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The Structure and Thermomechanical Properties of Blends of Trans-polyisoprene with Cis-polyisoprene

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The present work reports the structural and thermomechanical properties of cis- and trans-polyisoprene blends. These blends have been prepared using the solution casting method. The effect of blending on thermomechanical properties such as glass transition temperature, damping and storage modulus and mechanical properties such as toughness, elastic modulus, tensile strength and elongation of present blends has been studied. Besides these, the effect of blending on structure has also been studied. It was observed that elastic moduli, tensile strength and toughness of the TPI/CPI blends decreases with increased CPI percentage. The study also presents a relation between T_g and crystallinity.

Keywords: dynamic mechanical analyzer (DMA), strength, stress/strain curves, thermomechanical properties, X-ray diffraction (XRD)

INTRODUCTION

Blending of two or more types of polymers is a useful technique for preparing and developing materials with properties superior to those of the individual constituents. The state of mixing of polymer blends is important especially from the industrial point of view [1,2]. Elastomers are blended with other polymers to improve the physical and mechanical properties, processability and cost [3,4]. These polymers may be either another elastomer with some special properties or a

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crystalline or amorphous plastic. The mechanism by which the second polymer improves the physical properties in compatible or incompatible blends is not clear since the properties of the blended elastomers are influenced by many complex factors [5]. These factors are: (1) the thermodynamic compatibility that controls the phase separation and domain size, (2) the viscosity of the elastomer blend that controls the diffusion of one polymer into another, (3) the molecular weight of the polymers that controls domain interfaces, and (4) the distribution of additives that affects their function.

Trans-polyisoprene (TPI) is one of the widely used polymers for various products with some specific properties different from those of cis-polyisoprene (CPI). TPI is known to have the ability to crystallize in two crystal forms, i.e., monoclinic and orthorhombic [6]. Blends of TPI with CPI is one of the mixtures of interest, an ideal compatible blend having comparable individual glass transition temperatures [7]. In this direction, Cooper and Vaughan [8] reported that admixture of CPI and TPI caused a marked reduction in the rate of crystallization, but the melting points and the volume fractions of TPI, which were crystallized in the unstretched state, were not reduced. These blends exhibit a single glass transition temperature [9] and complete thermodynamic miscibility at all compositions [10]. Uncrosslinked solution blends of natural rubber (hevea) and TPI were studied by Manzur [11], in order to show the effect of the molecular weight of TPI on the strain-induced crystallization (SIC) of the CPI, and found that the molecular weight of TPI plays an important role in the rate of the strain-induced crystallization.

Boochathum and Prajudtake [9] have reported the cure characteristics and crosslink distribution of accelerated sulfur vulcanization for TPI, CPI and their blends. In general, it was found that CPI had lower crosslink density than those of TPI. Boochathum and Chiewnawin [6] have also reported crystallization characteristics and properties of TPI and CPI blends and found that the variation of TPI content in the vulcanized blends could cause lower tensile strength and modulus.

In this paper, the effect of blending on thermomechanical properties (modulus, toughness, tensile strength, damping properties and elongation) of TPI and TPI/CPI blends are being studied without vulcanization in greater detail. However, there have been few studies [9,10] about the relationship between the state of TPI/CPI blend, glass transition and its crystallization, but there is no quantitative X-ray data on the relationship between the glass transition and TPI and TPI/CPI blend crystallinity. Therefore wide-angle X-ray scattering (WAXS) experiments also have been done in this paper to see the effect

of blending on crystallinity of TPI, because this method has the advantage of providing direct information about TPI molecules.

EXPERIMENTAL

Materials

The basic materials used in this work are given here: Cis-polyisoprene (CPI), in liquid gel form, and trans-polyisoprene, in granular form, were obtained from Sigma–Aldrich Japan.

Preparation of Samples

Both CPI and TPI of known polymer composition were separately dissolved in toluene and then mixed at the TPI/CPI weight ratio of 100/0, 75/25, 50/50, and 25/75. The solutions were slowly cast on a petri dish and kept for drying in air for a period of 2–3 days. To assure that the sample did not contain solvent, the films were further dried in vacuum for 2 days at ambient temperature. Films were prepared with thickness of approximately 0.5 mm for all blends. Uniformity of the thickness of the film has been ensured by measuring the same at different points of the film.

Structural Characterization

Structural characterization of TPI and its blends with CPI have been performed by WAXS. These measurements were carried out on a Philips X'pert X-ray diffractometer using copper target (Cu, K_{α}) at a scanning rate of 3° per min between 10 to 50° .

The degree of crystallinity, X_c , and amorphous content, X_a , have been calculated using the following relationship:

$$X_c = I_c / (I_a + I_c), \quad X_a = I_a / (I_a + I_c) \quad (1)$$

where I_c and I_a are the integrated intensities of the crystalline and the amorphous phase, respectively, which can be determined by drawing the line of demarcation in such a manner as to be congruent with the spectrum profile of the blend [12,13]. In this usual method, the area above the demarcation curve is taken to be proportional to the intensity of crystalline scattering, I_c , and the area between the baseline and the demarcation curve is taken to be proportional to the intensity of amorphous scattering, I_a . The 2θ values between 10 to 30° were considered for crystallinity measurements.

The interplanar distance (d) were calculated as follows:

$$d = \lambda/2\sin \theta \quad (2)$$

where λ is the wavelength of the X-ray radiation (1.540 Å for Cu).

Thermomechanical Characterization

Both thermomechanical and mechanical properties have been measured using dynamic mechanical analysis (DMA). This is a sensitive technique that characterizes the mechanical response of materials by monitoring property changes with respect to the temperature and frequency of an applied sinusoidal stress. With the use of this technique, a force is applied to the sample and the amplitude and phase of the resulting displacement are measured [14]. The details of the technique are discussed elsewhere [15].

For DMA measurements, film samples were cut to 4–6 mm width and 8.05 mm length and were applied in tension mode. The variation of glass transition temperature (T_g) and the storage modulus as a function of temperature were studied in liquid nitrogen atmosphere. The temperature covered was from -100 to 20°C .

RESULT AND DISCUSSION

Wide Angle X-Ray Scattering Study

The X-ray scattering curves of pure TPI and TPI/CPI blends are shown in Figure 1. The XRD pattern of TPI shows that the material is partially crystalline [16]. The interplanar spacing has been calculated using Eq. (2) and has been shown in Figure 1 from which the crystalline form was identified as of the high-melting form [9,17]. On the other hand CPI is reported [9] to be an amorphous material. So in binary systems, the presence of an amorphous polymer (CPI) affects the crystalline character of the other crystalline polymer (TPI) substantially [18]. From Figure 1, it is observed that crystalline peaks of TPI continues to be present at the same position of 2θ for all the compositions, while new peaks at $2\theta = 14^\circ$ and $2\theta = 16^\circ$ have appeared in all three blends due to the presence of CPI content. Formation of these two new peaks in all three blends is due to the splitting of amorphous peak of CPI at $2\theta = 18.88^\circ$ after blending. The XRD measurements also inferred that the percentage of crystallinity of the blends decreases with the addition of CPI as given in Table 1. This is due to the decrement of the number of nucleation sites with the increment of CPI content in the blends [16].

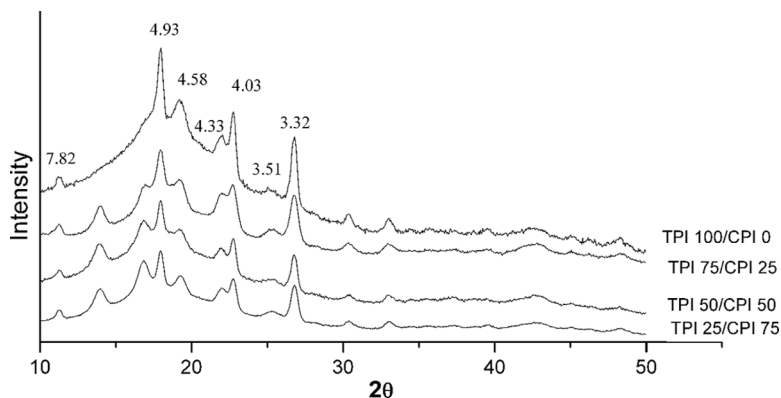


FIGURE 1 XRD pattern of TPI and TPI/CPI blends.

Thermomechanical Study

The variation of $\tan \delta$ and storage modulus as a function of temperature for pure TPI and TPI/CPI blends are shown in Figures 2 and 3, respectively. The plots of $\tan \delta$ against temperature show well-defined and symmetric peaks corresponding to the relaxation associated to the transition from glassy state to the elastic state of the rubber. The characteristic temperature corresponding to the peak point is identified as glass transition temperature T_g [19]. The T_g of pure TPI was found to be -57°C . However, T_g for conventional TPI is around -62°C as reported by Sigma–Aldrich. This difference in the value of T_g could be explained in the following manner. Normally, during the casting and drying procedures, the majority of toluene solution is removed from the samples and the samples become dry. However, owing to the formation of hydrogen bonds along the backbone of the polymer chain, loose structures are produced. As a result, there is a shifting in the transition to a higher temperature as was observed by various

TABLE 1 Values of Glass Transition Temperature and Percentage Crystallinity of the Samples

Composition (W/W)	Glass transition temperature ($^\circ\text{C}$)	% Crystallinity
TPI 100/CPI 0	-57	14.45
TPI 75/CPI 25	-54	11.84
TPI 50/CPI 50	-46	11.14
TPI 25/CPI 25	-45	9.01

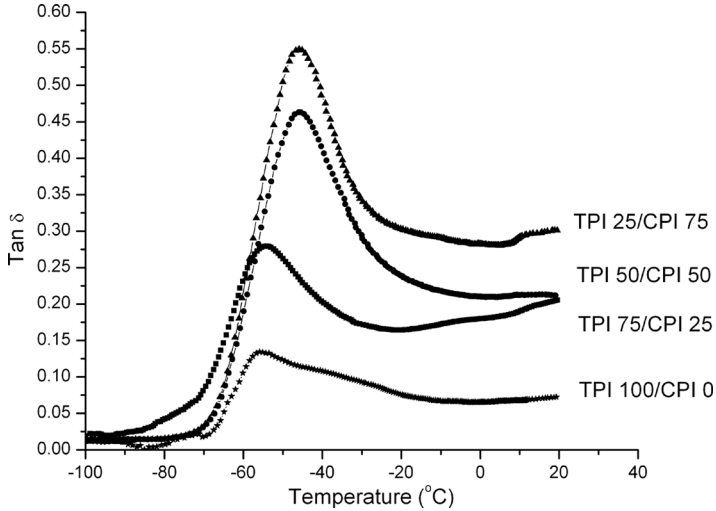


FIGURE 2 Tan δ vs. temperature curve of TPI and TPI/CPI blends.

researchers in the case of toluene solvent [20]. All the blends show a single but separate glass transition temperature, which confirm that all blends are miscible as reported by other researcher [6,9].

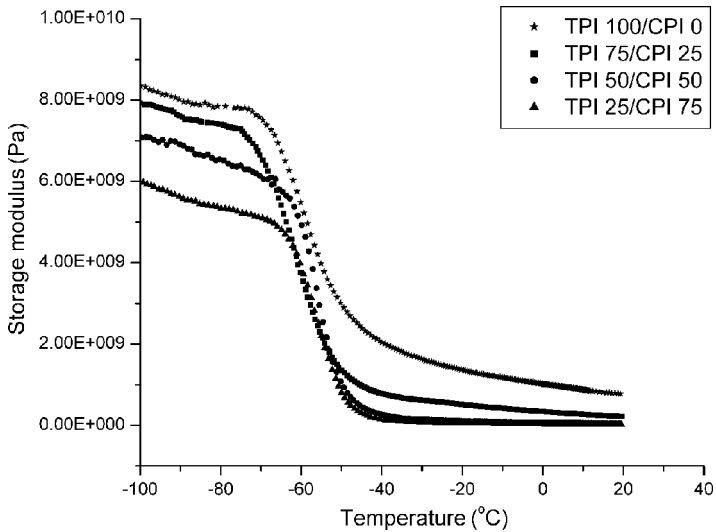


FIGURE 3 Storage modulus vs. temperature curve of TPI and TPI/CPI blends.

From Figure 2 three things are worth noting: (1) the shifting of glass transition temperature, (2) the height of $\tan \delta$, and (3) the broadening of $\tan \delta$ peak.

It is observed from Figure 2 that there is a considerable shift towards higher temperature with decreasing TPI content. On the other hand, $\tan \delta$ of blends was found to be vastly superior to that of pure TPI showing higher damping properties. The superior $\tan \delta$ for TPI/CPI blends might be attributed to the lower crosslink density of CPI than that of TPI [6]. It has been observed that the glass transition temperature depends upon the crystallinity, as also reported elsewhere [21]. This can also be explained on the basis of WAXS measurements. As the crystallinity decreases with decreasing TPI content, the T_g increases (Table 1), and as a result material goes from tough phase to soft phase. This has also confirmed in further studies in this paper.

In the case of pure TPI, the broadness of $\tan \delta$ peak is high and as the concentration of CPI increases, the broadness decreases. This is due to higher concentration of CPI in the TPI matrix causing a lesser restriction of mobility of the polymer chains [22] in comparison with pure TPI. Also, CPI has higher viscosity than TPI.

The plot of storage modulus vs. temperature (Figure 3) shows that the modulus of pure TPI is higher than that of TPI/CPI blends. As the concentration of TPI decreases, the storage modulus decreases, too. This decrease can be explained as due to the fact that the damping property of material increases with the increase of CPI content. It has been observed that there is a small decrement in the value of storage modulus with temperature up to -65°C in all samples. As the temperature further increases, the storage modulus shows a sharp drop in almost all blends and then attains a constant value in the temperature region -40 to 20°C temperature. This phenomenon is due to fact that above is the molecules may be considered as a collection of mobile segments that have a higher degree of free movement.

At a lower temperature, the molecules of the solid material have lower kinetic energies and because their oscillations about a mean position are small, the material is glassy. Therefore, in this state, the restricted chain mobility reduces the ability of the chains to respond to a load or stress to which the sample is subjected [20,23] and the modulus is higher. However, at elevated temperature (near about T_g), the mobility of the chain segments increases. The motion of these chains produces more strain in the sample with applied load; hence, the modulus of the sample decreases in the temperature range -57 to -45°C which is the glass transition range for pure TPI and its blends with CPI.

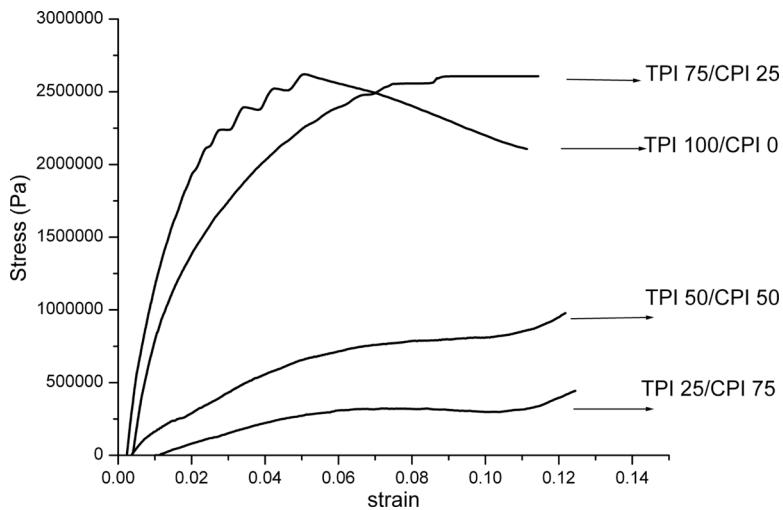


FIGURE 4 Stress-strain curve of TPI and TPI/CPI blends.

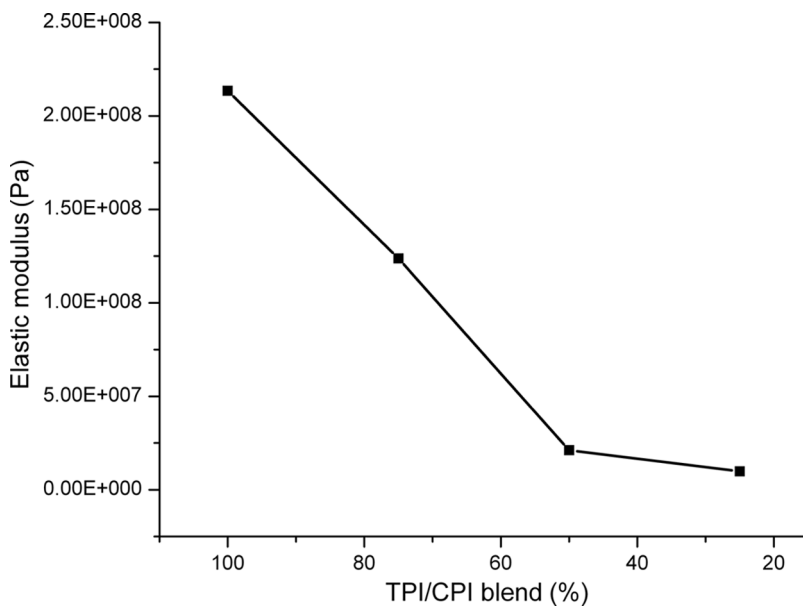


FIGURE 5 Variation of elastic modulus with TPI content.

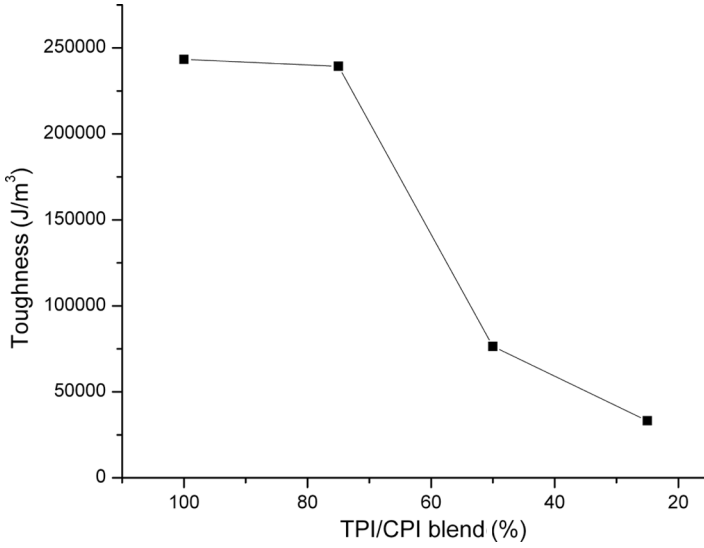


FIGURE 6 Variation of toughness with TPI content.

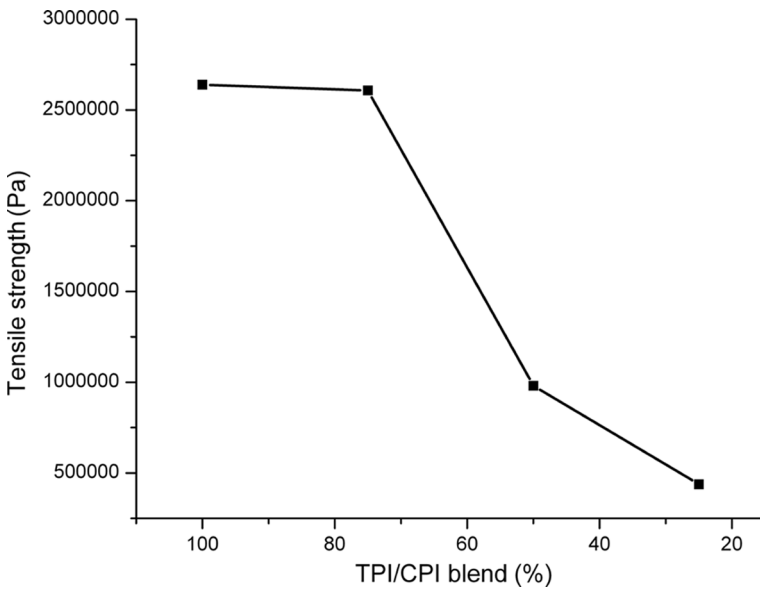


FIGURE 7 Variation of tensile strength with TPI content.

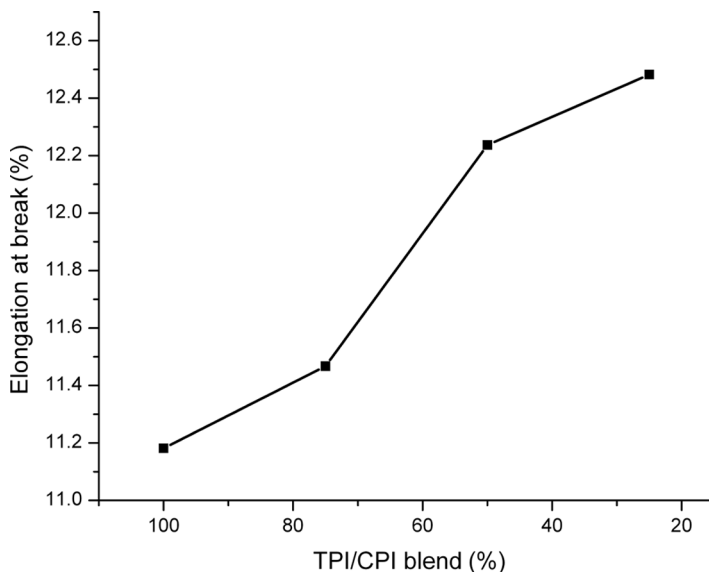


FIGURE 8 Variation of elongation at break with TPI content.

Mechanical Studies

Figure 4 represents the stress-strain behavior of TPI and its blends with CPI. It is clear that all the curves have rather similar behavior, but as the concentration of CPI increases, the plastic region increases while the elastic region decreases. All the mechanical properties—toughness, tensile strength, elastic modulus (Young's modulus) and elongation at break—have been calculated from these stress-strain curves.

From Figures 5–8, it was observed that blending of TPI with CPI reduces the modulus, tensile strength and toughness while enhancing the elongation at break. It was also observed that the blending of TPI with CPI induces a phase transition from a tough phase to a soft phase. This is due to the fact that the blending increases the glass transition temperature while decreasing the crystallinity, which ultimately results in a softer material. The crystallization characteristic of polymers [6] is therefore responsible for a change in all the mechanical properties of investigated elastomeric samples.

CONCLUSION

1. The decrease in crystallinity with the increase of CPI content in TPI/CPI blends is due to an increase of amorphous content of CPI.

2. Positive deviation in glass transition temperature (T_g) and damping property (height of $\tan \delta$ curve) of TPI/CPI blends with increasing CPI content are due to the fact that the restriction of movement of polymer (TPI) chains decreases with increasing CPI content. Also, experimental results of T_g and crystallinity show a relation between them.
3. Dependence of storage modulus on TPI content as well as on the temperature can be explained on the basis of damping property and variation in the chain mobility. Damping property of the material increases with the decrease of TPI content and chain mobility increases with the increase in temperature. This increase in the chain mobility is responsible for the decrease in storage modulus.

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