

STUDY ON THE MISCIBILITY OF DYNAMICALLY VULCANIZED EPDM/PP BLEND BY POSITRON ANNIHILATION SPECTROSCOPY^{*}

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Abstract Positron annihilation spectroscopy (PAS) was utilized to investigate the relationship between the free-volume hole properties and miscibility of dynamically vulcanized EPDM/PP blend. The results showed that the noncrystalline region of PP and EPDM in the blend was partially miscible and the miscibility of the blend became worse when the weight percent of EPDM was <50%. This was also demonstrated by DMTA and mechanical properties of the blends with various compositions.

Keywords EPDM, PP, Dynamic vulcanization, Miscibility, PAS

INTRODUCTION

Since the last few decades, it has been realized that many physical and mechanical properties of polymers can be significantly improved by a process of blending^[1]. Miscibility and phase-separation phenomena of polymer blends have received significant attention in polymer applications^[2]. In order to predict and enhance the mechanical properties of blends, it is important to understand the atomic-scale microstructure and interaction between the two phases of the blend.

The research shows that the volume of a polymer includes the occupied volume and the free volume^[3]. The so-called free volume is a random distribution of holes, which exist between molecular chains of polymers in order to supply necessary space for molecular chain motions. Many physical and chemical properties of polymers are related to their free volume^[4, 5]. In recent years, positron annihilation spectroscopy (PAS) has emerged as a unique and potent detector for characterizing the free volume properties of polymers^[6-8]. The unique sensitivity of PAS is due to the fact that the positronium (Ps) atoms are preferentially localized and annihilated in the free volume holes in the amorphous regions of the polymers. Positron annihilation lifetime (PAL) measurements can be used to determine the free-volume hole sizes, fractions and concentrations^[9].

The concept of the free volume is employed to model qualitatively and quantitatively the polymeric behavior such as physical aging^[10], sorption and transport^[11] plasticization^[12] and miscibility of blends^[13]. In this paper, we present the results of PAL measurement on vulcanized EPDM, pure PP and dynamically vulcanized EPDM/PP blends and discuss the relationship between the free-volume properties and miscibility of two phases in dynamically vulcanized EPDM/PP blend.

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EXPERIMENTAL

Materials

The polymers used in this study are listed in Table 1. The polypropylene (PP) and the ethylene propylene diene monomer (EPDM) with ethylidene norbonene (ENB) as a termonomer were all commercially available grades. A curing system including zinc oxide (ZnO), stearic acid, sulfur, tetramethylthiuram disulfide (TMTD) and dibenzothiazyl disulfide (DMBT) were of C.P. grades.

Table 1. Materials and their characteristics

Materials	Characteristics		Commercial name and supplier
PP	MFI	2.5g/10min	F401
	ρ	0.91g/cm ³	GanSu LanGang Chemical Industrial Co., Ltd.
EPDM	ML ₁₊₄ ^{121°C}	71~80	3080
	iodine value (ENB)	10-16	JiLin Chemical Industrial Co., Ltd.
	(g/100g)		
	Ethylene content(wt %)	72	

Preparation of Blends

PP was blended with EPDM on a mixing roll in the molten state at 180°C for 2 min. After adding curing agents, EPDM was dynamically cured under shear in the presence of PP; a smooth and uniform film of the blend was formed in 10 min and then removed. Before measurement, the prepared EPDM/PP blend was pre-heated for 5 min at 190°C and cooled down slowly to <100°C under a pressure of 15 MPa on the vulcanizer.

Measurements

PAS measurement

A 20 μ Ci ²²Na positron source sealed by aluminium foil (0.8 mg cm⁻²) was placed between two discs of the same sample. Positron lifetime measurements were performed using a conventional fast-fast coincident system with high-efficiency BaF₂ detectors. The time resolution of the system was determined to be 235 ps from the prompt curve of a ⁶⁰Co source. The samples for positron lifetime measurement had a size of 8×8×2 mm³.

DMTA measurement

Dynamic mechanical thermal analysis (DMTA) was performed under liquid nitrogen using an MI III dynamic mechanical thermal analyzer made in England. The samples for DMTA measurement were 3~5 mm in width and 0.3~0.4 mm in thickness. The conditions of measurement are as follows: rate of heating: 3 K/min, experiment frequency: 5Hz, experiment temperature range: -100~150°C.

DSC measurement

Differential scanning calorimetry (DSC) was applied to characterize the crystallinity of PP in dynamically vulcanized EPDM/PP blends. The heats of fusion (ΔH_f) of PP in the blends were measured using a Perkin-Elmer DSC-7. Samples weighing 15~20 mg were heated at a rate of 10 K/min, and the scanning temperature was from -60°C to 260°C.

Mechanical properties measurement

The mechanical properties of the blends were determined on test specimens by an AG-10KNA material tester. All tests were conducted using the standard ASTM methods such as ASTM D638 for tensile strength and ASTM D638 for ultimate elongation.

RESULTS AND DISCUSSION

Miscibility Measurements by PAS

Each PAL spectrum was resolved into three lifetime components using the computer program PATFIT^[14]. After the background and source correction were subtracted, the variance of fit (χ^2) was less than 1.2. The shortest

lifetime component ($\tau_1 \approx 0.12$ ns) is temperature independent which is attributed to the para-positronium (p-Ps) annihilation^[7] and free positrons. The intermediate lifetime component ($\tau_2 \approx 0.38$ ns) arises from positron annihilation in the defects of crystalline regions^[15]. The longest lifetime component τ_3 has strong temperature dependence and is attributed to the ortho-positronium (o-Ps) pick-off annihilation in free-volume holes in amorphous regions of the polymers^[16]. According to the free-volume model, we employ the results of o-Ps lifetime (τ_3) to obtain the average free-volume holes radius (R) by the following semiempirical equation^[17]:

$$\tau_3 = \frac{1}{\lambda} = \frac{1}{2} \left[1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin \left(\frac{2\pi R}{R_0} \right) \right]^{-1} \tag{1}$$

where τ_3 and R are expressed in ns and nm, respectively, R_0 equals $R + \Delta R$. Where ΔR is the fitted empirical electron layer thickness ($= 1.66$ nm).

The fractional free volume F_v is expressed as an empirically fitted equation as ^[18] $F_v = CV_f I_3$, where V_f (in nm³) is the volume of free-volume holes calculated by using the spherical radius (R) of Eq. (1) from τ_3 (in ns), I_3 (in %) is its concentration, and C is an empirical constant. For convenience, we define a relative fractional free volume

$$F_r = V_f I_3 \tag{2}$$

The PAL spectra in vulcanized EPDM, pure PP and dynamically vulcanized EPDM/PP blends were measured at room temperature. The results for the o-Ps lifetime (τ_3) and intensity (I_3) as a function of weight percent of EPDM (wt%) in dynamically vulcanized EPDM/PP blends are shown Fig. 1. The variations of o-Ps intensity (I_3) reflect the change of free-volume hole concentration. Here, the intensity of o-Ps (I_3) denotes the concentration of free-volume holes. Free-volume hole radius (R) and relative fractions (F_r) are calculated according to Eq. (1) and (2) in a spherical-hole model and are shown in Fig. 2.

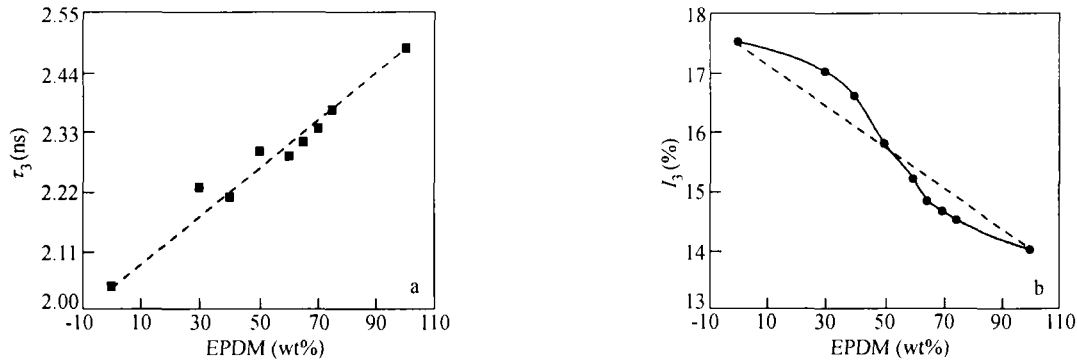


Fig. 1 (Left) the o-Ps lifetime (τ_3) and (right) intensity (I_3) of dynamically vulcanized EPDM/PP blends versus wt% of EPDM
Solid lines were drawn through measured data points and dashed lines represent the linear additive relationships

In Fig. 1, it was found that the concentration of free-volume holes (I_3) decreased with increasing weight percent of EPDM (wt%) in dynamically vulcanized EPDM/PP blends. The concentration of free-volume holes (I_3) is lowest in vulcanized EPDM and highest in PP. I_3 has a positive deviation in the blend at wt% < 50%, but a negative deviation at wt% > 50%.

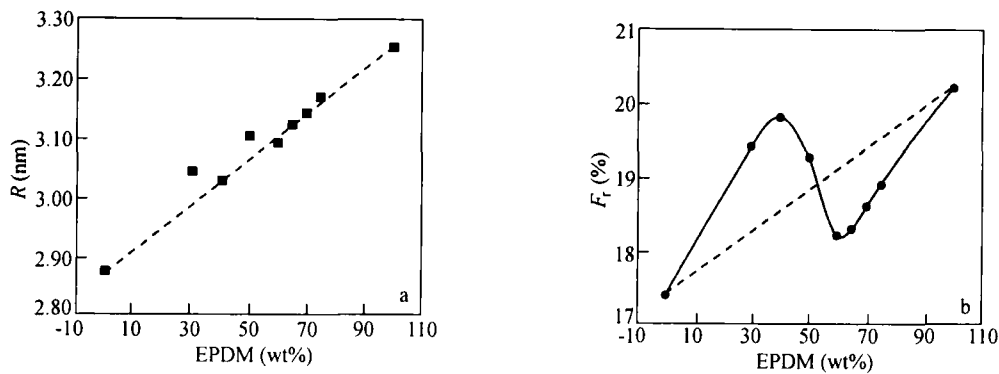


Fig. 2 (Left) R and (right) F_r of free-volume in dynamically vulcanized EPDM/PP blends versus wt% of EPDM
Solid lines were drawn through measured data points and dashed lines represent the linear additive relationships

As shown in Fig. 2, the free-volume radius (R) increased with the weight percent of EPDM (wt%) in dynamically vulcanized EPDM/PP blends. F_r has the same variation tendency as I_3 .

During the mixing of EPDM and PP, if there is no interaction between the two phases, the hole concentration (I_3) and the relative fractional free volume (F_r) will have a linear relationship with the specific volume fraction^[8]. When interaction exists between the two phases, I_3 and F_r will be lower than calculated on the basis of simple mixing. From the above results, we presume that the noncrystalline region of PP and EPDM in dynamically vulcanized EPDM/PP blend are partially miscible. The stronger interaction was found in the blend with EPDM > 50% (wt%) and the weaker interaction with wt% of EPDM < 50%. This phenomenon can be explained by similarity in the chemical structure of EPDM and PP, as PP is a semicrystalline polymer, while EPDM is a noncrystalline polymer, which has propylene segments. Molecular chains of both components diffuse and entangle with each other between the amorphous region of EPDM and noncrystalline region of PP. However, molecular chain motion in the noncrystalline region of PP is seriously restricted by that in the crystalline region. On increasing the weight percent (wt%) and crystallinity of PP, this restricted action becomes more obvious. ΔH_f of EPDM/PP blends are shown in Table 2. It suggests that the crystallinity of PP in the blend become higher with increasing wt% of PP.

Table 2. ΔH_f of blends with various compositions (measured by DSC)					
EPDM/PP (weight ratio)	80/20	70/30	60/40	40/60	30/70
ΔH_f (J/g)	14.8	26.0	72.8	74.8	83.4

When the wt% of EPDM becomes lower than 50%, the crystallinity of PP in the blends is high. The molecular chains in amorphous regions of each component diffuse with difficulty and even repel each other, so that F_r and I_3 in the blends are larger than the ones calculated on the basis of specific volume fraction. The miscibility of the two components in dynamically vulcanized EPDM/PP blend becomes worse. Due to the presence of the crystalline region and an increase in the crystallinity of PP which is related to the molecular packing and chain motions in the amorphous region^[19, 20], the miscibility of dynamically vulcanized EPDM/PP blend varies with the wt% of EPDM.

Miscibility Measurements by DMTA

Miscibility of the polymer blend is studied by measuring the change of glass transition temperature (T_g) of each component. The blend with only a single T_g demonstrates that both components are miscible, while the blend with two T_g s suggests that the components are immiscible or partially miscible. When the values of two T_g s of the blend are close to each other, it implies that the blending system is partially miscible^[2] and the approachability of

the two T_g s denotes the degree of the miscibility of the two components.

Figure 3 shows that the presence of two T_g in the dynamically vulcanized EPDM/PP blend is attributed to the two components. Compared to the T_g of PP and vulcanized EPDM, the two T_g peaks in the blend approached each other and demonstrated that the noncrystalline regions of PP and EPDM in the blend are partially miscible.

In Fig. 4, it can be observed that the T_g peaks of EPDM in the EPDM/PP blends moved towards the low temperature domain on increasing the wt% of PP, but the T_g peaks of PP did not vary. This also shows that the miscibility of dynamically vulcanized EPDM/PP blend became worse with the increase of the wt% of PP. The crystallinity and wt% of PP in the blend affect its glassy state properties, such as glass transition temperature (T_g) of EPDM according to the degree of interaction between two phases^[13].

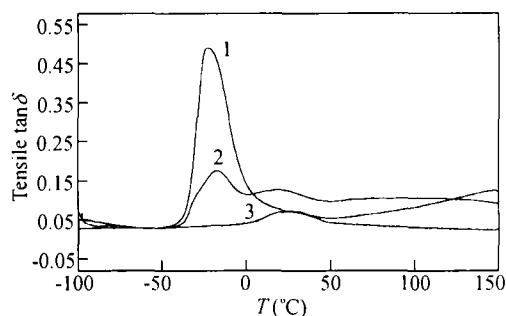


Fig. 3 $\tan\delta$ - T curves of a series
1) vulcanized EPDM, 2) dynamically vulcanized EPDM/PP blend, 3) PP

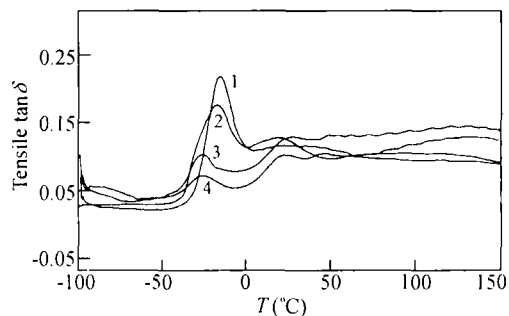


Fig. 4 $\tan\delta$ - T curves of dynamically vulcanized EPDM/PP blends with different ratio of rubber to plastics
1) 70/30, 2) 60/40, 3) 40/60, 4) 30/70

Mechanical Properties of Blends

The mechanical properties of many miscible or partially miscible blend systems, such as strength and modulus, lie above a line representing linear addition of the values of the two pure components because of the interaction between the polymer macromolecules^[21, 22].

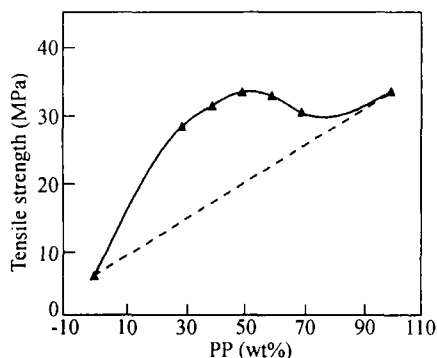


Fig. 5 Tensile strength of dynamically vulcanized EPDM/PP blends with different ratio of rubber to plastics
Solid lines were drawn through measured data points and dashed lines represent the linear additive relationships

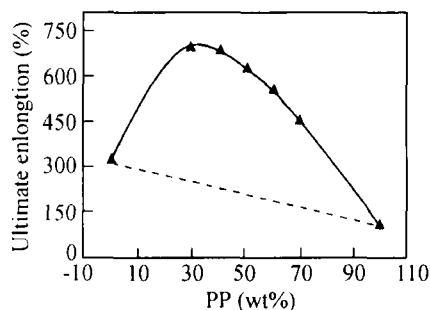


Fig. 6 Ultimate elongation of dynamically vulcanized EPDM/PP blends with different ratio of rubber to plastics
Solid lines were drawn through measured data points and dashed represent the linear additive relationships

The results shown in Fig. 5 and Fig. 6 indicate that the tensile strength and ultimate elongation values for the blends of all compositions show positive deviations from linear addition. As discussed previously, these trends of mechanical properties can be attributed to the changes in molecular packing and interaction that occurred on blending. The mechanical properties of various compositions showed that the interaction of two phases became

relatively weaker with increasing wt% of PP. It showed that the mechanical properties of dynamically vulcanized EPDM/PP blends became worse when the wt% of PP was $> 50\%$ because of the bad miscibility of the blends. In order to attain better mechanical properties of the blend, we should control the relative amounts of EPDM/PP = 70/30~50/50.

CONCLUSIONS

On use of the PAS technique to probe the free-volume hole properties in the dynamically vulcanized EPDM/PP blend, it showed that the hole concentration (I_3) and the relative fractional free volume (F_f) deviated positively from linear additivity when the wt% of EPDM is $< 50\%$, but deviated negatively when the wt% of EPDM is $> 50\%$. These results demonstrated that the noncrystalline regions of PP and EPDM in the blend were partially miscible. The miscibility of the blends was influenced by the weight percent and crystallinity of PP. The measurements of DMTA and the tests of mechanical properties of various compositions showed that both components in the blend were partially miscible because of their interaction between two phases.

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