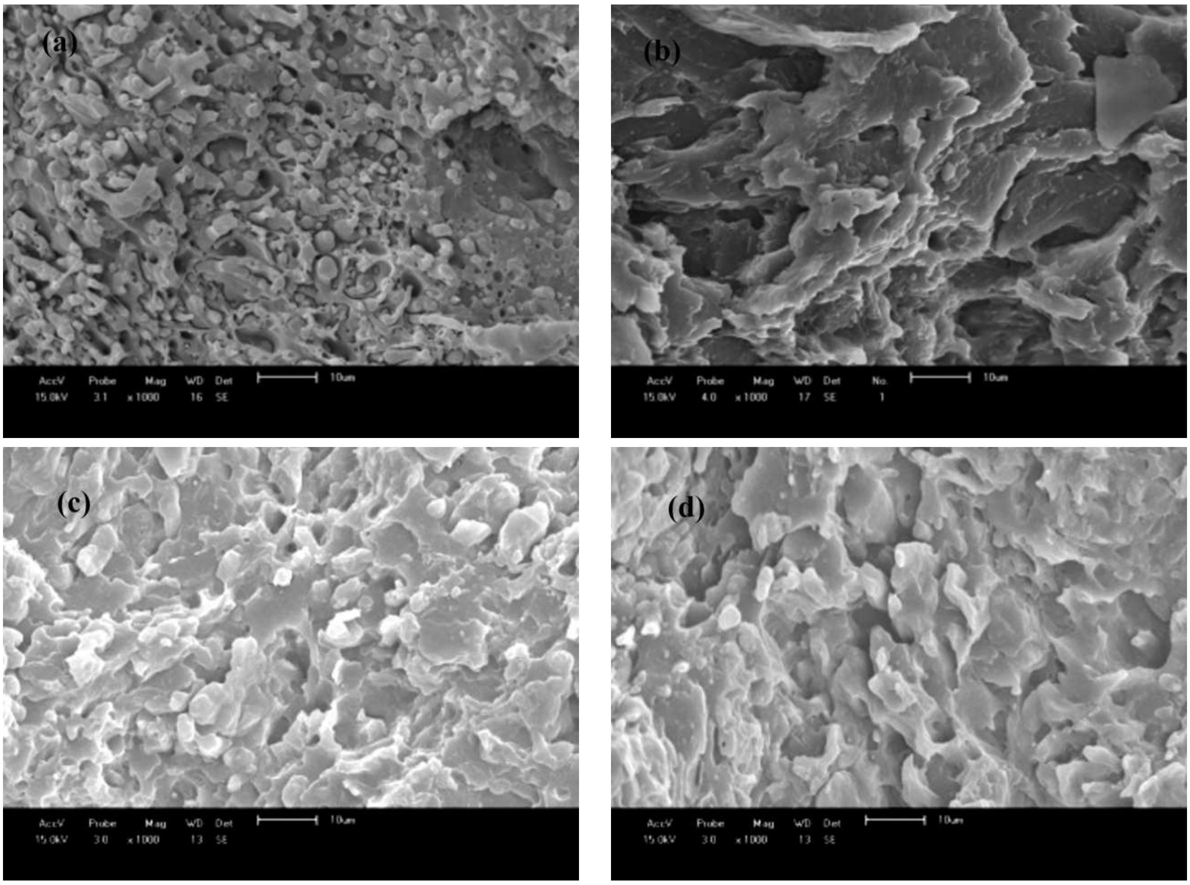

Fig. 3: Phase morphology of the polymer blend PA6,12/EVA (a) without addition of DCP, (b) with addition of 1 phr DCP, (c) with addition of 4 phr DCP and (d) with addition of 8 phr DCP.

TABELA I: Mechanical properties and gel content

Sample	Tensile strength (MPa)	Elongation at break (%)	Hardness (Shore D)	Gel content (wt.%)
PA6,12	43.7 ± 6.6	424.0 ± 50.4	59.4 ± 0.5	0.0 ± 0.5
PA6,12/EVA 50/50	18.1 ± 3.4	484.7 ± 159.1	41.6 ± 0.5	0.0 ± 0.5
PA6,12/EVA 50/50 1 phr	21.8 ± 2.7	321.1 ± 71.7	47.0 ± 1.0	2.7 ± 0.3
PA6,12/EVA 50/50 4 phr	15.0 ± 0.9	271.2 ± 20.9	46.6 ± 0.5	17.0 ± 1.7
PA6,12/EVA 50/50 8 phr	11.6 ± 1.1	196.5 ± 40.5	47.2 ± 0.8	10.5 ± 0.8
EVA	4.5 ± 0.3	375.6 ± 162.0	28.4 ± 0.5	0.0 ± 0.5

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