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Dynamic Vulcanization of Thermoplastic Elastomers Based on Poly(Epichlorohydrin-*Co*-Ethylene Oxide) and Polypropylene

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Unvulcanized and dynamically vulcanized blends of poly(epichlorohydrin-*co*-ethylene oxide) elastomer and polypropylene have been prepared by melt mixing in an internal mixer. The solvent resistance, morphology, dynamic mechanical and mechanical properties of these blends were studied with special reference to the effect of the crosslinking agent content. The swelling behaviour shows that the blends, with and without dynamic vulcanization, present excellent resistance to solvents ASTM A, B, C and D, at room temperature. Morphology study by scanning electron microscopy of the cryofractured surface and analysis of the dynamic mechanical properties of the system indicate that the uncrosslinked blend is immiscible and form a two-phase structure, where the rubber phase was dispersed as domains in the continuous polypropylene matrix. The mechanical properties of the crosslinked blends do not improve by increasing the doses of crosslinking agent.

Introduction

The emergence of thermoplastic elastomers (TPE) is one of the important developments in the area of polymer science and technology, because these materials posses the elasticity of a rubber, at ambient conditions, and the thermoplasticity and processability of a plastic.[1,2] Thus, these materials offer a substantial economic advantage with respect to the fabrication of finished parts by methods such as extrusion and molding. Generally, the elastomer/thermoplastic combination in a single material lead to an immiscible blend, and consequently a technological compatibilization is necessary to improve the mechanical properties of the blends, and to produce commercially relevant materials.[3,4]

A typical method to improve the rubber performance and stabilize the morphology of blends for the thermoplastic elastomer is dynamic vulcanization, also called dynamic curing or dynamic crosslinking, introduced by Fischer.[5-8] This method describes the process of vulcanization of the elastomer during melt-mixing with a molten plastic. This technology has led to a significant number of products commercialized after the end of the 1980s, such as Santoprene® and Geolast®.[9] The ductility of polypropylene was enhanced by melt blending with different rubbers and the brittle-ductile transition temperature was shifted toward lower temperatures. The impact strength of the thermoplastic at low temperature was also improved. [10,11]

Several researchers had studied the rheological behaviour of isotactic propylene and nitrile rubber blends due to the oil-resistance properties of nitrile rubber and excellent processability and mechanical properties of polypropylene. However, these blends are immiscible with poor mechanical properties due to the weak physical and chemical interactions between the phases. Thus, several studies were done to attain a technological compatibilization, improving the mechanical and reological properties of the blends for commercial uses.[12-15] George *et al.*[16] studied the effect of the dynamic vulcanization of isotactic polypropylene and nitrile rubber blends, using sulfur, peroxide and a mixed system, on its viscoelastic behaviour. Among these systems, the researchers observed that the peroxide system lead to blends with the highest values of the storage modulus and the sulfur system the lowest. In addition, for the same system, Kuriakose *et al.*[17] investigated the effect of the dynamic vulcanization of the blend on its viscoelastic properties. They found that the increase in storage modulus and decrease in loss modulus became more remarkable as the extent of crosslinking increased.

The effect of dynamic vulcanization on the rheological behaviour of various rubber-plastic blends has been investigated in several studies, observing that the viscosity of the blends increased as a function of the curing agent content**,** and that a high entanglement density (lower M_c values) gave the higher quality blends.[2,17] Also, in these studies, was observed that the dynamic vulcanization of the rubber phase gives compositions with improved mechanical properties, compared to uncured compositions. This is attributed to the stabilization of the rubber particle morphology, resulting from crosslinking.

Among the different types of elastomers, the poly(epichlorohydrin-*co*-ethylene oxide) has attracted much interest, because its vulcanized form offers an attractive combination of properties, such as heat resistance, fuel and oil resistance, ozone resistance, and low glass transition temperature (-41 ^{o}C). These properties leaded to its use in many consumer and engineering applications.[18] The most important crosslinking agent for the poly(epichlorohydrin-*co*-ethylene oxide) elastomer is 2-mercaptoimidazoline, also called ethylenethiourea. In this system, the elastomer readily undergoes nucleophilic-substitution reactions at the pendant chloromethylenic group, which is the site for the crosslinking. Vulcanized poly(epichlorohydrin-*co*-ethylene oxide) exhibits resistance to ozone and heat aging and resistance to a variety of fluids including lubricating oils and fuels. Thus, the largest single area for application of this material is in the automotive industry, in fuel, air and pressure hoses, and tubing, and many other automotive parts.[18]

According to the previous discussion, the blends of poly(epichlorohydrin-*co*-ethylene oxide) elastomer with isotactic polypropylene should present the oil resistance and flexibility of an elastomer and the excellent processing characteristics and mechanical properties of polypropylene. Thus, the purpose of the present study is to investigate the effect of the dynamic vulcanization of the poly(epichlorohydrin-*co*-ethylene oxide)/polypropylene (70/30) blend, specifically the effect of 2-Imidazolidinethione concentration on the morphology, mechanical and dynamic mechanical properties, and solvent resistance of the blend.

Experimental

Raw materials

The Epichlomer-C elastomer sample, poly(epichlorohydrin-*co*-ethylene oxide) (50/50), Epichlomer-C®, was supplied by Daiso Co., Ltd. (Osaka; Japan). Isotactic propylene, PPi, H503 (MFI 3.4 g 10 min^{-1} at 230 °C and 2.16 Kg cm^{-2}) was supplied by Braskem S.A. (Triunfo, Brazil). 2-Imidazolidinethione (Ethylenethiourea, ETU), Aldrich, was used as the curing agent for the vulcanization. ZnO, Carbon black, Zinc stearate were used as received. Immersion fluids for the swelling test were Chloroform (Merck), Toluene (Merck) and iso-octane (Merck). Toluene and iso-octane at different volume ratios were mixed to prepare the ASTM fuels (A, B, C, D and E), according to ASTM D471-93 standard.

Preparation of Epichlomer-C®/PPi thermoplastic elastomers

The blends of Epichlomer-C® and PPi were prepared by mechanical mixing in Haake Rheocord 90 internal mixer equipped with counter rotating rotors and a mixing chamber of 69 mL. PPi was first molten for 2 min at 180 °C and 60 rpm in the presence of stearic acid and ZnO, followed by the addition Epichlomer-C and curing agent in the same conditions. The total mixing time was 6 min. The unloading of the mixing chamber was followed by the lamination of the sample in an open roll mill at controlled temperature at 70 °C. After that, the samples were vulcanized at 200 °C and 5 MPa of pressure for 10 min in a Jasco model HP3 Hot Press. Details of the mixes are given in Table 1. The amount of the curing agent is based on the rubber phase.

Table 1: Formulation of dynamically vulcanized Epichlomer-C/PPi (70/30) blends (parts per 100 parts of rubber by weight).

Components	**Blends**				
	BVD	**BVD1**	**BVD2**	**BVD3**	**BVD4**
Ethylenethioureia (ETU)	-	1	2	3	4
ZnO	1	1	1	1	1
Carbon black	0.5	0.5	0.5	0.5	0.5
Zinc stearate	2	2	2	2	2

Characterization of Epichlomer-C®/PPi thermoplastic elastomers

Gel fraction (GF) measurements of the blends were done by swelling test at room temperature in chloroform during 8 days. GF was calculated from the weight ratio of the dried sample before and after extraction. The solvent resistances of the blends were also done by swelling test, according to ASTM D471-93 standard, using a disk of 20 mm radius, die cut from 2 mm thick molded sheets. These were accurately weighed and immersed in the solvents at room temperature. After the specified time of swelling, the specimens were removed from the solvents, blotted and weighed in a glass-stoppered bottle. The solvent resistance of the blend was calculated from the difference of the dried sample mass before and after swelling in the ASTM solvent.

The morphology of the blends was studied by scanning electron microscopy (SEM) in a Jeol JSM-T3000 microscope operating at 20 kV. The samples for morphology study were prepared by cryogenic fracture in liquid nitrogen. The fracture surfaces of the samples were then coated with Pd/Au alloy in a Balzer MED 020 machine.

Dynamic mechanical measurements were made over rectangular bars (6.9 x 1.9 x 5.8 mm cut from the compression-moulded sheets) using a TA 983 DMA equipment operating at a frequency of 1 Hz with a sinusoidal deformation and a heating rate of 2 ^{o}C min^{-1} over a temperature range of –100 to 100 ^{o}C.

Stress-Strain tests were done using EMIC DL 2000 equipment, according to DIN 53504 standard, using a crosshead speed of 200 mm min^{-1} and a cell of 500 N.

Results and discussion

Processing characteristics

The variation in mixing torque and temperature with time during the blend preparation was recorded. The mixing time-torque curves for Epichlomer-C$^{®}$/PPi blends uncrosslinked and dynamically cured are given in Figure 1. In all cases, only one peak is observed, and it is clear that at first the torque is high as we are introducing cold material to the mixing chamber. Once the material attains the set temperature and melts, the torque decreases indicating the complete melting of the phases. In addition, the small difference between them can be explained by the different time of chamber loading. After that, there is a stabilization of the mixing torque *vs.* the processing time for all blends vulcanized dynamically. In this case, we observe a stabilization of the torque as a result of two effects: increase of the torque due to higher viscosity as a result of crosslinking rubber phase during mixing with the molten PPi and decrease of the torque due to degradation of the blend components by shearing. In the unvulcanized dynamically (BVD) was observed that the torque curve decrease with the time. This behavior is due to the degradation of the polymer materials by thermal and mechanical process.

Also, in the figure 1 we observe that the torque at equilibrium value is depending of crosslinking agent content. Hence, the torque values at the end of mixing stage (6 min) were plotted versus crosslinking agent concentration and the results are shown in

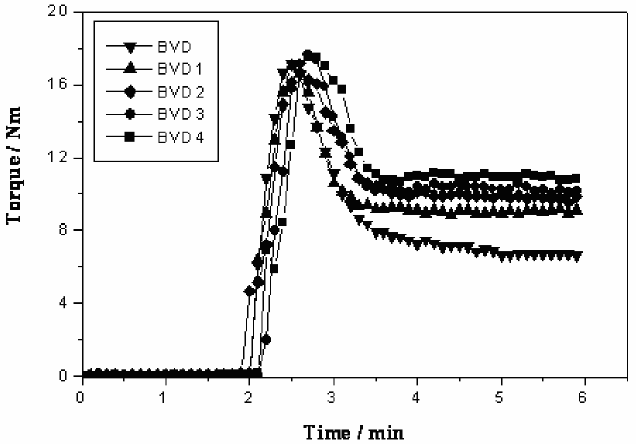

Figure 1: Time-torque curves of the Epichlomer-C$^{®}$/PPi (70/30) blends containing different levels of ETU.

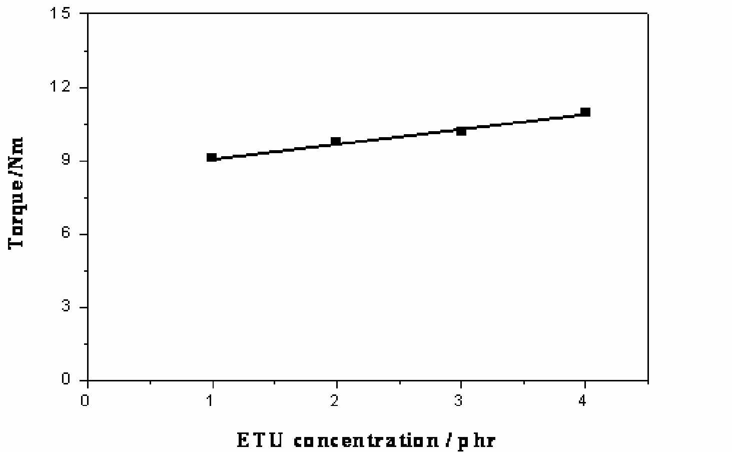

Figure 2: Effect of ETU concentration on the final torque values of Epichlomer-C®/PPi blends containing different levels of crosslinking agent.

Figure 2. It can be seen that the torque increases linearly with the crosslinking agent content. The increase in torque is due to crosslinking of the rubber phase and thereby exerting greater resistence to the rotation of branbender mixing rotors, this means that higher energy input is required for melt processing of dynamically vulcanized blends.

The temperature *vs.* time plots obtained during the blend preparation show two temperature drops, Figure 3. Initially the temperature falls due to the introduction of the plastic phase (PPi), and then the temperature increases as the melting of the plastic occurs. Addition of the rubber causes the second drop in temperature. Again, as the mixing progresses, the temperature increases. In this figure we also observe that the set temperature is achieved at the end of mixing time for all the blends, and that there is a substantial increase, c.a. 10 °C, for the set temperature values for the dynamically vulcanized blends in comparison to the uncrosslinked blend. This increase is due to

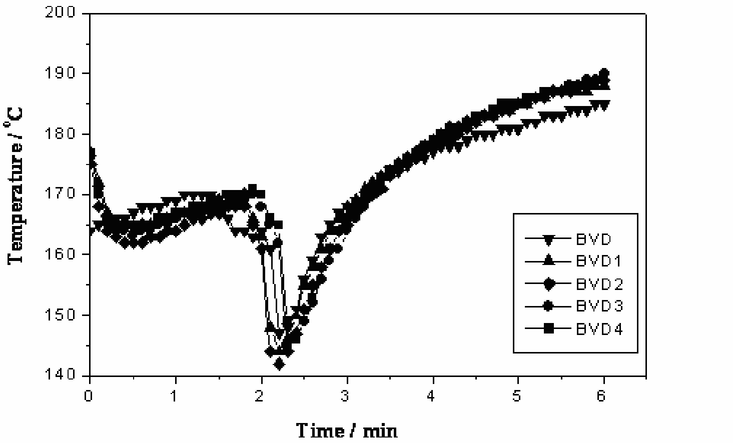

Figure 3: Time-Temperature curves of the Epichlomer-C®/PPi (70/30) blends containing different levels of ETU.

the crosslinking of the rubber phase. However, it may also be due, in part, to the resistance to rotation offered by the crosslinked rubber particles, thereby resulting in frictional heat development. Nevertheless, for the vulcanized blends was not observed an increasing in the set temperature as a function of the crosslinking agent content. In our case, this can be due to uncompleted crosslinking, due to b the short processing time.

Effect on solvent resistance

The extent of swelling in a particular solvent is expected to be sensitive to changes in the structure of the component polymer phases, and it is related to the properties of the polymer chains such as molecular mobility and phase interaction. Thus, the extent of crosslinking of the elastomer phase in the Epichlomer-C®/PPi (70/30) blends containing different levels of ETU was studied by the gel fraction (GF) determination. The variation of the GF values of the blends with ETU concentration is shown in Table 2. In this table we observe that the GF values are nearly constant, despite the increase in the crosslinking agent concentration in the blend. From this result we observed that this test do not allow to know the extent of crosslinking of the rubber phase for thermoplastic elastomers. This can be due to the fact that the thermoplastic precludes an overall swelling of the rubber phase.

Resistance behaviour of the dynamically vulcanized Epichlomer-C®/PPi (70/30) blends to the ASTM solvent at 25 °C is shown in Table 2. In this study we observe that the blends present high resistance to gasoline, based onto ASTM fuels A, B, C, and D. Also, we do not observe that an increase in the crosslinking density of the rubber phase improves substantially the solvent resistance of the blends. According to our results, the dynamically vulcanized Epichlomer-C®/PPi (70/30) blends present the same solvent resistance as the Epichlomer-C rubber and the dynamically vulcanized nylon-6/acrylate rubber (40/60) blend. [19]

Table 2: Variation of the gel fraction (GF) and of the weight in percent of the dynamically vulcanized Epichlomer-C/PPi blends after swelling test according to ASTM D 471-93.

		ASTM fuels / ΔM %				
Blends	**GF (%)**	**A**	**B**	**C**	**D**	**E**
BVD	54 ± 2	0.20 ± 0.50	0.45 ± 0.65	0.73 ± 0.56	0.23 ± 0.89	41.80 ± 1.50
BVD 1	87 ± 1	1.33 ± 0.88	1.70 ± 0.50	0.61 ± 0.75	0.60 ± 0.82	10.53 ± 0.85
BVD 2	79 ± 4	1.50 ± 0.50	1.75 ± 0.60	1.50 ± 0.70	2.92 ± 0.79	8.60 ± 1.23
BVD 3	84 ± 1	1.05 ± 0.32	1.70 ± 0.06	2.79 ± 0.62	1.98 ± 0.02	9.71 ± 0.19
BVD 4	85 ± 2	1.34 ± 0.06	1.61 ± 0.09	1.99 ± 0.21	1.87 ± 0.04	6.77 ± 0.20

A: Iso-octane, B; Iso-octane – Toluene (70/30), C: Iso-octane – Toluene (50/50), D: Iso-octane – Toluene (60/40), E: Toluene, Δ M (%): difference of dried sample weight before and after swelling, in percent.

Morphological changes

The scanning electron micrographs of unvulcanized and dynamically vulcanized blends are shown in Figure 4. This figure shows the morphology of the uncrosslinked Epichlomer-C®/PPi (70/30) blend as the blank sample. It can be seen that the rubber phase is dispersed as domains in the continuous PPi matrix, and that the dispersed phase present irregular and elongated domains. The observation of a continuous PPi phase is consistent with the melt processability of these blends. Hence, the blend is typically an immiscible blend, which is undoubtedly attributed to a large polarity difference, and by the high interfacial tension present we can postulate that it presents poor mechanical properties. In Figure 4 we also observe that the dynamic vulcanization leads to a drastic change in the morphology of the blend as a result of crosslinking of the rubber phase. This is due to a higher torque during the dynamic vulcanization, when the rubber particles are crosslinked, which leads to particles breaking-up and, consequently, to a better mixing between the rubber and the thermoplastic phase. In addition, we do not observe a decrease of the particle size of the rubber phase with the increase of the crosslinking agent concentration in the blend, Figure 4.

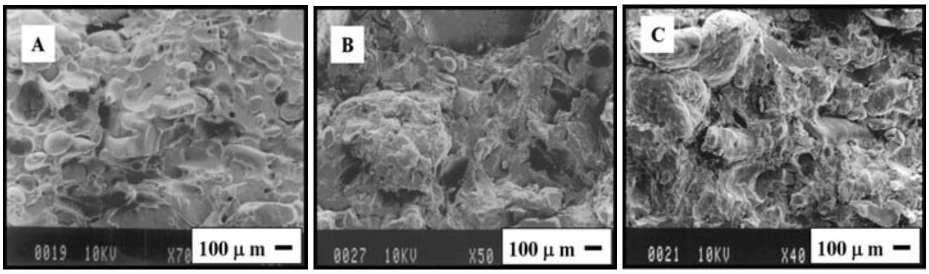

Figure 4: Scanning electron micrographs of the dynamically vulcanized Epichlomer-C$^{®}$/PPi blends: A) BVD, B) BVD1, and C) BVD4.

Dynamic mechanical analysis

The variation of the storage modulus (*E'*) with the temperature for the Epichlomer-C$^{®}$/PPi blends is shown in Figure 5. In this figure we observe that, for all the blends, uncrosslinked and crosslinked with ETU, the *E'* decrease with the increase of the temperature. Also, it is observed that the uncrosslinked blends shows the maximum values for storage module in the regions below -45 ^{o} C and above -30 ^{o}C, and the lowest values in the regions between -45 ^{o} C and -30 ^{o}C. But in the case when the blends are dynamically crosslinking between -45 ^{o} C and -30 ^{o}C, the decrease in the storage modulus is much lower and the onset of segmental mobility starts at a higher temperature. The variation of the loss modulus (*E''*) as a function of temperature are shown in Figure 6. In this case two distinct peaks were observed with increasing temperature. This is explained by the fact that, when the temperature is approaching the glass transition temperature of the rubber or thermoplastic, energy dissipation takes place and a corresponding peak is observed in the loss mudulus values. The unvulcanized blend present the two loss maxima *E''* at -45 ^{o}C and about -5 ^{o}C, and the vulcanized blends from -40 and -30 ^{o}C and from 5^{o}C to 10 ^{o}C, depending on the crosslinking agent content in the blend. The first loss correspond to the the glass transition temperatures (*Tg*) of the Epichlomer-C$^{®}$ and the second to PPi.

The temperature dependence of the tan δ for the blends is shown in Figure 7. Two peaks can be observed in the curve related to the Epichlomer-C$^{®}$/PPi blend without crosslinking agent, indicating the immiscibility of the system. This is consistent with the micrographic observation, Figure. 4. In this study we also observe that the *Tg* of the Epichlomer-C$^{®}$ phase in the crosslinked blends is shifted to a higher temperature upon the first addition of curing agent but the effect levels off at higher loadings, Figure 7. The results indicate that the vulcanization decreases chain mobility, hence making the rubbery phase more rigid. Also, in Figure 7 we can observe that the crosslinked blends present higher damping than the uncrosslinked blend. In addition, the *Tg* corresponding to the PPi component of the crosslinked blend is slightly shifted to a lower temperature. A parallel scanner differential calorimetric analysis indicated that the crystallinity of the PPi phase in these crosslinked blends is essentially constant (17 ± 3 %), which rules out the possibility of increased tan δ peak intensity due to decreased crystallinity.

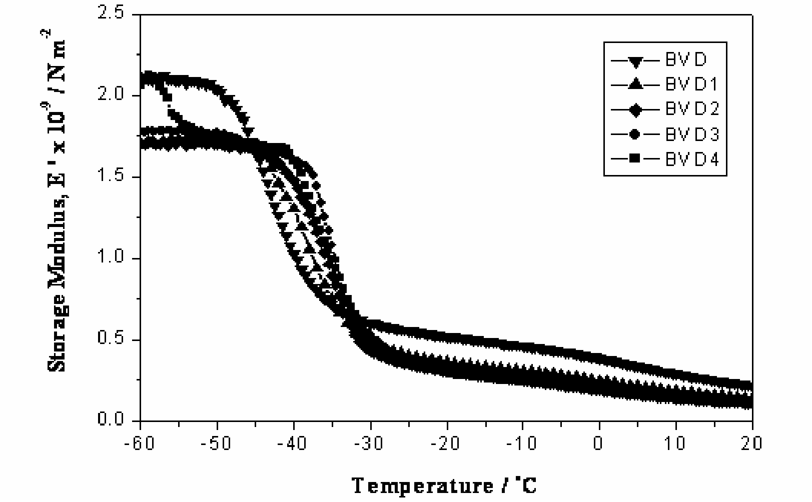

Figure 5: Variation of store modulus (E') with temperature of dynamically vulcanized Epichlomer-C®/PPi blends.

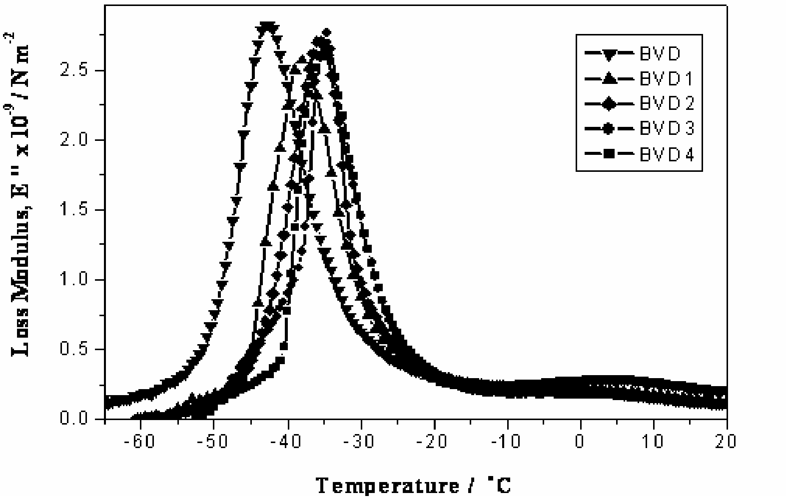

Figure 6: Loss modulus (E") vs. temperature plots of dynamically vulcanized Epichlomer-C®/PPi blends.

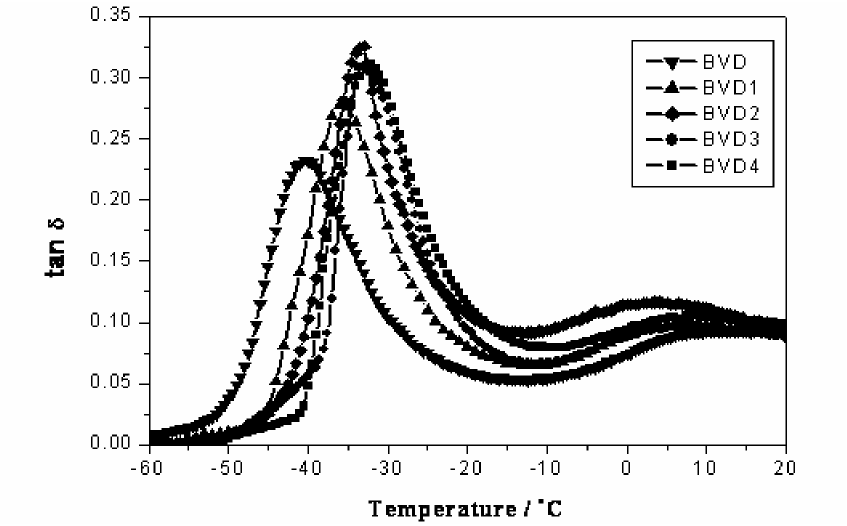

Figure 7: Loss factor (tan δ) - temperature curves of dynamically vulcanized Epichlomer-C®/PPi blends.

Mechanical properties studies

The stress-strain curves of the Epichlomer-C®/PPi (70/30) blends containing different levels of crosslinking agent are shown in Figure 8. We observe that the crosslinked blends present lower mechanical properties, specifically Young modulus, tensile stress and elongation at break, than the uncrosslinked blend, Table 3. This behavior can be explained on the basis of morphological changes that occur during the dynamic vulcanization. Also, the mechanical properties did not improve because the particle size of the rubber phase was not drastically reduced with the increase of the

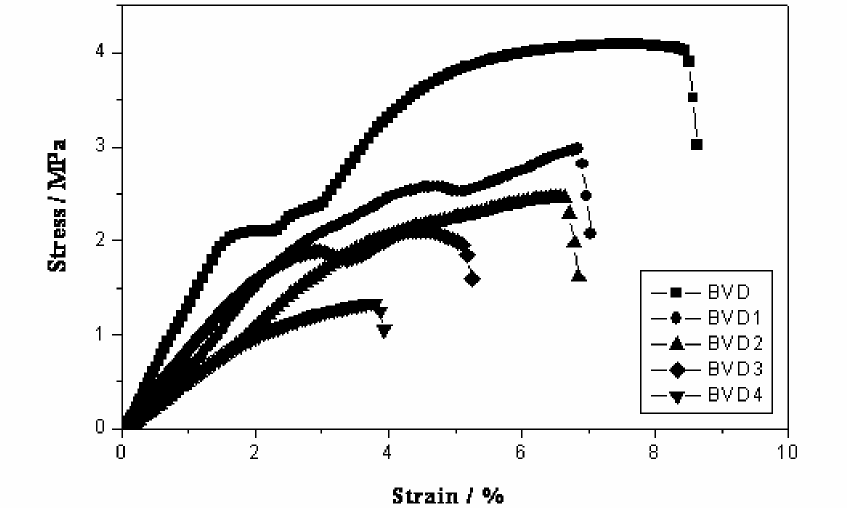

Figure 8: Stress-strain curves of dynamically vulcanized Epichlomer-C®/PPi blends.

crosslinking agent concentration. This was probably caused by the short mixing time, Figure 4. In addition, in the dynamically vulcanized blends occur a cavitation phenomenon, which to lead to production of voids at the rubber-rigid polymer interface and, hence, decreasing substantial on elongation at break. [20]

Table 3: Variation of mechanical properties with blend composition.

Blend	Young's Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
BVD	1.67 ± 0.33	4.21 ± 0.61	7.72 ± 1.18
BVD1	0.70 ± 0.14	2.67 ± 0.32	6.86 ± 0.25
BVD2	0.61 ± 0.16	2.61 ± 0.53	6.58 ± 1.02
BVD3	0.94 ± 0.06	2.79 ± 0.50	6.48 ± 1.07
BVD4	0.58 ± 0.11	1.44 ± 0.18	3.77 ± 0.37

Conclusions

This investigation indicated that the Epichlomer-C®/PPi (70/30) blend is immiscible, as shown by the presence of two relaxation peaks corresponding to the *Tg* of Epichlomer-C and PPi. The morphology of the blend shows a two-phase structure, in which the rubber phase is dispersed in the continuous PPi matrix. The analysis of the variation of mechanical properties with the crosslinking agent content indicated that the crosslinked blends present lower mechanical properties than the uncrosslinked sample. The swelling behavior of Epichlomer-C®/PPi (70/30) blends, uncrosslinked and crosslinked, in various ASTM solvents indicated that these materials present a high resistance to the solvents ASTM A, B, C and D at 25 °C. Thus, from the results obtained in this work, we can propose the use of the uncrosslinked Epichlomer-C®/PPi (70/30) blend for the construction of fuel hoses for room and sub-room temperature uses.

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