Influence of Curing Agent and Compatibilizer on the Physicomechanical Properties of Polypropylene/Nitrile Butadiene Rubber Blends Investigated by Positron Annihilation Lifetime Technique

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ABSTRACT: A series of thermoplastic vulcanizates of polypropylene (PP)/nitrile butadiene rubber (NBR) (50/50) have been prepared by melt-mixing method, using phenolic resin/$SnCl_2$ as the curing system and maleic anhydride-functionalized PP (PP-g-MA) and carboxylated NBR (NBRE-RCOOH) as the compatibilizing system. Triethylenetetramine was also employed to promote the reaction between the functionalized polymers. The effects of curing agent and compatibilizer on the mechanical and morphological properties have been studied. A novel technique based on positron annihilation lifetime spectroscopy has been used to measure the free volume parameters of these systems. The positron results showed minimum free volume size and free volume fraction at 5.0% of the curing agent suggesting some crosslinking in the rubber phase. The reduction in free volume holes at 2.5% of the compatibilizer is interpreted as improvement in the interfacial adhesion between the components of the blend. The observed variation of free volume fraction is opposite to the tensile strength and exhibits the correlation that, lesser the free volume more is the tensile strength at 2.5% of the compatibilizer in the blend. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4672–4681, 2006

Key words: polypropylene/nitrile butadiene rubber; thermoplastic vulcanizate; compatibilizer; mechanical properties; *ortho*-positronium; free volume

INTRODUCTION

Thermoplastic elastomer blends are materials with the processing behavior of thermoplastic but having the mechanical properties and elastic recovery similar to vulcanized blends.[1,2] For many end uses, these materials should have a morphology characterized by the rubber phase finely dispersed in a relatively small amount of the plastic. In addition, the elastomer particles must be crosslinked to promote elasticity. These characteristics are better achieved by adding a small quantity of crosslinking system during the melt mixing of elastomer with a molten plastic. This *in situ* vulcanization process of the dispersed rubber particle is called dynamic vulcanization and was first described by Gessler[3] and then developed by Fisher[4] and Coran et al.[5–8] As a result of dynamic vulcanization, fine dispersion of the elastomeric phase and more stable morphology can be achieved even with relatively low proportion of plastic. The thermoplastic vulcanizates (TPVs) behave like rubber at room temperature and can be processed at elevated temperature as normal thermoplastics.[9] Hence, TPVs are important from the economic as well as ecological points of view as they can be readily recycled or reground without any pretreatment, keeping their properties practically intact.[10–16]

Among several systems employed on the development of TPVs, those based on blends of polypropylene (PP) and nitrile rubber (NBR) are of particular interest for hot oil-resistant applications. However, PP and NBR are highly incompatible because of their

large difference in surface energy. This makes them difficult to attain small rubber particle size during dynamic vulcanization, which is necessary for good mechanical properties. Therefore, a compatibilizer is required to overcome the interfacial tension between the elastomeric and thermoplastic phases and enable a fine dispersion of highly crosslinked rubber particles. A 1982 patent by Coran and Patel describes a number of possibilities of PP/NBR blend compatibilization by using PP-NBR copolymer prepared *in situ* during the melt-blending.[7] Some of them include: the prefunctionalization of PP with dimethylolphenolic derivative and posterior melt-mixing with (a) NBR or (b) NBR containing amine groups; and the prefunctionalization of PP with maleic anhydride (PP-g-MA) and posterior melt-mixing with (c) NBR containing amine groups or (d) carboxylated NBR. The effect of these compatibilization systems on PP/NBR vulcanizates was lately studied by Coran and Patel[8] and George et al.[17,18] Zhang et al. have also published another compatibilization method for these blends based on a combination of glycidyl methacrylate-grafted PP and low molecular weight amino compounds.[19]

The interfacial action of a compatibilizer in a polymer blend influences the microscopic free volume parameters at atomic and molecular scale. There exists strong theoretical base relating the mechanical behavior of glassy polymers on free volume available for chain slippage and chain mobility. For example, the ability of a polymer to deform and dissipate energy under impact depends on the ability with which the chains can slide past each other or chain conformation via in-chain rotations.[20] Finding a correlation between microstructure and macroscopic properties of these materials has been of interest for many years. In the amorphous regions of a polymer, structural changes can be characterized in statistical terms, by density fluctuation or concentration and average size of the free volume holes.[21] There exist many physical probes for characterizing the structures and properties of polymers. However, only a limited number of probes are available for characterizing free volume properties. In recent years, positron annihilation technique has emerged as a unique and potent tool for characterizing the free volume properties of polymers.[22] Positron lifetime technique is one of the sophisticated tools available for determining directly the nanometer sized free volume holes and their relative number density (concentration) in polymers.[23–26] This technique has proved to be useful on studies regarding diffusion kinetics in electron-irradiated polycarbonate,[27] water sorption in contact lens polymers,[28] sorption in poly(vinyl alcohol),[29] polymers containing silver nanoparticles,[30] structural relaxation/physical aging in polymers,[31,32] etc. Even though positron annihilation lifetime spectroscopy (PALS) has been successfully used in the study of polymers for more than two decades, only recently it has been used to study microstructural behavior of polymer blends.[33,34]

The aim of this article is to study the influence of curing agent concentration and compatibilizer on physicomechanical performance of PP/NBR vulcanizates and correlate these properties with the variation of free volume size, using the PALS. For this purpose, a curing system based on phenolic resin and stannous chloride was employed. For the compatibilization system, two functional polymers, PP-g-MA and carboxylated NBR (NBR-COOH), were used. Since both anhydride and carboxyl groups can not react with each other, triethylenetetramine was also employed to promote the reaction between these functional groups according to the scheme illustrated in Figure 1.
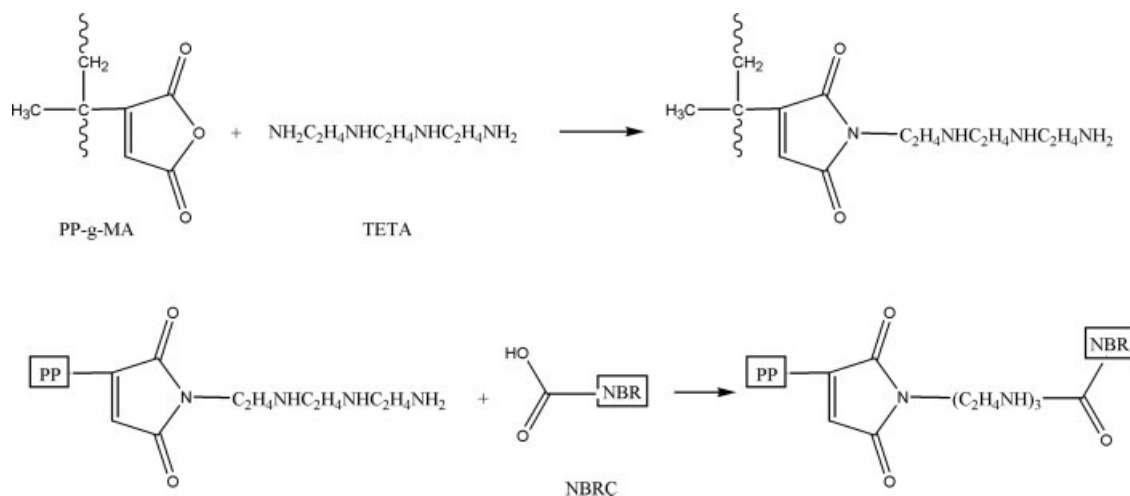

Figure 1 Reaction scheme for reactive compatibilization during melt-mixing of PP and NBR in the presence of PP-*g*-MA, TETA, and NBR-COOH.

EXPERIMENTAL

Materials

Nitrile rubber (NBR) [33 wt % acrylonitrile; Mooney viscosity (ML 1 + 4 at 100°C) = 50] and NX43G carboxylated nitrile rubber (NBR-COOH) was kindly supplied by Petroflex Ind. Com. S.A., Brazil. Polypropylene (MFI = 3.5 g/10 min at 230°C) was supplied by Brasken S.A., Brazil. Maleic anhydride-modified polypropylene (PP-g-MA) (MFI = 51.9 g/10 min at 230°C) was prepared, according to the standard procedure.[35] The maleic anhydride content of PP-g-MA is 2.4 mmol %. The reagents employed on the polymer functionalization were used as received (from Merck, India). Other chemicals employed as the vulcanization components such as phenolic resin (SP-1045), stannous chloride (SnCl$_2$), and triethylenetetramine (TETA) were of the laboratory reagent grade and were purchased from the local Industries.

Melt blending

The PP and NBR homopolymers were mixed in the ratio of 50/50 wt %, at 185°C and 80 rpm in the mixing chamber of a Haake Rheometer type RC90. After blending PP and NBR for 4 min, the vulcanizing agent (phenolic resin) and coagent (stannous chloride) were added and mixing was continued for further 4 min. After completion of the mix, the batch was passed through a two roll mill, to make easy the milling of the material for further injection step. The samples were prepared with different amounts of vulcanizing agent and compatibilizer to study their influence on the performance of the blends. The specimens for tensile property were injection-molded under pressure of 140 psi at 240°C. In the case of compatibilized blends, the mixture of PP, PP-g-MA, NBR, NBRC, and TETA were added to the Haake machine and mixed for 4 min, then a calculated amount of phenolic resin with stannous chloride curing agents were added and mixing was continued for 4 min. The composition of all samples is listed in Table I.

Mechanical properties

The density and surface hardness were measured as per ASTM D 792 and ASTM D 2240, respectively. The tensile behaviors like tensile strength and tensile modulus were measured using Instron 5569 Universal testing machine as per DIN 53504 method.

Sorption experiment

Swelling of PP/NBR TPVs samples in toluene were measured by immersing a known weight of the samples in airtight containers for 7 days at room temperature. The change in weight of the samples was measured to a good accuracy and reported in Table II.

Morphological behavior

The morphology of the samples were determined by scanning electron microscopy on a JEOL equipment model JSM 5300 with 10 kV of voltage acceleration. All samples were coated with thin layer of gold and microphotographs were recorded.

Positron annihilation lifetime measurements

In the following paragraph we briefly outline the positron lifetime method. When positrons from a radioactive source (commonly Na-22) are injected into a molecular medium, they interact with the surrounding molecules through inelastic collisions and reach thermal energy in a very short time (around 1 ps). During such a slowing down process and at nearly thermalized stage, a positron, the antiparticle of the electron, may pick up an electron from the medium and annihilate as a free positron, or get trapped into defects present in crystalline, crystalline–amorphous interface regions and then annihilates, or form a bound state with an electron of the medium (e$^+$e$^-$) called the positronium (Ps) atom. Ps exists in two allowed spin states: if the spins are aligned antiparallel to each other, it is called *para*-positronium (*p*-Ps), which has a lifetime of 125 ps; the other spin state is called *ortho*-

TABLE I
Composition of PP/NBR (50/50) Thermoplastics Vulcanizates

S. no.	Phenolic resin (wt %)	SnCl$_2$ (wt %)	PP	NBR	PP-g-MA (wt %)	PP-g-MA mmol MA	NBR-COOH (wt %)	TETA (wt %)	TETA mmol −NH$_2$
1	1.0	0.05	50	50	–	–	–	–	–
2	2.0	0.1	50	50	–	–	–	–	–
3	5.0	0.25	50	50	–	–	–	–	–
4	10.0	0.5	50	50	–	–	–	–	–
5	10.0	0.5	50	50	0.5	0.12	0.5	0.2	2.6
6	10.0	0.5	50	50	1.0	0.25	0.5	0.2	2.6
7	10.0	0.5	50	50	2.5	0.62	0.5	0.2	2.6
8	10.0	0.5	50	50	5.0	1.25	0.5	0.2	2.6

TABLE II
The Effect of Curing Agent Concentration on Physicomechanical Properties of PP/NBR (50/50) Vulcanizates

S. no.	Density (g/cc)	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)	Surface hardness (Shore A)	Weight gain in toluene (%)
1	0.9763	21.5 ± 0.5	52 ± 1.5	22.6 ± 0.7	94	67.7
2	0.9768	20.3 ± 1.0	44 ± 0.9	25.2 ± 1.9	94	67.0
3	0.9824	18.2 ± 0.5	34 ± 0.8	23.4 ± 1.3	95	63.5
4	0.9844	18.8 ± 0.5	33 ± 0.5	25.4 ± 2.6	95	60.0

positronium (o-Ps), in which the spins are parallel, and annihilates with a lifetime of 140 ns in free space. However, in molecular media like polymers, the positron of o-Ps picks up an electron from the surrounding medium and annihilates, thereby its lifetimes gets shortened to a few nanoseconds. Since o-Ps is preferentially localized in the free volume holes of polymer systems,[23–33,36–38] the Ps parameters τ_3 and I_3 have been widely used over the last few years in the study of microstructural behavior of this class of materials. It is usual to correlate the free volume characteristics to the viscoelastic properties of the system under investigation.

Positron annihilation lifetime spectra were recorded using PALS. The positron lifetime spectrometer consists of a fast–fast coincidence system with BaF$_2$ scintillators coupled to photo multiplier tubes type XP2020/Q with quartz window as detectors. The BaF$_2$ scintillators were shaped conical to achieve better time resolution. The two identical pieces of the sample were placed on either side of a 17 μCi ^{22}Na positron source, deposited on a pure kapton foil of 0.0127 mm thickness. This sample–source sandwich was placed between the two detectors of PALS to acquire the lifetime spectrum. The Co^{60} prompt spectrum gave 180 ps as the resolution function. However, to improve the counting rate, the spectrometer was operated at 220 ps. All lifetime measurements were performed at room temperature and two to three positron lifetime spectra with more than a million counts under each spectrum were recorded within a time of 1 to 2 h. Consistently reproducible spectra were analyzed into three lifetime components with the help of the computer program PATFIT-88[39] with proper source and background corrections. Source correction term and resolution function were estimated from the lifetime of well-annealed aluminum using the program RESOLUTION.[39] Three Gaussian resolution functions were used in the present analysis of positron lifetime spectra for the polymer blend samples to get better convergence.

RESULTS AND DISCUSSION

Noncompatibilized blends

PP/NBR (50 : 50 wt %) noncompatibilized blends were prepared by dynamic vulcanization, using different proportions of the curing system (phenolic resin/SnCl$_2$), but keeping constant the weight ratio between them (resin/SnCl$_2$ = 20.0). The mechanical properties of these blends are summarized in Table II. The increase of curing agent concentration resulted in an increase in density, as a consequence of the increase of crosslink density. This behavior also reflects in the decrease on swelling ability in toluene. The increase of curing agent proportion also resulted in a decrease in both ultimate tensile strength and elongation at break until a concentration corresponding to 5.0 phr of phenolic resin. Additional amount of the curing system did not affect these properties. The decrease on elongation at break in rubber vulcanizates is normally related to an increase in crosslink density. But in this system, the decrease of both ultimate tensile strength and elongation at break may be associated to the high incompatibility between the blend components. The tensile modulus did not show any substantial variation, which stayed within the experimental error for all blends. The surface hardness was not influenced by the crosslink density of the rubber phase. The dynamic vulcanization process results in vulcanized rubber particles dispersed inside the thermoplastic matrix. Since both tensile modulus and surface hardness are governed by the polypropylene phase, it is expected that the crosslink density of the rubber phase has no influence on these properties, as it is observed in this work. These morphological characteristics will be discussed in following section.

Compatibilized blends

For the compatibilization of PP/NBR blends, two functional groups, PP-g-MA and NBR-COOH, were employed together with TETA to promote the reaction between them. Both the functionalized polymers are quite miscible in PP and NBR phases, respectively, because of the low content of functional groups in these polymers and also because of the low amount of them used in the blends. Table III presents the mechanical properties and other characteristics of dynamically vulcanized PP/NBR blends as a function of the PP-g-MA concentration. In spite of the higher reactivity between anhydride and amino groups, the

TABLE III
The Effect of PP-g-MA Concentration on Physicomechanical Properties of PP/NBR (50/50) Vulcanizates

S. no.	Density (g/cc)	Elongation at break (%)	Surface hardness (Shore A)	Weight gain in toluene (%)
1	0.9844	33 ± 0.5	95	60.0
2	0.9979	30 ± 1.0	94	59.7
3	0.9921	59 ± 1.3	94	61.6
4	0.9978	67 ± 1.1	95	55.9
5	0.9883	82 ± 2.1	95	59.1

concentration of amino groups was substantially higher than anhydride groups in all studied blends. Therefore, even if all anhydride groups present in PP-g-MA reacted with amino groups, there would be enough free —NH_2 groups to react (or interact) with the carboxyl groups of NBR-COOH. From Figure 2 one can observe a slight increase in ultimate tensile strength and a decrease in tensile modulus with the increase in PP-g-MA content until a concentration corresponding to 2.5 phr. Also the swelling ability in toluene showed a minimum at this concentration, which can be related to the increase on entanglements between the components at the interface, as a consequence of the reaction between the functional groups, which is expected to occur at the interface. This supposition was based on the lower viscosity of PP-g-MA (higher MFI) and lower viscosity of NBR-COOH, compared to the corresponding polymer blend components. Both of them and TETA, a low molecular weight compound, have enough mobility to reach the interface where the reaction must take place.

The entanglement of NBR flexible chains on the PP matrix, close to the interface associated to the increase of the interphase region (because of the lower interfacial tension and smaller particle size of the rubber dispersed phase) also contributes for the decrease in modulus.

The elongation at break was strongly affected by the compatibilization. Indeed, a substantial and continuous increase in this property was observed as the PP-g-MA concentration increases.

Positron annihilation lifetime results

The acquired lifetime spectra were resolved into three lifetime components τ_1, τ_2, and τ_3 with intensities I_1, I_2, and I_3, respectively. All the lifetime spectra were resolved into three lifetime components, since this gave better χ^2 value and standard deviations than the two- and four-component analyses. The attribution of these lifetime components is as follows.[24] The shortest lifetime component τ_1 with intensity I_1 is attributed to para-positronium (p-Ps) and free positron annihila-

tions. The intermediate lifetime component τ_2 with intensity I_2 is usually considered to be mainly due to annihilation of positrons trapped at the defects present in the crystalline regions or trapped at the crystalline–amorphous interface regions. Since τ_2 is not the main focus of the work, the second lifetime is not discussed in this article. The longest-lived component τ_3 with intensity I_3 is due to pick-off annihilation of the ortho-Positronium (o-Ps) in the free volume sites present mainly in the amorphous regions of the polymer matrix.[40] The o-Ps lifetime τ_3 is related to the free volume hole size by a simple relation given by Nakanishi and Jean,[41] which was developed on the basis of theoretical models originally proposed by Tao[42] for molecular liquids and later by Eldrup et al.[43] In this model, positronium is assumed to be localized in a spherical potential, which has an infinite potential barrier of radius R_o with an electron layer in the region $R < r < R_o$. The
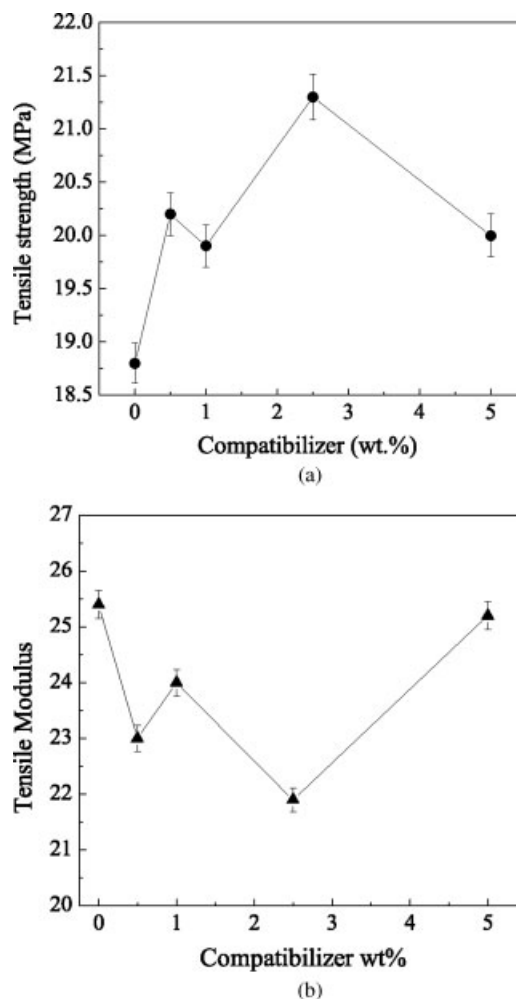

Figure 2 Plot of (a) tensile strength and (b) tensile modulus as a function of compatibilizer concentration (solid line is to guide eye).

relation between τ_3 and the radius R of the free volume hole or cavity is:

$$(\tau_3)^{-1} = 2\left[1 - \frac{R}{R_o} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_o}\right)\right]\ ns^{-1} \quad (1)$$

where, $R_o = R + \delta R$ and δR is an adjustable parameter. By fitting eq. (1) with τ_3 values for known hole sizes in porous materials like zeolites, a value of $\delta R = 0.1657$ nm was obtained. With this value of δR, the free volume radius R has been calculated from eq. (1) and the average size of the free volume holes V_f was evaluated as $V_f = (4/3)\pi R^3$. The fractional free volume or the free volume content (F_v) can then be estimated as:

$$F_v = C\ V_f I_3 \quad (2)$$

where C is the structural constant, V_f and I_3 are the parameters described above. The parameter C has to be estimated from a different experiment. In the present case, we use the relative fractional free volume defined as $F_{vR} = V_f I_3$ in the absence of measured C value, to understand the changes in fractional free volume. Since the Ps atom probes the local molecular environment and the free volume is the result of it, the PALS results are more appropriate for understanding the interactions at molecular level.[22]

The effect of curing system concentration on positron parameters (τ_3, I_3, V_f, and F_{vR}) is illustrated in Figure 3. The curing agent concentration exerted different influence on o-Ps lifetime τ_3 [Fig. 3(a)]. The addition of up to 2% of curing agent resulted in small increase in τ_3, which suggests a rearrangement of dispersed NBR phase in the PP matrix. More addition of the curing agent resulted in a decrease in this parameter, which means a decrease on free volume hole size (V_f), as a consequence of the increase in crosslink density. However, when 10% of the cur-
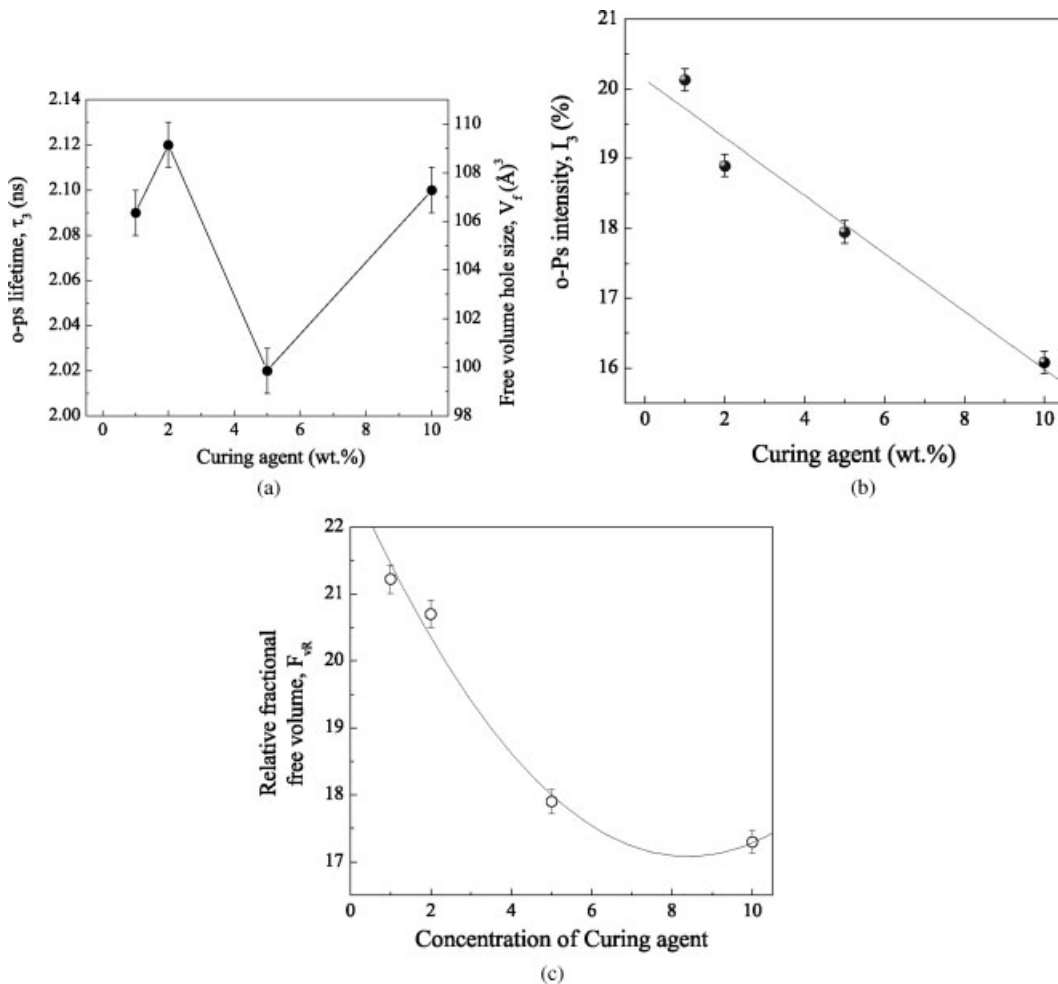

Figure 3 (a) Plot of o-Ps lifetime τ_3 and free volume hole size V_f as function of curing agent concentration (solid line is to guide eye). (b) Plot of o-Ps intensity I_3 as function of curing agent concentration (solid line is to guide eye). (c) Plot of relative fractional free volume F_{vR} as a function of curing agent concentration (solid line is to guide eye).

ing agent was employed, the free volume hole size increased again, in spite of the increase in crosslink density, as indicated by the decrease in swelling ability in toluene (Table II). This behavior may be attributed to the increase in free volume at the interface between PP and NBR, probably because of the contraction of the NBR phase promoted by a higher crosslink density. The increase in the curing system also resulted in a gradual decrease in o-Ps intensity (I_3) [Fig. 3(b)]. This behavior may be attributed to the inhibiting nature of chlorine in the $SnCl_2$ with regard to o-Ps formation probability. This effect was also observed in literature for other systems containing chlorine,[44] and is expected to occur in our system, since the decrease in I_3 was observed with increase in $SnCl_2$ concentration. The o-Ps intensity may also be related to the number of holes in the

material. The increase in crosslink density of the dispersed NBR phase may also cause a decrease in the number of holes. Even with 10% of the curing agent, the number of holes is lower in spite of their larger size (V_f). This behavior is due to the strong incompatibility and poor interfacial adhesion of the blends.

The effect of the compatibilizing agent concentration on positron parameters was also evaluated and the results are illustrated in Figure 4(a–c). Both o-Ps lifetime (τ_3) and free volume size (V_f) decrease with the increase of compatibilizer content and present a minimum at 2.5 wt % of the compatibilizer. Similarly, at this concentration, it was observed a maximum value in tensile strength and minimum value in modulus. These results suggest an improvement on interfacial adhesion between the blend compo-
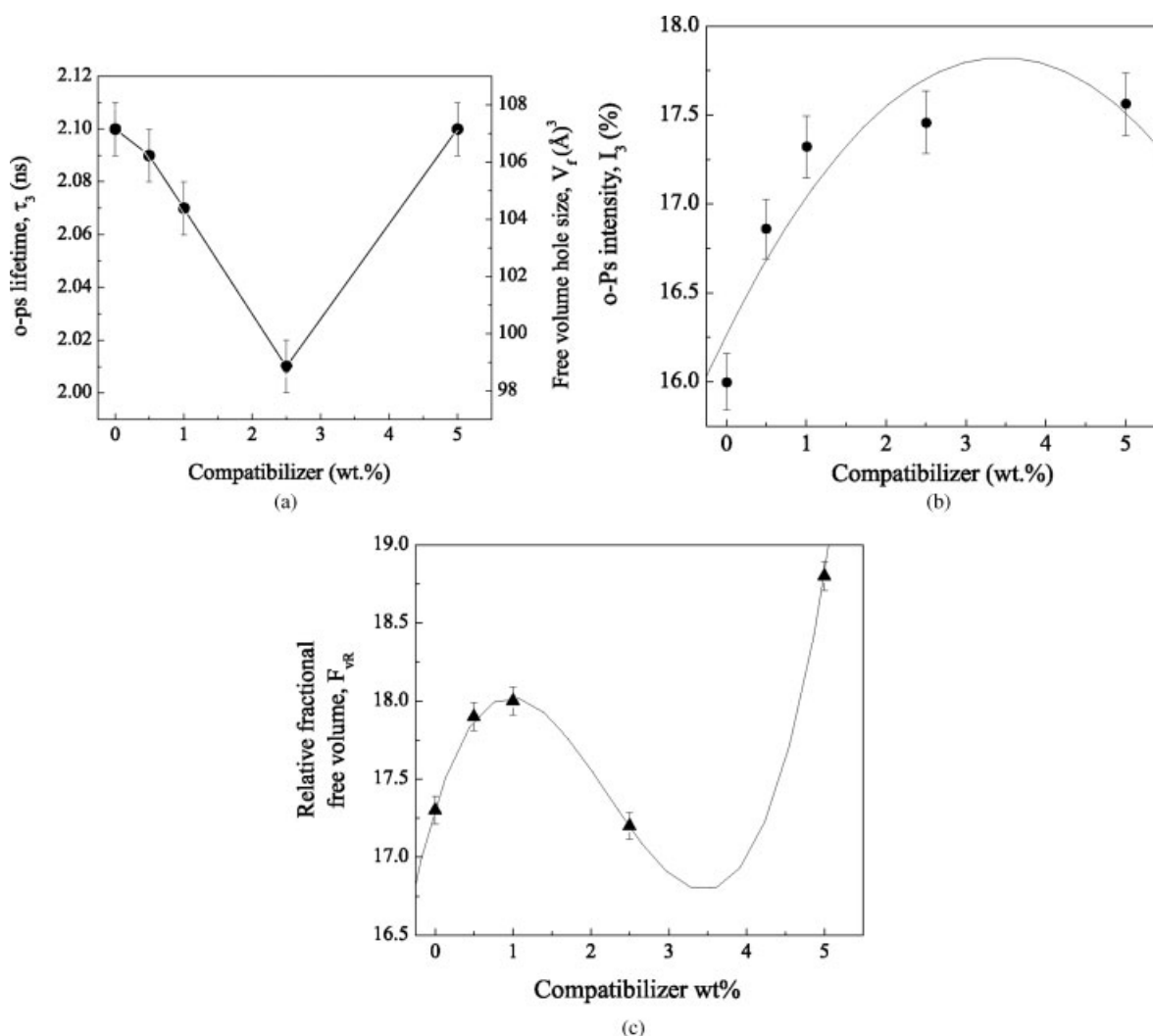

Figure 4   (a) Plot of o-Ps lifetime τ_3 and free volume hole size V_f as function of compatibilizer concentration (solid line is to guide eye). (b) Plot of o-Ps intensity I_3 as function of compatibilizer concentration (solid line is to guide eye). (c) Plot of relative fractional free volume F_{vR} as function of compatibilizer concentration (solid line is to guide eye).

nents until a concentration of compatibilizer corresponding to 2.5%, and an increase on entanglements at the interface, contributing for a decrease in free volume hole size. Attempts to correlate molecular structure and the available free volume with chain mobility and mechanical properties have led to the general belief that any process, which reduces free volume, also reduces chain mobility, increases tensile strength, and reduces tensile modulus.[34] The higher V_f for blend with 5% of PP-g-MA is somewhat intriguing, since this blend presented the highest value of elongation at break [Fig. 2(b)]. This phenomenon may be attributed to a plasticizing effect of PP-g-MA because of its high MFI.

It is important to point out that the increase in PP-g-MA concentration resulted in a decrease in free volume size but a small increase in the o-Ps intensity, I_3. The I_3 parameter is related to the number of holes present in the sample. This behavior may be interpreted as follows: the compatibilization decreases the interfacial tension, giving rise to smaller rubber particle size. Consequently, the interfacial area becomes higher. Therefore, the interfacial adhesion resulted in a decrease in free volume hole size but the higher interfacial area contributes for an increase in the number of these small holes at the interface. This reflects on the increase in I_3 value [Fig. 4(b)].

The effect of curing agent as crosslinker and the compatibilizer can effectively be observed by comparing the relative fractional free volumes of unvulcanized and vulcanized blends of PP/NBR (50/50). The relative fractional free volume of pure PP is 23.3 and that of NBR is 19.1. Using the following linear additivity rule given by Kelly and Bueche,[45] the predicted value of relative fractional free volume for 50/50 blend can be calculated as

$$F_{vR} = F_{vR1}w_1 + F_{vR2}w_2 \qquad (3)$$

where F_{vR}, F_{vR1}, F_{vR2} are the relative fractional free volumes of blend and its constituent polymers 1 and 2, respectively, w_1 and w_2 are the weight fractions of component polymers 1 and 2 in blend. From the above linear additive relation, the predicted value of relative fractional free volume turns out to be 21.2. The experimentally determined value for this blend is also 21.2. It is evident from the literature that immiscible or incompatible blends always result in the relative fractional free volume equal to or greater than the linear additive values.[46] Based on this, it can be concluded that PP/NBR is an incompatible system. From Figure 3, we observe that F_{vR} decreases with the addition of curing system and these values are less than 21.2% suggesting the effect of curing system through possible crosslinking. This results in the improvement of compatibility of the

system. Further, when compatibilizer is added to the system having 10 wt % of curing agent, it is observed that F_{vR} shows slight minimum at 2.5 wt % of compatibilizer. The effect of compatibilizer is not very significant, otherwise we could have observed noticeable decrease in F_{vR} as a result of improved phase compatibility. However, 2.5 wt % of the compatibilizer can be considered as optimum concentration for the present system to achieve moderate compatibilization.

Morphological aspects

Figure 5 compares the morphology of dynamically vulcanized PP/NBR blends obtained by SEM. The white region corresponds to the rubber phase, which was selectively stained by OsO_4. In all blends, the polypropylene (dark region) constitutes the matrix containing the rubber particles (white region) dispersed inside it. This morphological situation explains the results observed for surface hardness. This property was not influenced either by curing agent concentration or compatibilization because the PP matrix governs it. The compatibilization decreased significantly the rubber particle size and this behavior was more pronounced in blend containing 5% of PP-g-MA. In addition, this blend presented a more homogeneous distribution of rubber particles, and a higher interfacial area, which may explain the best results observed for elongation at break and also the results observed from positron annihilation experiments.

CONCLUSIONS

The effect of curing agents and the PP-g-MA compatibilizer concentration on the phase morphology and mechanical properties of PP/NBR blends has been studied. The positron results showed minimum V_f and F_{vR} values at 5.0% of the curing agent concentration, suggesting an ordering of the dispersed phase and a stabilized structure through vulcanization process. With regard to the compatibilization effect, there is a continuous improvement of elongation at break as the amount of PP-g-MA in the blend increase. From positron data, it was observed that the concentration of PP-g-MA corresponding to 2.5 wt % resulted in minimum values of V_f and F_{vR}, and also a maximum on tensile strength and a minimum on the percent change of weight after toluene swelling, which agree with the smaller free volume hole size. The higher value on elongation at break with 5% of PP-g-MA associated to higher value of free volume hole size were attributed to the increase in interfacial area between the blend components.
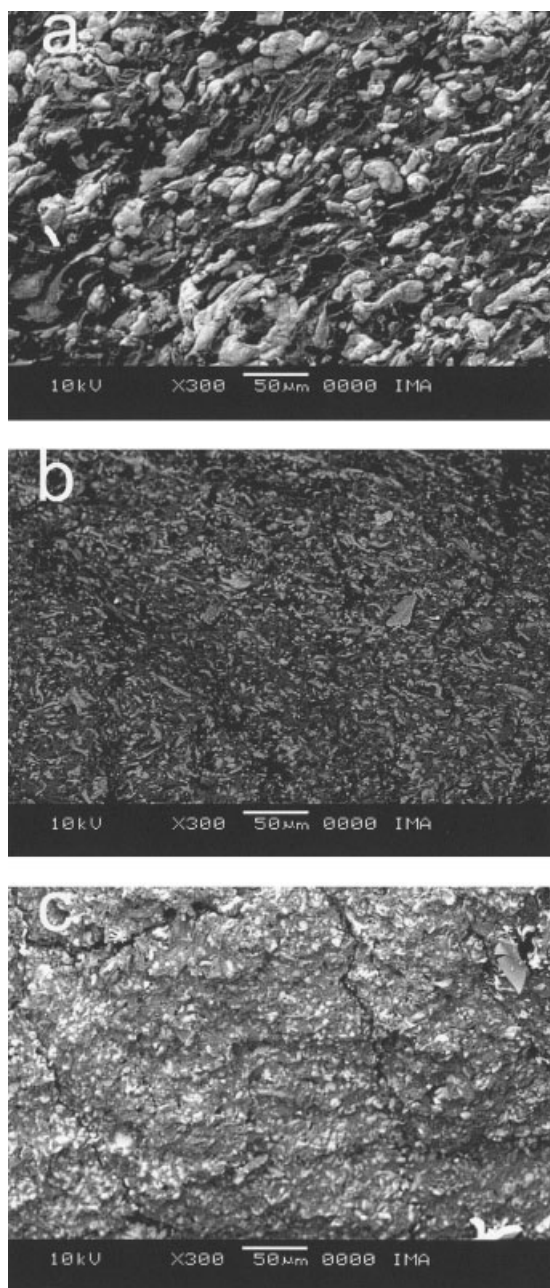
Figure 5 SEM micrographs of dynamically vulcanized PP/NBR (50 : 50 wt %) blends: (a) noncompatibilized; (b) with 2.5% PP-*g*-MA; (c) with 5% PP-*g*-MA.

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