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Activation energy and thermo-mechanical properties of trans-polyisoprene and liquid cis-polyisoprene blends

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ABSTRACT

In this study, elastomeric blends of trans-polyisoprene and liquid cis-polyisprene have been prepared by solution casting. Wide angle X-ray scattering (WAXS) measurements have been performed in order to determine crystallinity. The dynamic mechanical analyzer (DMA) technique has been used to obtain the storage modulus and glass transition temperature of the blends. The apparent activation energy of the glass transition temperature has also been determined using Vogel–Fulcher–Tammann (VFT) equation. Results indicate that crystallinity, storage modulus and apparent activation energy decrease with decreasing trans-polyisoprene content while glass transition temperatures show opposite behavior.

1. Introduction

Cis-polyisoprene (CPI or NR) and trans-polyisoprene (TPI) are well-known elastomers because of their wide range of application in the industrial and automotive world. CPI is purely amorphous material and is known to crystallize both on stretching and cooling. TPI on the other hand has some specific properties different from those of CPI and it has the ability to crystallize in two crystal forms – monoclinic and orthorhombic [1]. Mixtures of cis- and trans-polyisoprene have attracted increasing attention in last few years from both technological and scientific point of view as the glass transition temperature of both are comparable, the melting points of their crystals are close [2] and TPIs are inexpensively available in both synthetic and naturally occurring forms.

Cooper and Vaughan [3] have used cis- and trans-polyisoprene blends and have reported that a mixture of CPI and TPI causes a marked reduction in the rate of crystallization of CPI. Carter et al. [4] have also studied the same blends and found a single glass transition temperature at all compositions. Bhomic et al. [5] through their studies on WAXS of TPI/CPI blends found that TPI did not act as a nucleating site for crystallization of CPI. Strain-induced crystallization (SIC) in blends of CPI and TPI was studied by Manzur [6] and results showed that the presence of TPI in CPI promoted the SIC and seemed to indicate that the number of nucleation sites increased with increasing TPI content. More recently, Boochathum et al., in two different studies [1,7], reported the cure characteristics, cross-link distribution, crystallization characteristic and mechanical properties. According to Corish [8] there are many factors that influence the properties of blended material like (1) the molecular weight of the polymers that controls domain interfaces, (2) the thermodynamic compatibility that controls the phase separation and domain size, (3) the viscosity of the elastomer blend that controls the diffusion of one polymer into another and the distribution of additives that affects their function. The influence of crystallinity on the glass transition temperature of TPI/CPI blends has also been investigated by Baboo et al. [9] and results showed that T_g increases with decreasing crystallinity.

A plethora of work has been done on the rate of crystallization of CPI, glass transition temperature, strain-induced crystallization (SIC), cure characteristics and cross-link distribution of TPI and CPI blends but very little efforts have been made to study the crystallinity and glass transition temperature of these blends. The present paper reports the correlation between cross-link densities, crystallinity and glass transition temperature of these blends. The effect of these parameters on thermo-mechanical properties has also been studied. Besides these, an effort has also been made to determine the apparent activation energy of these glass transitions.

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2. Experimental

2.1. Materials

The basic materials used in this work are given below:

Cis-polyisoprene (CPI), which is in liquid–gel form and trans-polyisoprene, which is in granular form, were obtained from Sigma–Aldrich Japan.

2.2. 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, 25/75 and 0/100. The solutions were slowly cast on petri dish and kept for drying in air for a period of 1–2 weeks. 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 0.52 mm for all blends. Uniformity of the thickness of the film has been ensured by measuring the same at different points of the film.

2.3. Characterization

X-ray diffraction measurements were carried out on a Philips X' pert X-ray diffractometer using copper target (Cu, K_α) at scanning rate of 3°/min between 10° and 50°. All the data were recorded in reflection mode.

Thermo-mechanical properties of the blends were analyzed using a Tritec Instrument (DMA 2000 model) in tensile mode. The dynamic mechanical analyzer (DMA) is a well-known method for determining viscoelastic properties by applying a controlled sinusoidal stress to a sample and measuring the resulting strain. The measurements were carried out at a heating rate of 2 °C/m from −100 °C to +20 °C at a fixed frequency of 1 Hz. The samples for the test were rectangular shape having width of 4–6 mm, thickness of 0.52 mm and length of 8.05 mm.

3. Theory

3.1. Determination of crystallinity

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

$$X_c = \frac{I_c}{I_a + I_c}, \quad X_a = \frac{I_a}{I_a + I_c} \tag{1}$$

where I_c and I_a are the integrated intensities of the crystalline and the amorphous phases, 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 [2,3]. 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° and 30° have been considered for crystallinity measurements.

The interplaner distance (d) was calculated as follows:

$$d = \frac{\lambda}{2\sin\theta} \tag{2}$$

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

3.2. Determination of cross-link density

Cross-link density is an important parameter which influences the thermo-mechanical properties of elastomeric blends. The cross-link density (ρ) has been determined according to the rubber elasticity theory as follows [10]:

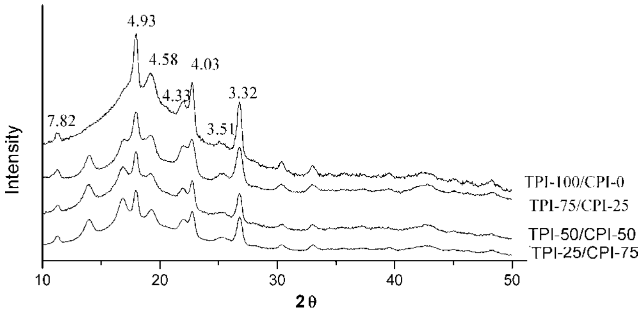

Fig. 1. XRD pattern of TPI and TPI/CPI blends.

$$\rho = \frac{G}{3\varphi RT} \tag{3}$$

where G is the storage modulus at $T_g + 50\,°\mathrm{C}$, φ is a front factor (assumed as $\varphi = 1$), R is the gas constant and T is the absolute temperature at $T_g + 50\,°\mathrm{C}$.

3.3. Determination of activation energy and glass transition temperature

The glass transition temperature (T_g) and the apparent activation energy for the glass transition of elastomeric blends have been obtained by measuring the dynamic storage modulus and assuming non-Arrhenius behavior [11,12]. Although the curve of tan δ obtained by DMA exhibits a definition of temperature for glass transition in the blend but the curve corresponding to the temperature derivative of storage modulus shows more accurate definition of the temperature where relaxations occur. So for accurate analysis of glass transition temperature, the derivative curve of storage modulus has been obtained.

According to Angell and co-workers [12], all organic polymers exhibit a non-Arrhenius (fragile) behavior and this behavior can be represented by Vogel–Fulcher–Tammann (VFT) equation of the form:

$$\eta = \eta_0 \exp\left[\frac{1}{K\{(T/T_0) - 1\}}\right] \tag{4}$$

and

$$K = \frac{E_a}{2.303 R T_g} \tag{5}$$

where η is the viscosity and K is the fragility. T_0 is defined as the VFT temperature which is roughly 50 °C below the glass transition temperature (T_g) and at which viscosity (η) reaches its maximum value. Temperature dependence of viscosity has been obtained from the temperature dependence of storage and loss modulus which have been measured using DMA.

Fragility K is determined from the slope of the linear fit of the curve between log η and $1/(T - T_0)$. Using so obtained value of K apparent activation energy (E_a) has been calculated from Eq. (5).

4. Result and discussion

4.1. Wide-angle X-ray scattering study

The X-ray scattering pattern of pure TPI and TPI/CPI blends are shown in Fig. 1. The XRD pattern of TPI shows that the material is partially crystalline. The interplaner spacing has been calculated using Eq. (2) and has been shown in Fig. 1 from which the crystalline form was identified as the high-melting form. Similar results were

Table 1
Values of percentage crystallinity, cross-link density and glass transition temperature of the samples.

Composition (W/W)	Percentage crystallinity	Cross-link density (mole/m^3)	Glass transition temperature (°C)
TPI-100/CPI-0	14.45	134.25×10^{-3}	−59
TPI-75/CPI-25	11.84	52.34×10^{-3}	−56
TPI-50/CPI-50	11.14	16.89×10^{-3}	−52
TPI-25/CPI-75	9.01	3.64×10^{-3}	−50

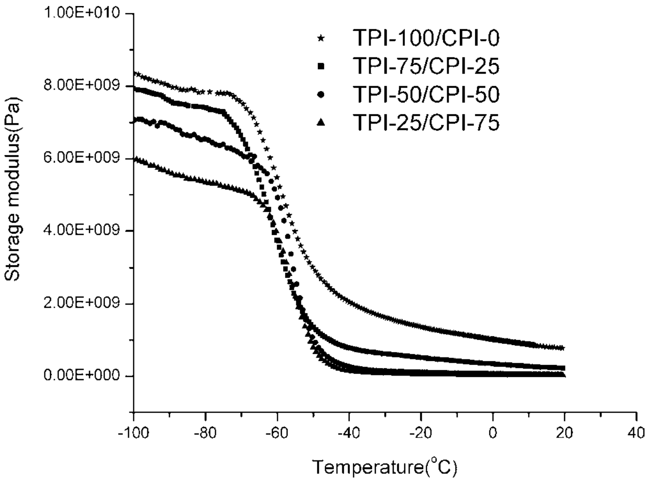

Fig. 2. Variation of storage modulus with temperature.

also reported by other researchers [6,7,13]. It is reported that CPI is an amorphous material and its presence in binary system affects the crystalline character [14] of other polymers (TPI). From Fig. 1, it is also observed that crystalline peaks of TPI continue to be present at the same position of 2θ for all the compositions, while new peaks at $2\theta = 14°$ and $2\theta = 17°$ 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 $2\theta = 18.88°$. 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 number of nucleation sites with the increment of CPI content in the blends [6].

4.2. Glass transition and storage modulus

Fig. 2 shows the variation of storage modulus with temperature while Fig. 3 shows the variation of dG/dT with temperature. From Fig. 3, it is clear that there is a considerable shift in glass transition towards higher temperature with decreasing TPI content as is also shown in Table 1. This shift in T_g value towards the higher temperature side may be described on the basis of increasing crystallinity with the decrease of TPI content.

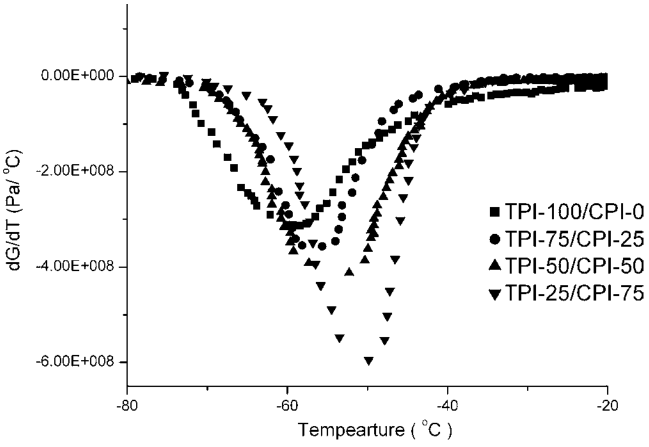

Fig. 3. Variation of derivative curve of storage modulus with temperature.

It has been reported [9] that the glass transition temperature depends upon the crystallinity and increases with the decrease of crystallinity of the sample (as confirmed by WAXS measurements). This can also be explained on the basis of structure of material. At room temperature, TPI has a rigid structure while CPI has a loose viscous structure. In TPI/CPI blends, when CPI is added at the cost of TPI, the material converges towards a rubbery elastic phase. The higher the CPI content, the more softer is the blend. When a blend with lower CPI content is subjected to low temperature, the free volume of molecules of chains in the blend decreases and hence more energy is required to make a transition from rubbery phase to glassy phase. As a result T_g obtained in this case is higher (magnitude only) than that obtained in pure TPI. When the CPI content increase in the blend, material has a more viscous form as compared to the one mentioned before and hence when this material is subjected to low temperature, the decrease in free volume is not as much as observed in previous case. Therefore, in this case, energy required for motion of chains and hence for transition is less and material makes a transition at lower temperature.

It can also be seen that the maximum transition rate, namely the peak height in the derivative curves increase with decreasing TPI content, which shows higher damping property. This behavior can be explained on the basis of cross-link density which decreases as the TPI content decreases (Table 1).

The plot of storage modulus with temperature (Fig. 2) shows that modulus of pure TPI is higher than that of TPI/CPI blends. As the concentration of TPI decreases storage modulus also decreases. This decrease is 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 decrement in almost all blends and then attains a constant value in the temperature region −40 °C to 20 °C. This phenomenon is due to fact that the molecules may be considered as a collection of mobile segment that have higher degree of free movement. At a lower temperature, the molecules of the solid material have lower kinetic energies and their oscillations about a mean position are small; the material is tightly compressed. Therefore, in this state, the lack of free volume restricts the possibility of motion in various directions; hence, the molecules are unable to respond to a load or stress to which the sample is subjected [15,16]. As a result there is a high value of the modulus. However, at elevated temperature (near about T_g), the free volume of the chain segments increases, thereby resulting in an increment of mobility of molecular segments. 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 −59 °C to −50 °C which is glass transition range for pure TPI and their blends with CPI.

4.3. Activation energy

It is observed that activation energy (Fig. 4) for pure TPI is higher than that of TPI/CPI blends. As the concentration of TPI decreases

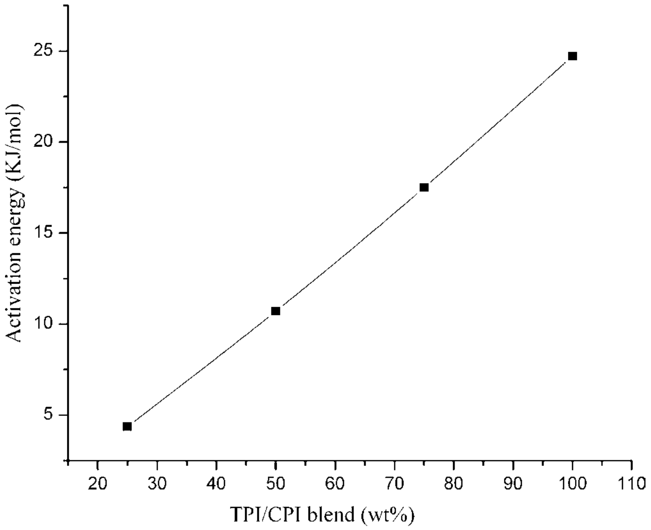

Fig. 4. Variation of activation energy with TPI content.

activation energy also decreases. This is due to the fact that in glass transition region, the motion of molecules is governed by the cross-link density. The decrease in TPI content decreases the cross-link density, which inturn increases the free volume and oscillations of molecules about mean position. This implies that decrease in TPI content enhances the motion of chains and therefore less energy is required to make molecule mobile. This phenomenon is also confirmed by the behavior of storage modulus which decreases with the decreasing TPI content (Fig. 2).

5. Conclusions

The systematic study of activation energy and thermo-mechanical properties of elastomeric blends on trans-polyisoprene and liquid cis-polyisoprene leads to the following conclusions:

1. The TPI/CPI blends exhibited a single glass transition which indicates the miscibility and better compatibility of these blends for industrial application.
2. The drop in initial value of storage modulus and increase in glass transition temperature with respect to TPI content is due to decrease in cross-link density and crystallinity.
3. The decrease in value of activation energy and increase in glass transition temperature with decrease in TPI content infer that less energy is required for a transition from a glassy state to rubbery state.

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