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### Effect of Storage on the Mechanical Properties of Propylene-Ethylene Copolymers

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## **EFFECT OF STORAGE ON THE MECHANICAL PROPERTIES OF PROPYLENE-ETHYLENE COPOLYMERS**

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**Key Words:** Propylene-ethylene Copolymers, Mechanical Properties, Storage, Secondary Crystallization

### **ABSTRACT**

The effect of storage at room temperature on the mechanical properties of the low ethylene content propylene-ethylene copolymers was investigated. The experimental results showed that the storage modulus increased and the loss tangent decreased on storage. The glass transition temperature shifted to higher temperature compared to unstored samples. From the tensile results, it was seen that storage produced a stiffer and more brittle material. The stress relaxation behavior was investigated. It is suggested that all the effects resulted from the occurring of secondary crystallization during the storage process.

### **INTRODUCTION**

Most plastic materials are used because they have desirable mechanical properties at an economical cost. For this reason, the mechanical properties may be considered the most important of all properties of high polymers and determines

most of their applications. There are numerous structural factors which determine the nature of the mechanical behavior of polymer materials. These factors, in addition to the chemical composition, include molecular weight, crosslinks and branches, crystallinity and morphology, copolymerization, molecular orientation etc. In addition to the above structural and molecular factors and some environmental or external variables, storage is also an important factor in determining mechanical behavior [1-2].

Semicrystalline polymers quenched from temperatures above their melting point, and amorphous glasses quenched from temperatures above their glass transition temperature  $T_g$  are not normally in thermal equilibrium [3-4] but can approach it over extended periods in a limited temperature region.

Since material properties of the quenched polymer change continuously with the extent of storage, the process has considerable commercial importance and has been widely studied.

The effect of storage at room temperature on the creep properties in isotactic polypropylene has been described by several researchers [5-6]. In the present work, the effect of storage at room temperature on the dynamic mechanical response, impact and tensile properties, as well as the stress relaxation of low ethylene content propylene copolymers have been studied.

## EXPERIMENTAL

### Materials

The low ethylene content block, random propylene-ethylene copolymers and polypropylene homopolymer were supplied by SOLVAY, their grade numbers were RV210, KV202 and HV202, respectively. Samples were pressed on a hot-press at 200°C for 15 minutes and quenched from the melt to room temperature water, and then stored at 24°C in air in a constant temperature room.

### Apparatus

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 used. The temperature was controlled using a Polymer Laboratories temperature programmer. Sample dimensions, geometry and predetermined calibration constants were entered into the DMTA analyzer, which allowed the computer to calculate the storage and loss moduli, and  $\tan \delta$  as a function of frequency or temperature.

An Instron floor standing tester model TT-BM, maximum load 2500 kg, was used to measure the tensile properties of samples. The instrument was calibrated using standard weights. The test were carried out in a constant temperature room at  $295 \pm 1$  K. Dumb-bell shaped specimens were used.

The energy to failure of PP and its copolymers under high strain rate ( $3.5 \text{ m s}^{-1}$ ) was investigated using a Zwick impact tester. The dumb-bell shaped specimens used were identical to those used in Instron tests except they were about 2.5 mm thick.

## RESULTS AND DISCUSSION

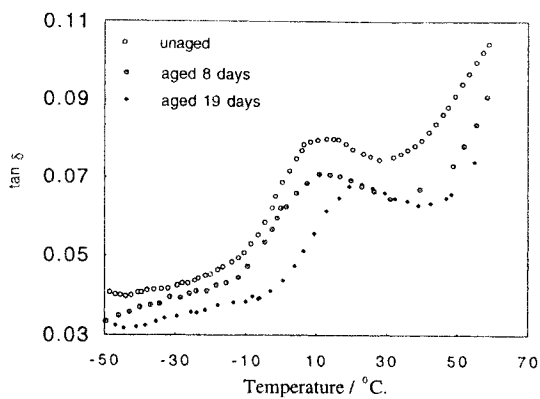
### Effect of Storage at Room Temperature on Dynamic Mechanical Properties

More recent investigations of isotactic polypropylene (i-PP) have shown that changes in structure associated with storage at  $T > T_g$  can substantially influence the relaxation behavior [5-7]. One of the general facts observed in dynamic tests on storage samples is an increase in modulus and a decrease in loss tangent.

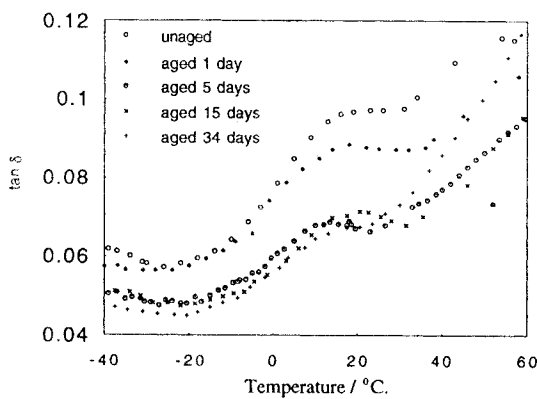
Figures 1(a, b, c) shows the effect of storage at  $240^\circ\text{C}$  on the DMTA spectra at 10 Hz damping of i-PP and propylene copolymers. It can be found that for i-PP and copolymer samples, the  $\tan \delta$  values decreased with the storage time and the  $T_g$  peaks have a little shift to higher temperature. At the same time, the damping peaks become broader after storage, which can be observed obviously by  $\log E'' - T$  curves (Figure 2). From these results, it can be suggested that storage in amorphous phase decrease the loss tangent. Since the storage temperature is above the glass transition temperature, there is no physical aging happened in amorphous phase during the storage process [1-4]. It is suggested that secondary crystallization may happen in the storage process, which make the amorphous phase constrained so that the  $T_g$  has a little shift to higher temperature and make the peak broader.

Figure 3 shows the effect of storage at room temperature on real modulus  $E'$ . It can be seen that the real modulus increased after storage.

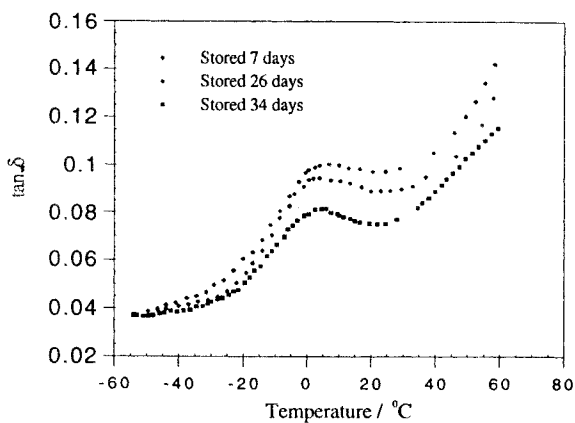
The secondary crystallization behavior was studied by DSC. The thermal history involved in this work is given below. Samples were melted at 470 K for 5 minutes in DSC cell, quench to the storage temperature ( $T_s = 290 \text{ K}$ ) at cooling rate of  $80 \text{ K min}^{-1}$ , and storage at 290 K for  $t_s$  minutes. The samples were quenched to 285 K, again at  $80 \text{ K min}^{-1}$ , and then heated at  $10 \text{ K min}^{-1}$ . A small melting peak was observed at lower temperature apart from the main melting peak at higher temperature for stored samples. Figure 4 showed the subtracted DSC



(a) i-PP.

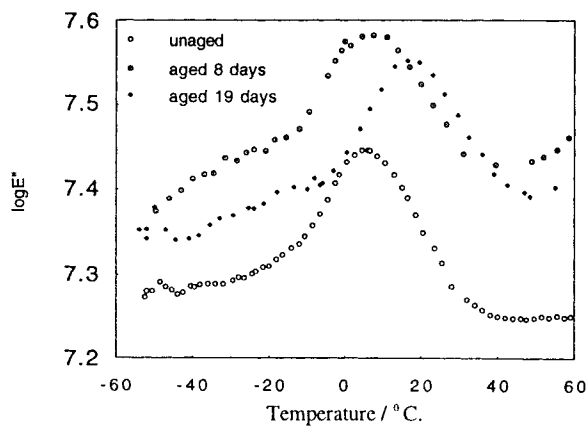


(b) Block copolymer.

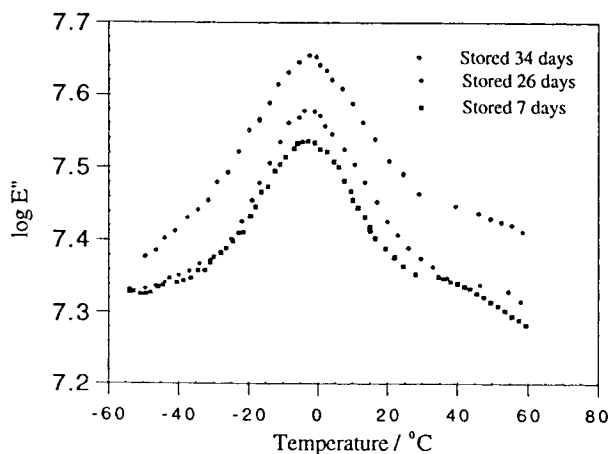


(c) Random copolymer.

**Figure 1.** Effect of Storage on the 10 Hz Damping ( $T_g = 24^\circ\text{C}$ ).



(a) i-PP.

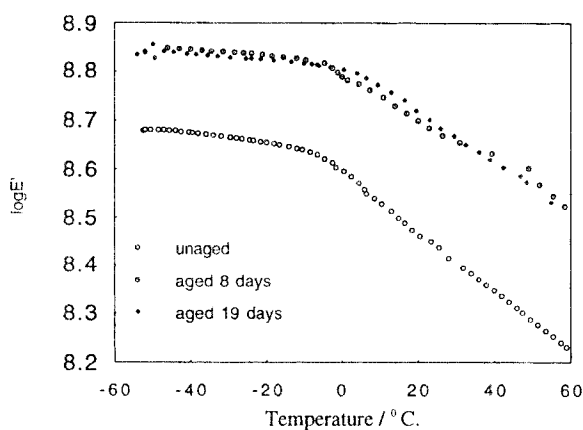


(b) Random copolymer.

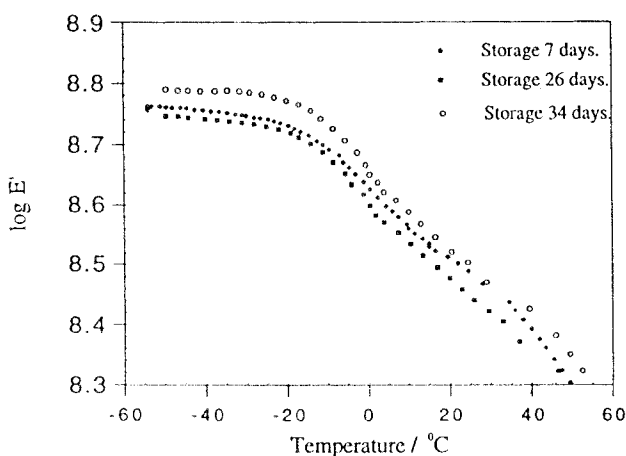
**Figure 2.** Effect of Storage on Log  $E''$  ( $T_g = 24^\circ\text{C}$ ).

curves of stored samples with unstored sample. From these curves, it can be seen that the peak temperature increased with the increasing of storage time. It is noticeable also from Figure 4 that these peaks become increasingly broad as the storage time increased.

According to Hutchison's suggestion [6], and in contrast to the situation in amorphous polymers below  $T_g$ , it would appear instead that the enthalpy relaxation behavior of i-PP could be best understood in terms of a type of 'ordering' or 'partial crystallization' of the amorphous fraction, in an interfacial region close to the surfaces of the crystalline lamellae. On storage, this interfacial



(a) i-PP.



(b) Random copolymer.

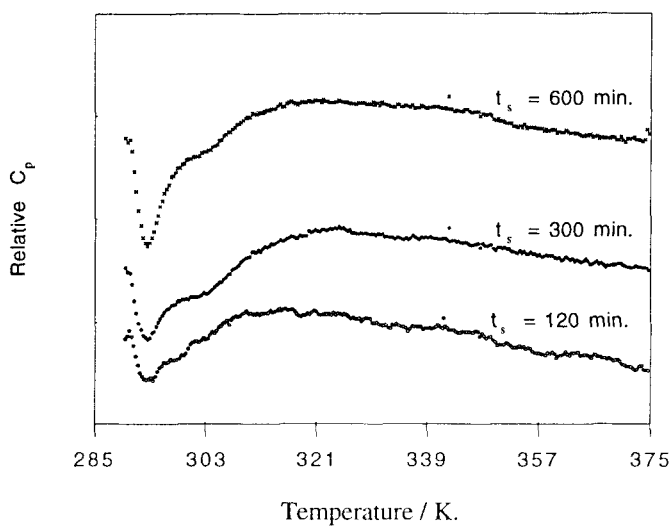
**Figure 3.** Effect of Storage on Log  $E''$  (10 Hz).

region becomes increasingly more ordered, and the corresponding DSC heating scans show what is effectively a melting endotherm. The effect of this progressive ordering in the interfacial regions during storage is to restrict, to an increasing extent, the bulk amorphous material in the interlamellae regions. Thus, with increasing storage time, the glass transition moves to higher temperature.

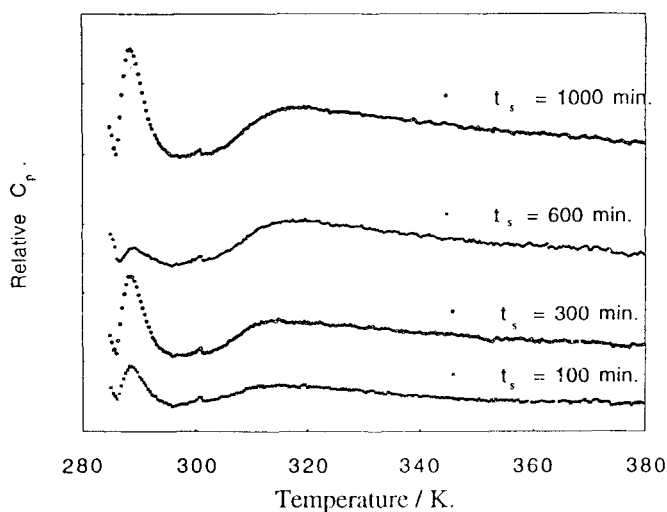
### Effect of Storage at Room Temperature on Mechanical Properties

#### *Impact Properties*

Figure 5 shows the effect of storage on impact energy of samples. It can be seen that for all three types of samples, the breaking energy decreased with the



(a) Block copolymer.

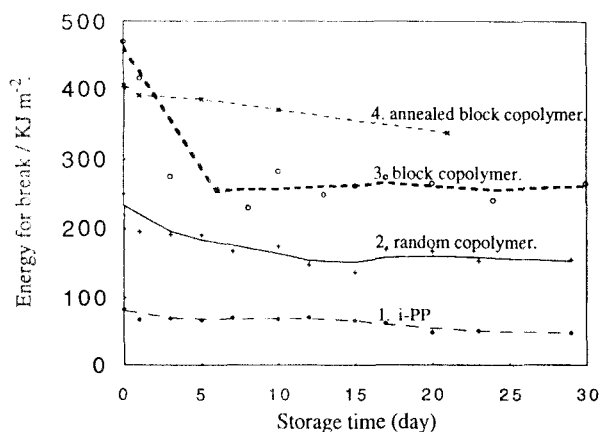


(b) i-PP.

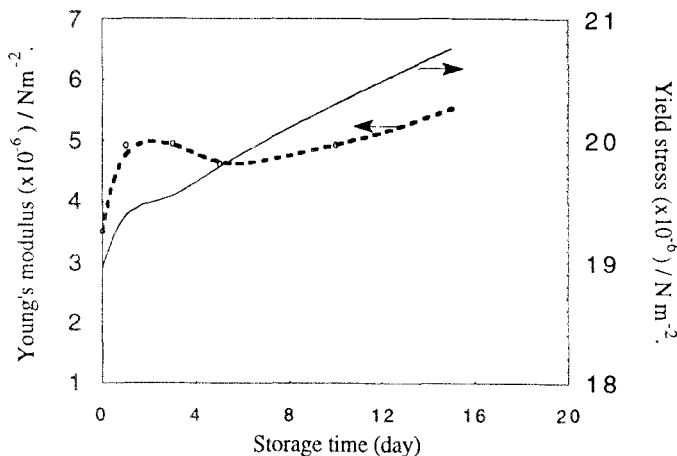
**Figure 4.** DSC Curve of Stored i-PP with Unstored Sample Subtract.

increasing of storage time. But for block and random propylene-ethylene copolymers, it was found that the energy to break decreased sharply with aging time, and then approach equilibrium. For iPP, the breaking energy did not change much. For block propylene-ethylene copolymer sample annealed at  $110^{\circ}\text{C}$  for 45 minutes, storage at  $24^{\circ}\text{C}$  is unlikely to induce secondary crystallization and





**Figure 5.** Effect of Storage on Impact Properties (stored at 24°C).

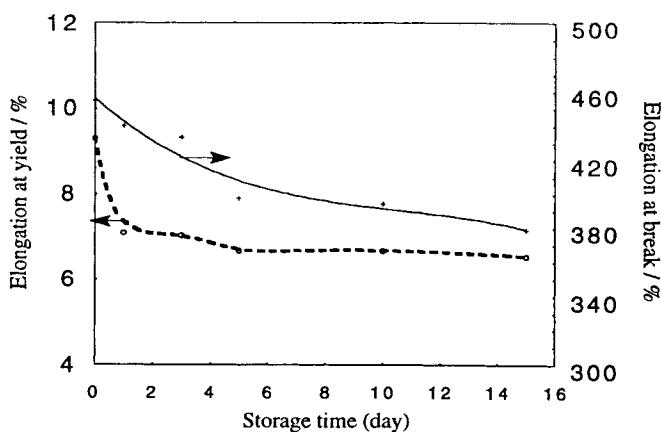


**Figure 6.** Effect of Storage on Young's Modulus and Yield Stress of the Block Copolymer.

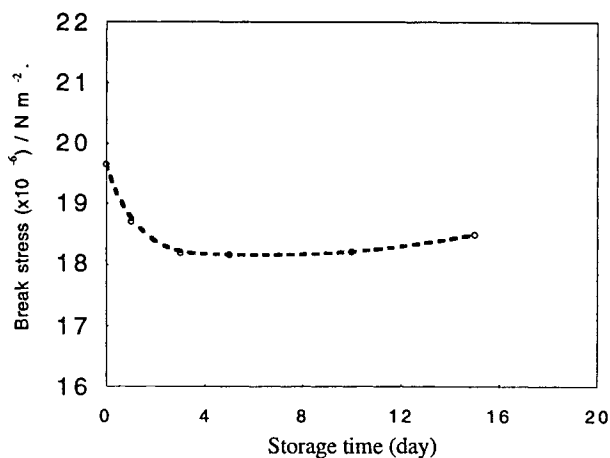
changes in crystallinity. Hence, in this situation, the structural changes during storage at 24°C will come from the molecular rearrangements in the amorphous phase. From Figure 5 it can be seen that the breaking energy has little change with storage time. So it was suggested that the decrease of breaking energy as storage time comes from secondary crystallization in amorphous phase.

#### *Extension Properties*

Figure 6 shows the effect of storage on the Young's modulus and the variation of yield stress for the block copolymer. With an increase in storage time,



**Figure 7.** Effect of Storage on Elongation of Block Polymer.

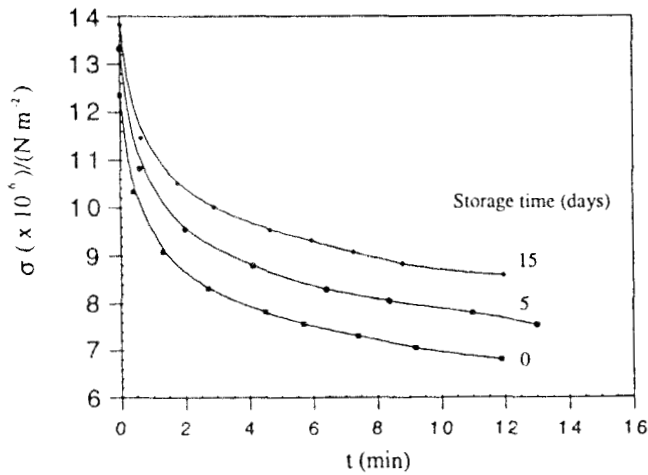


**Figure 8.** Effect of Storage on Stress at Break of Block Copolymer.

the Young's modulus increased, and this is in agreement with the results obtained by other authors for other semicrystalline polymers [8]. The yield stress increased with the storage time, but the elongation at yield decreased (Figure 7). For ultimate behavior, it was found that the elongation decreased with storage time (Figure 7), and the stress decreased as well (Figure 8). From these results, it can be seen that storage produced a stiffer, more brittle material.

#### *Stress Relaxation*

Stress relaxation experiments were carried out below yield strain. Figure 9 shows the stress relaxation of samples stored at 24°C for different times. Each is



**Figure 9.** Stress Relaxation Curves for the Stored Block Propylene-ethylene Copolymer.

an average of 5 specimens. The experimental time and the corresponding tensile force data were treated using the Maxwell-Voigt function:

$$\sigma = \sigma_0 e^{-(t/\tau)} \quad (1)$$

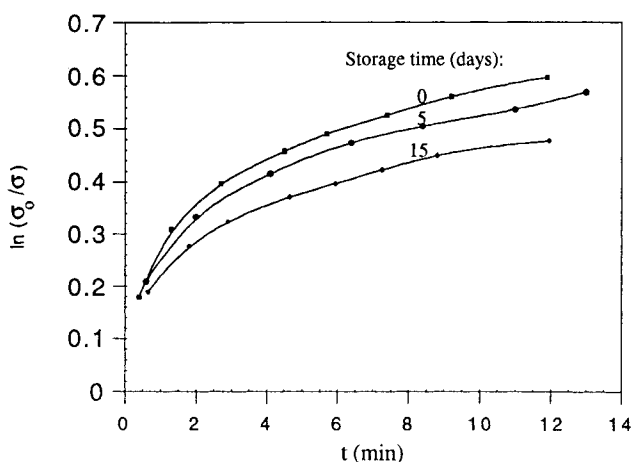
where  $\sigma$  is the stress at time  $t$ ,  $\sigma_0$  is the stress at time  $t = 0$ ,  $\tau$  is relaxation time. Rearrangement of the equation yield:

$$\ln\left(\frac{\sigma_0}{\sigma}\right) = \frac{t}{\tau} \quad (2)$$

A plot of  $\ln(\frac{\sigma_0}{\sigma})$  vs.  $t$  should yield a straight line of slope  $\frac{1}{\tau}$ , and intercept at zero point.

Figure 10 showed the experimental  $\ln(\frac{\sigma_0}{\sigma})$  vs.  $t$  relationship. It can be seen that the Maxwell-Voigt function does not fit the experimental data, and a Williams-Watts relaxation function [9], which had been used successfully to describe various relaxation phenomena in the glass state, was used. The function has been used successfully to fit the stress-relaxation data of many polymer systems [10]:

$$\varphi_t = E/E_0 = \sigma/\sigma_0 = e^{-(t/\tau)^\beta} \quad (3)$$



**Figure 10.** Relationship Followed Maxwell-Voigt Function.

where  $0 \leq \beta \leq 1$ . Chow and Prest [11] have shown that the relaxation phenomena described by the Williams-Watts equation are controlled by continuous relaxation spectra. The parameter  $\beta$  describes the breadth of the relaxation spectrum. The higher the value of  $\beta$ , the narrower is the spectrum, and in the extreme case of  $\beta = 1$  (Maxwell-Voigt model), there is only one relaxation process.  $\tau$  is an average characteristic relaxation time. The Williams-Watts equation yields:

$$\ln\left(\frac{\sigma_0}{\sigma}\right) = \left(\frac{t}{\tau}\right)^\beta \tag{4}$$

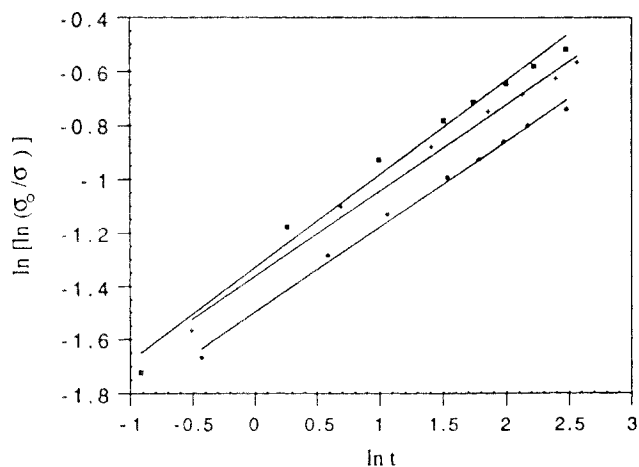
Taking logarithms:

$$\ln\left[\ln\left(\frac{\sigma_0}{\sigma}\right)\right] = \beta(\ln t - \ln \tau) \tag{5}$$

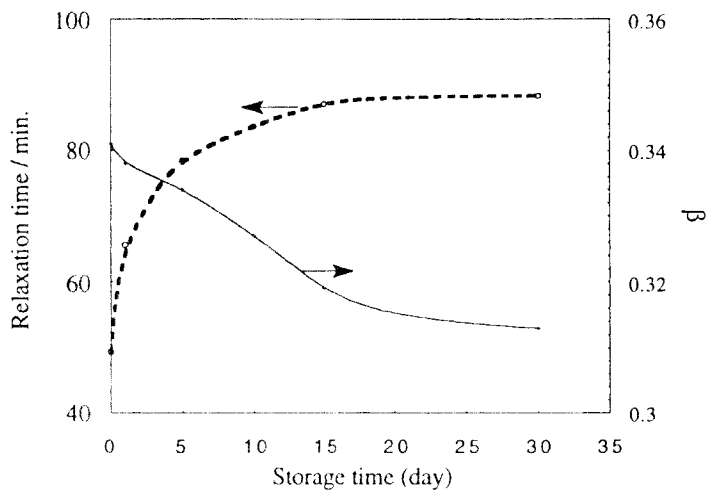
A plot of  $\ln\left[\ln\left(\frac{\sigma_0}{\sigma}\right)\right]$  versus  $\ln t$  yielded a straight line of slope  $\beta$  and intercept of  $-\beta \ln \tau$  at  $t = 1.0$ . The effect of storage on stress relaxation behavior was to change both  $\beta$  and  $\tau$ .

Figure 11 showed a plot of  $\ln\left[\ln\left(\frac{\sigma_0}{\sigma}\right)\right]$  and  $\ln t$ , from which it was concluded that the relationship fitted the data very well indeed.

Figure 12 showed the variation of stress relaxation time ( $\tau$ ) with storage time for the block copolymer. It was found that the stress relaxation time increased with storage time. Since secondary crystallization happened during the storage



**Figure 11.** Relationship Followed Williams-Watta Equation.



**Figure 12.** Effect of Storage on Relaxation Parameters.

Table 1. Stress-relaxation Parameters for Random Copolymer

| Storage Time (days) | $\tau$ (min.) $\pm 5$ | $\beta \pm 0.01$ |
|---------------------|-----------------------|------------------|
| 0                   | 104                   | 0.31             |
| 1                   | 117                   | 0.30             |
| 3                   | 130                   | 0.29             |
| 6                   | 165                   | 0.28             |
| 10                  | 169                   | 0.28             |
| 16                  | 208                   | 0.27             |

process, the molecular rearrangements decreased the mobility of the polymer chains. Inevitably, it took more time to relax to a corresponding stress, so the relaxation time increased with storage time. On the other hand, the  $\beta$  value changed a little within the storage time within experimental error (Figure 12). Because  $\beta$  represents the broaden of relaxation time distribution, the decreasing of  $\beta$  means that polymer structure becomes more 'ordered' after storage resulting in the narrower relaxation time distribution. For the random copolymer, we observed the same trend (Table 1).

## CONCLUSIONS

Storage effects have been studied on bulk semicrystalline low ethylene content block and random propylene-ethylene copolymers. It was found that secondary crystallization of the amorphous fraction happened in an interfacial region between the crystalline lamellae. Experimental results showed that after storage, the Young's modulus increased and loss tangent decreased. The glass transition temperature had shifted to higher temperature compared to the unstored specimens. The impact energy decreased with storage time but reached a limiting value. The effects of storage on extension property suggested that the storage increased the stiffness of the copolymers. Stress relaxation behavior were investigated. It was found that the stress relaxation time increased with storage time. The  $\beta$  value, representing the broadening of relaxation time distribution, decreased with storage time, which suggested that the polymer structure becomes more 'ordered' after storage.

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