Dynamic Mechanical Behavior Analysis for Low Ethylene Content Polypropylene Copolymers

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ABSTRACT: Dynamic mechanical behavior of low ethylene content propylene−ethylene copolymers was studied. It was found that there exists ethylene-propylene rubber component in the block copolymer, which is accordance with the component analysis. It is suggested that it is because of the existence of the ethylene−propylene rubber component that the block copolymer exhibits high impact strength. The relaxation temperature shifted to lower temperature for copolymers compared with homopolymer, and the damping peak was broadened by copolymerization, consistent with the increased chemical heterogeneity of the copolymers. Effects of thermal history and frequency on the relaxations were studied. The activation enthalpy for relaxation was determined. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 395−401, 1998

Key words: dynamic mechanical behavior; low ethylene content polypropylene copolymers; impact strength

INTRODUCTION

The phenomenon of mechanical relaxation has been studied extensively on isotactic polypropylene (i-PP) to elucidate the nature of molecular motion.[1,2] It is well known that melt-crystallized i-PP exhibits α-, β-, and γ-relaxation processed in the temperature range from -150 to $150°C$. The α-process is generally attributed to the crystalline phase. The β-process corresponds to the transition from the glassy to the rubber-like state, and the γ-process is usually assigned to the local mode relaxation in the amorphous phase.

i-PP is intrinsically brittle at low temperature and suffers from fracture problems in some applications. Products of greatly improved impact strength have been obtained by copolymerization of propylene with a small amount of ethylene using Ziegler-Natta catalysts. There are mainly two commercial propylene-ethylene copolymers in the market today: block and random copolymers. These copolymers, prepared by heterogeneous catalysts, exhibit compositional heterogeneity, and it is generally accepted that heterogeneous catalysts have a plurality of active species.[3] These copolymers contain a range of copolymers with a different composition and sequence distribution.[4]

There is little published information concerning the structure and morphology of these copolymers, and all that can be said for certain is that the two components are not present in a purely random copolymer or a block copolymer. It may be that the products are actually intimate blends. The actual copolymerization techniques used have not been disclosed, but they presumably involve the alternate feeding of ethylene and propylene into a Ziegler-Natta catalyst. These copolymers have superior impact strength at room temperature and low temperatures and improved moulding characteristics. At the same time, the hardness, stiffness, and softening point of the homopolymer are maintained.

In this article, dynamic mechanical behavior was studied for these low ethylene content polypropylene copolymers, and comparison was made

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Table I Propylene Copolymers

Name	Grade No.	Manufacturer
Block copolymer	RV210	SOLVAY
Random copolymer	KV202X6380	SOLVAY
Polypropylene homopolymer	HV202	SOLVAY

with polypropylene homopolymer. The source of improved impact strength for these copolymers will be analyzed.

EXPERIMENTAL

Samples

Commercially available polymers used in this study are listed in Table I.

Techniques

The mechanical relaxation spectra of samples were measured using a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA) controlled by an IBM PS-2 computer. Rectangular samples were clamped in the measuring head on a steel frame supported by ceramic pillars. They were flexed in a dual cantilever mode by a central clamp driven sinusoidal by an electromagnetic vibrator through a ceramic drive shaft. The temperature was controlled using a Polymer Laboratories temperature programmer. Subambient temperatures were achieved by filling a cooling jacket with liquid nitrogen. A temperature range of -150 to $300°C$ and heating or cooling rates between 0.1 to $20°C$ min^{-1} were available.

A scanning electron microscopy, model JOEL-J5200, was used to examine the morphology of the copolymers. The micrographs were recorded directly from the cathode ray tube display with a Yashica camera.

The energy to failure of the copolymers under high strain rate (3.5 m s^{-1}) was measured using a Zwick impact tester.

RESULTS AND DISCUSSION

The DMTA spectra of low ethylene content polypropylene copolymers and homopolymer are shown in Figure 1(a–c). At 1 Hz and in the temperature range between -100 and $100°C$, i-PP shows three dynamic mechanical relaxations. The
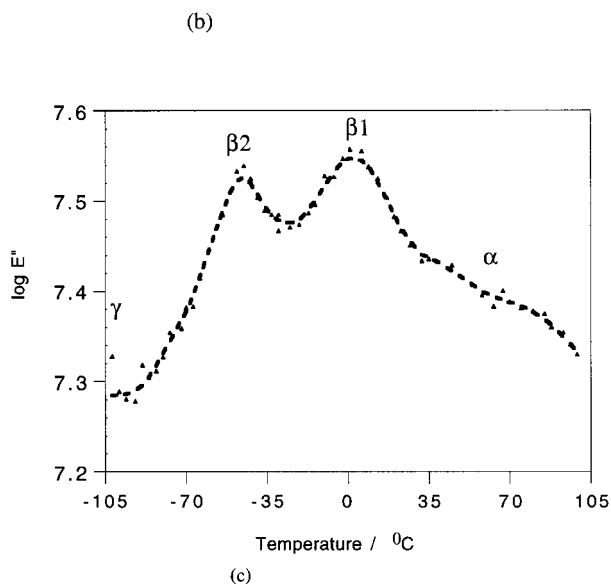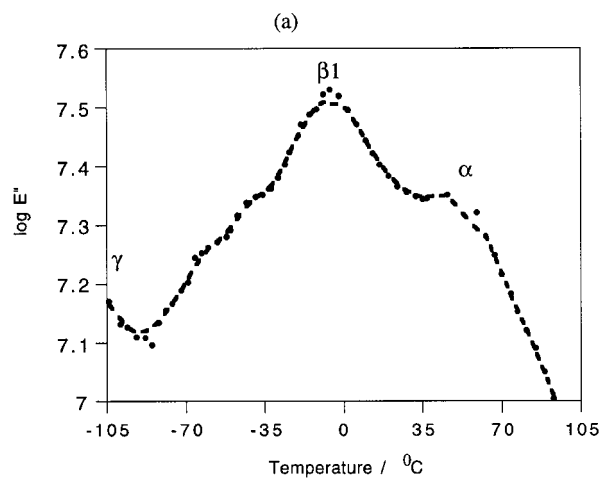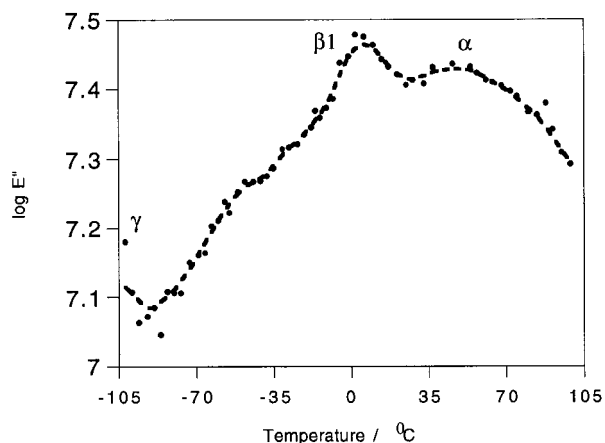
Figure 1 Dynamic mechanical spectrum of i-PP and its copolymers (1 Hz). (a) i-PP (1 Hz). (b) Random PP copolymer (1 Hz). (c) Block PP copolymer.
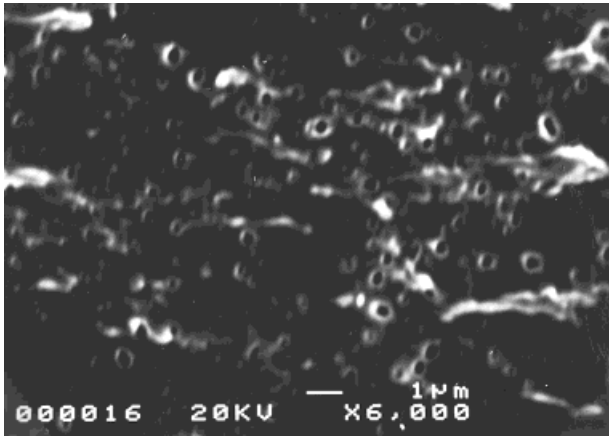
Figure 2 Scanning electron microscopic photograph of block propylene–ethylene copolymer etched in n-heptane.

Table II   Breaking Energy of i-PP and Its Copolymers

Samples	Energy for Break (kJ m^{-2})
i-PP	82
Random copolymer	190
Block copolymer	385

peak at about $-100°C$ is attributed to γ-relaxation associated with the onset of local mode relaxation. The dominant relaxation is the β_1-relaxation at about $0°C$, which is generally taken to be the glass transition of the amorphous regions in crystalline polypropylene. Another weak peak, which appears as a shoulder in the range of $35–90°C$, is associated with the crystalline regions of i-PP (α-relaxation). The DMTA spectrum of random copolymer is similar to that of the i-PP. However, because of the incorporation of ethylene comonomer into the propylene chain, the β_1-relaxation has been lowered about $5°C$ than that of i-PP. Log E'' associated with the β_1 transition are greater, implying that the random copolymer is less crystalline than i-PP.

Four relaxation processes appeared for block copolymer. Except the three relaxations as i-PP and random copolymer, there is another transition that appeared at about $-50°C$ (β_2). This transition is suggested that there is ethylene–propylene rubber (EPR) component existing in the block copolymer. The temperature rising elution fractionation and ^{13}C-NMR analysis confirmed this suggestion.[5] Quiescent melt ripening of the block copolymer was conducted at a melt temperature for a specified period of time, then etched in n-heptane at $70°C$ for 30 min. It can be observed that the two-phase system exists in the block copolymer (Fig. 2). The EPR is present as a minor fraction, and the multiphase system is composed of a continuous matrix of polypropylene and a discrete phase of EPR. Table II showed the comparison of impact strength of i-PP and the copolymers. It can be seen that the breaking energy of copolymers (especially block copolymer) is much higher

than that of i-PP. It is suggested that it is because of the existence of the EPR component that the block copolymer exhibits high impact strength.

Figure 3 showed the β_1-relaxation of i-PP, and block and random copolymers. Maximum values of log E'' for block and random copolymers are higher than that of i-PP, but the peak temperatures of the copolymers shifted to lower temperatures, compared with i-PP. This suggested that the amorphous content that is greater for copolymers determines the strength of the β_1-relaxation peak and the values of $T_{\beta1}$. It can be seen in Figure 3 that copolymerization tends to broaden the damping peak, consistent with the increased chemical heterogeneity of the copolymers.

The dynamic mechanical response of semicrystalline polymers is sensitive to the thermal history of the sample. Figure 4 showed the effect of annealing temperature on log E'' of the β_1-relaxation for i-PP and its copolymers. With increasing annealing temperature, the β_1-peaks increased in height for i-PP and block copolymer, whereas in the case of the random copolymer, the height changes only slightly but hardly changes in temperature. This has also been observed by others.[6,7] The reason for this is not clear, but may arise from the relaxation of constrained amorphous region on annealing. Quenched
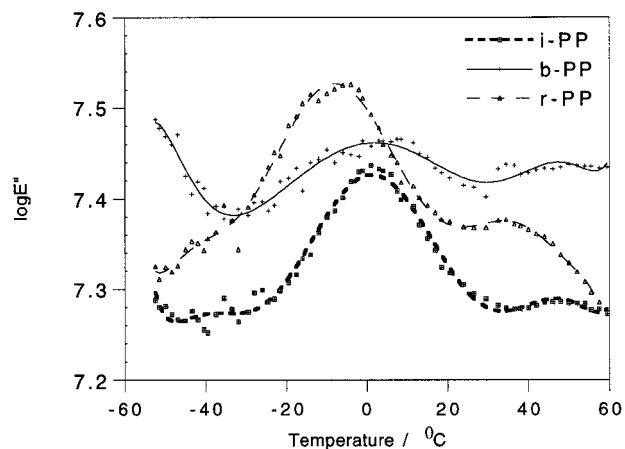

Figure 3 Effect of copolymerization on β_1-relaxation (1 Hz). b, block; r, random.

(a)

(b)

(c)
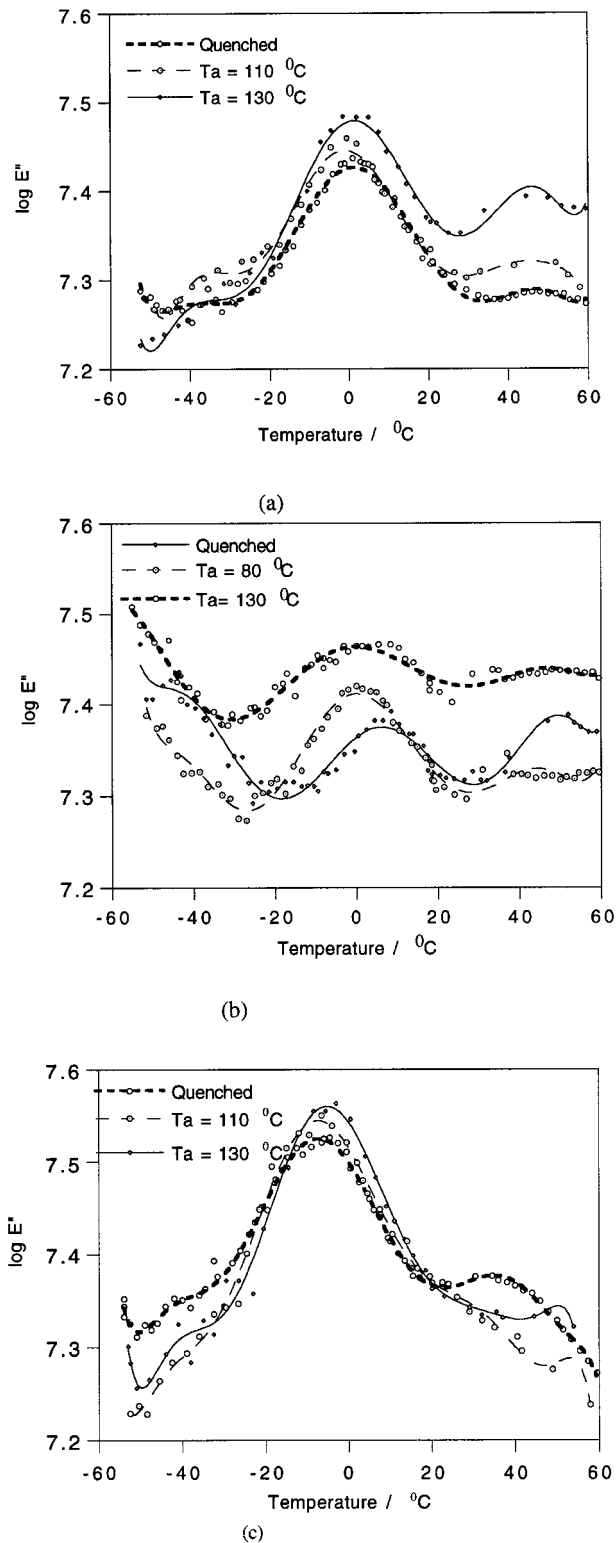
Figure 4 Effect of annealing temperature on β_1-relaxation of i-PP and its copolymers (1 Hz). (a) i-PP (1 Hz). (b) Block copolymer (1 Hz). (c) Random copolymer.

melt-crystallized samples are considered to contain a constrained amorphous phase, in which segmental motions are strongly depressed, in addition to

the ordinary crystalline and amorphous phases. In the amorphous phase, the constraints imposed on the segmental motions originate from several sources: tie molecules, loose loops, spatial restrictions imposed by surrounding crystalline phases and internal strains in the amorphous chains themselves. Spatial restriction imposed by the surrounding crystalline phases is the main cause of the constraints. On annealing, the constraints would be relaxed. If the change of lamellae thickness is not great at these annealing conditions, then the relaxation of constraints between lamellae play a main role and will increase the height of the β_1-peak.

(a)

(b)
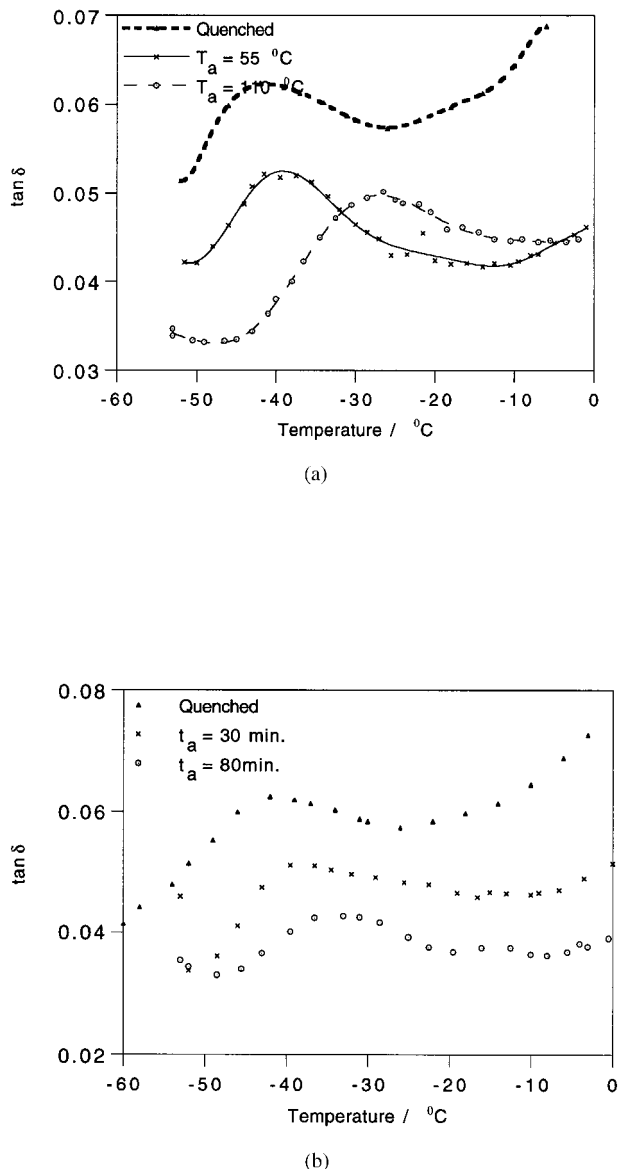
Figure 5 (a) Effect of the annealing temperature on the β_2-relaxation of block copolymer (10 Hz). (b) Effect on annealing time on β_2-relaxation of block copolymer (10 Hz) (Ta = 110°C).

From the structural analysis,[5] it was understood that the block copolymer studied herein was composed of components with polypropylene homopolymer and ethylene–propylene copolymer with different ethylene block lengths, some of which are crystallizable and others not. From Figure 1(c), it was found that the block copolymer exhibits two glass transitions: a primary transition at about room temperature (β_1) due to the matrix component and a secondary transition below room temperature (β_2) due to the dispersed rubber phase. Figure 5 showed the β_2-relaxation curves for annealed block copolymer. It was apparent that the damping peak decreased with annealing, and the transition temperature shifted to a higher temperature. It is suggested that these results come from the crystallization of propylene–ethylene copolymer within the amorphous phase during the annealing process.

The frequency dependence of molecular relaxations in block copolymer was studied. Figure 6 showed the change in the dynamic mechanical spectra of block copolymer at three frequencies: 0.1, 1, and 10 Hz. It can be seen that the relaxation peaks shifted to higher temperature with increasing frequency.

A superpositional master curve can be obtained by moving the tan δ, log E', and log E'' dependence on frequency horizontally along the log (frequency) axis. The shift factor a_T is related to the temperature through the Williams–Landel–Ferry equation[8,9]:

$$\log a_T = [-C_1(T - T_s)]/[C_2 + (T - T_s)], \quad (1)$$

where T_s is a reference temperature and C_1 and C_2 are universal constants. With different T_s, C_1 and C_2 have different values. When $T_s = T_g$, then $C_1 = 17.44$ and $C_2 = 51.6$. Studies, in general, have found that many polymers are not fitted by the equation with these constants. When T_s is taken at a temperature greater than T_g, then the combination of two constants, $C_1 = 8.86$ and $C_2 = 101.6$, fits many more polymers. In the present work, room temperature (296°K) was taken as T_s and $C_1 = 8.86$, $C_2 = 101.6$. Figure 7 showed the master curve for a reference temperature of 296°K. Reasonable superpositions were achieved over a wide frequency range. The main relaxations can be seen in the master curve that means the frequency dependence of tan δ, log E', and log E'' at the reference temperature 296°K. It is known that the conventional DMTA cannot cover such a large frequency range. The usual range is from 10^{-2} to 10^{11} Hz, so only the β_1-relaxation can be observed at 296°K on conventional DMTA.
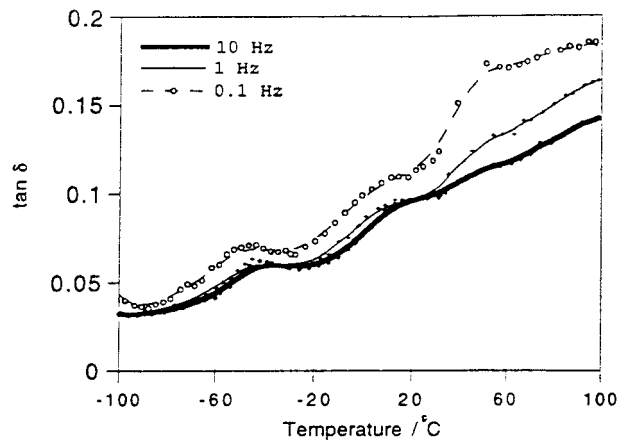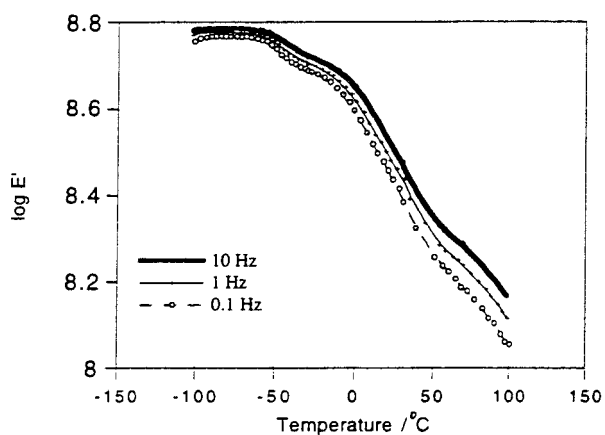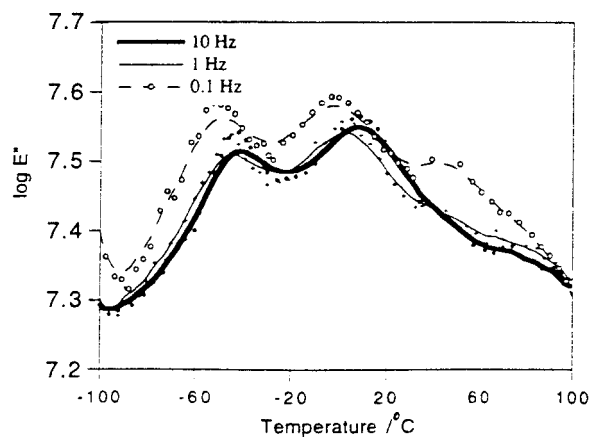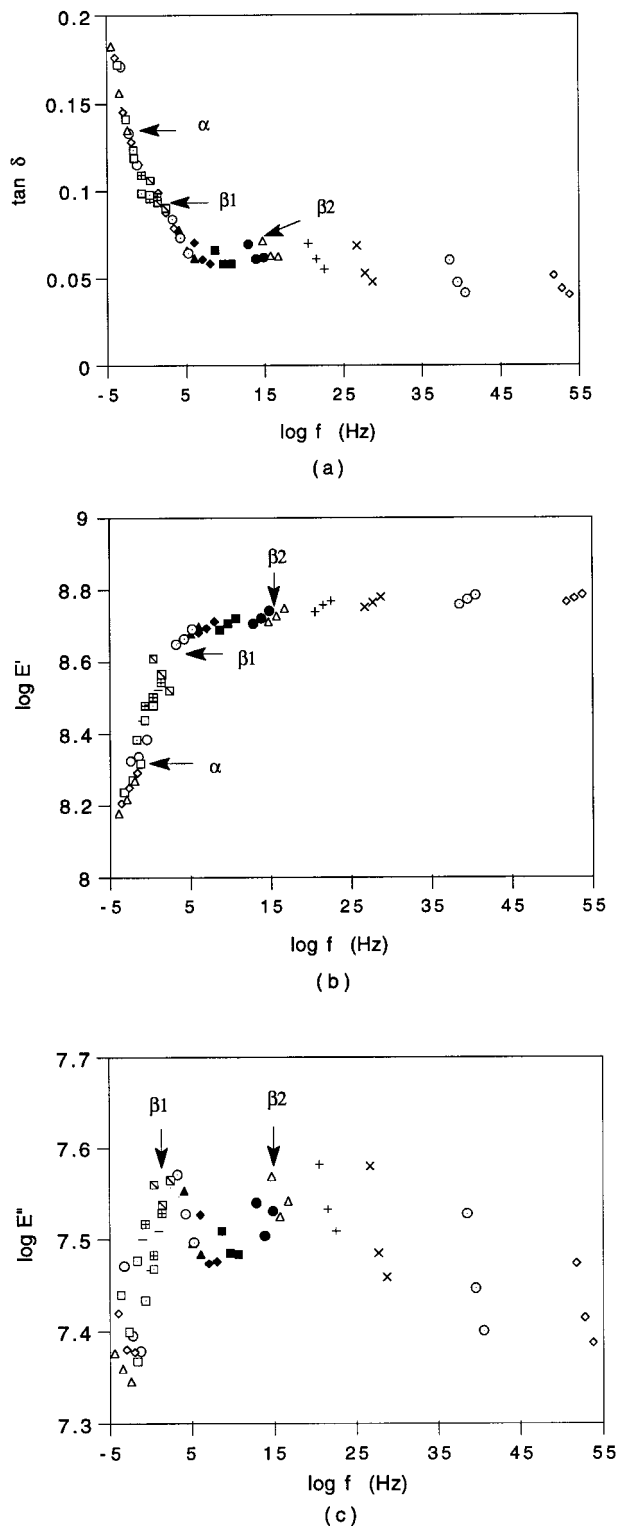

Figure 6 Effect of frequency on the DMTA spectra of bulk block copolymer.

The enthalpy of relaxation can be determined from the log-normal (ln) (frequency) against reciprocal T, using the Arrhenius equation:

Figure 7 Master curves for block copolymer at a reference temperature of 296°K.

$$\ln f = \ln A + \Delta H / R T_r \qquad (2)$$

where ΔH is the activation enthalpy of the relax-

ation and A is a constant. T_r is relaxation temperature. Table III showed the effect of annealing temperature on the activation enthalpy of α-, β_1-, and β_2-relaxations. The results showed that the ΔH for β_1 did not change with annealing temperature, whereas ΔH for α and β_2 increased slightly with annealing temperature. This indicated that the structure of block copolymer becomes more ordered on annealing, so there is more energy needed for relaxation. There was little or no difference in ΔH values for β_1 and β_2 processes, suggesting that they involve similar molecular relaxation processes. The similarity in the ΔH value is consistent with β_2 being a glass transition process.

CONCLUSIONS

Dynamic mechanical relaxation behavior was analyzed for low ethylene content polypropylene copolymers and homopolymer. The experimental results showed that the DMTA spectrum of random copolymer is similar to that of i-PP. However, the relaxation temperature has been shifted and broadened because of the incorporation of ethylene into propylene chain. The DMTA spectrum is more complex for block copolymer. Apart from the three relaxations similar to random copolymer, there is another relaxation (β_2) that appears at about $-50°C$ and is attributed to the glass transition of the EPR phase. Effect of annealing on β_1- and β_2-relaxation was studied. It was found that thermal treatment has some influence on the damping and temperature of β-relaxation, which indicated that the relaxation depends on crystal morphology. Frequency dependence of the molecular relaxation in block copolymer was studied, and the activation enthalpy for relaxation was determined using the Arrhenius equation.

Table III   Activation Enthalpy for Relaxations of Bulk Block Copolymer

Annealing Temperature (°C)	ΔH_α (kJ mol^{-1}) $\pm$ 50	ΔH_{β_1} (kJ mol^{-1}) $\pm$ 50	ΔH_{β_2} (kJ mol^{-1}) $\pm$ 50
Unannealed	550	350	240
80	580	410	320
110	650	400	350
130	690	410	380

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