Dynamic Mechanical Properties of Poly(vinyl chloride) After Complicated Thermal Histories

The effect of complicated thermal histories on the dynamic mechanical properties of poly(vinyl chloride) (PVC) has been investigated. The storage modulus E' increases and the loss tangent tan δ decreases as the material is subjected to sub-T'_g annealing. These physical aging phenomena are influenced by the crystallinity induced by annealing of the material at temperatures above T_g.

INTRODUCTION

In a previous paper,[1] the structural changes of poly(vinyl chloride) (PVC) that can be induced by thermal treatment above and below the glass transition temperature, T_g, was investigated. As the polymer is cooled from the melt to the glassy state through T_g, two different phenomena can occur that are strongly dependent of the thermal history of the material. Above T_g, crystallization processes can be carried out, whereas below T_g, physical aging phenomena related to the amorphous glassy phase take place.

More precisely, we have shown that the physical aging of PVC is affected by the crystallinity induced by annealing of the polymer at temperatures above T_g. Calorimetric measurements reveal that the enthalpy relaxation of the aged polymer depends strongly upon the crystallization conditions (T_c, t_c), as the induced crystallinity changes the composition of the amorphous phase, i.e., the extent of disturbed regions formed in the vicinity of the crystalline phase as well as the segmental mobility of the undisturbed amorphous domains.

In this communication, the influence of complicated thermal histories (i.e., successive annealing above and below T_g produced crystallinity and volume recovery to the material) to the dynamic mechanical properties of the polymer has been investigated. This work has been suggested in order to correlate the thermal properties of the polymer with the mechanical ones and to corroborate our previous findings reported elsewhere.[1]

On the other hand, these complicated thermal histories could be induced into the polymer during processing and storage, causing a practical interest as well.

EXPERIMENTAL

The polymer used was a commercial suspension-polymerized PVC obtained by EKO (Hellas) with M_n = 36,300 and M_w = 75,500 (M_w/M_n = 2.1).

Films were prepared by compression molding at 230°C under 5,000 psi pressure for 1–2 min and quenched to 0°C using white powder blended with 4% dibutultin dilaurate to prevent thermal degradation.

To assure a common thermal history, all samples were annealed at 210°C for 5 min and quenched to 0°C before any other thermal treatment. In the following, the samples were subjected to successive annealing according to the scheme

$$T_0 \nearrow T_c(t_c) \searrow T_0 \nearrow T_A(t_A) \searrow T_0$$

where T_0 is 0°C, T_c is 132°C ($> T_g$), t_c is the annealing time at T_c, T_A is 66°C ($< T_g$), and t_A is the annealing time at T_A.

Dynamic viscoelastic data were obtained between 30 and 120°C at 110 Hz using the Pheovibron (model DDV-IIC) viscoelastometer. The heating rate was close to 2°C/min.

RESULTS AND DISCUSSION

PVC samples made by compression molding were subjected to annealing at 132°C for 10 and 300 min followed by quenching to 0°C. As has been shown, this procedure gives specimens with different crystallinity percentages depending on the time and the crystallization temperature. In the following, the same specimens were annealed at 66°C ($< T_g$) for different times.

In Figure 1, the storage modulus E' of PVC samples with different thermal histories are illustrated. As shown, the modulus of the sample crystallized for 10 min is higher than that of the quenched sample. Furthermore, sub-T_g annealing at 66°C provokes a further increase of the modulus.[2] It is apparent that both phenomena, crystallinity and physical aging, though they arise from different mechanisms, influence the modulus in the same manner,
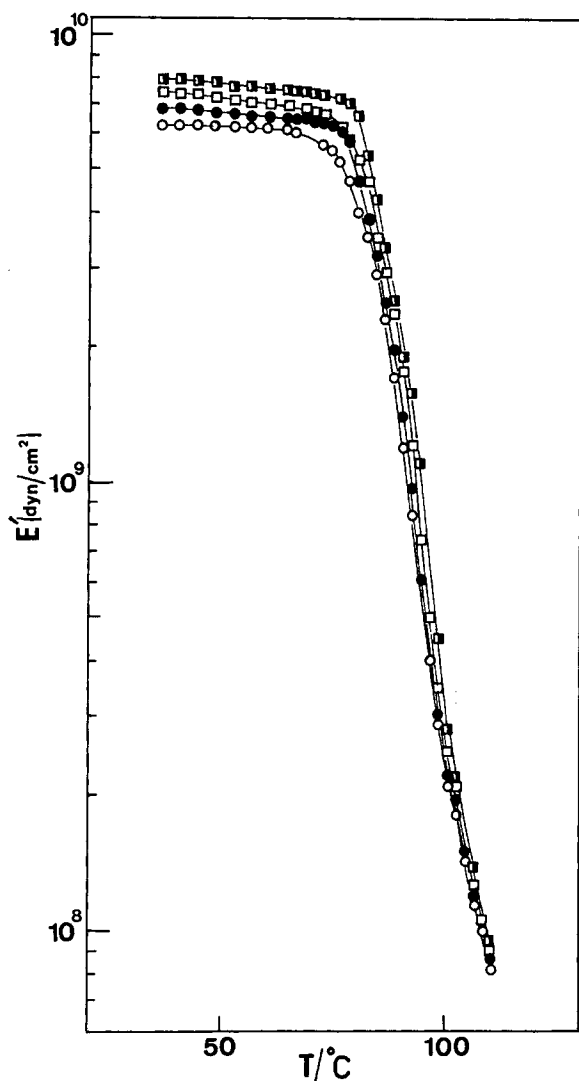
Figure 1 Temperature dependence of the storage modulus E' for PVC films with different thermal histories: (O) quenched from the melt; (●) annealed at 132°C for 10 min; (□) annealed at 132°C (10 min) and at 66°C (66 h); (■) annealed at 132°C (10 min) and at 66°C (161 h).

as both cause a further packing or a reduction of the segmental mobility. Of course, the second process (physical aging) depends on the remaining amorphous phase or the crystallinity percentage and therefore must be affected by the above-T_g annealing conditions.

Furthermore, the thermal history influences the damping, as illustrated in Figure 2. The loss tangent tan δ peak slightly drops and shifts toward higher temperatures owing to the crystallinity induced by annealing at 132°C. The damping continues to decrease with the aging time when the polymer is subjected to sub-T_g annealing.

Results concerning samples crystallized at the same

temperature but for 300 min (presenting higher crystallinity percentage) are given in Figures 3 and 4. In this case, the same phenomena are observed.

Analogous results concerning semicrystalline polymers are reported by Struik,[3] showing also that aging effects may occur at temperatures below as well as above the conventional T_g of the material. Also, it must be mentioned here that the same phenomena have been observed in partially semicrystalline, stereo regular biopolymer bacterial poly(D-b-hydroxybutyrate) reported recently by Scandola et al.[4]

Our attention is now focused on how the degree of crystallinity can affect the influence of the physical aging on the dynamic mechanical properties of the material. For that reason, we compare the storage modulus increase ($\Delta E'$) (measured at 80°C) owing to volume recovery that occurs during the annealing of the samples at 66°C for 66 h for the samples crystallized for 10 min and 300 min.
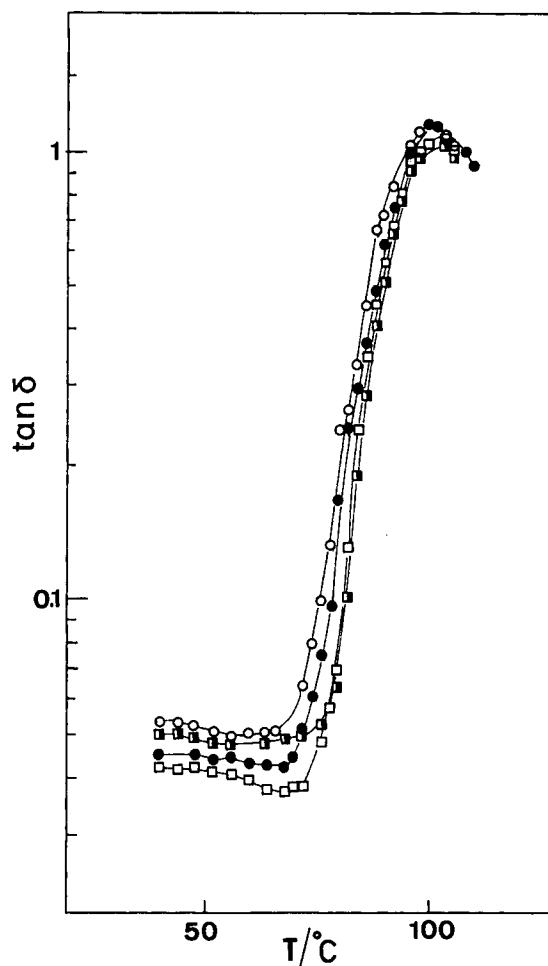

Figure 2 Temperature dependence of tan δ for PVC films with different thermal histories; symbols as in Figure 1.

As shown in Table I, $\Delta E'$ is higher for the sample crystallized for 300 min than for the sample crystallized for 10 min. This result is in excellent agreement with those already obtained by differential scanning calorimetry where the enthalpy relaxation of the sample for $t_c = 300$ min is higher than that of the sample for $t_c = 10$ min.[1] What one expects is that the sample with the lower crystallinity ($t_c = 10$ min) should undergo a more extensive physical aging and therefore should have a higher $\Delta E'$ than that of the sample with higher crystallinity ($t_c = 300$ min), as the former presents a more extensive amorphous phase.
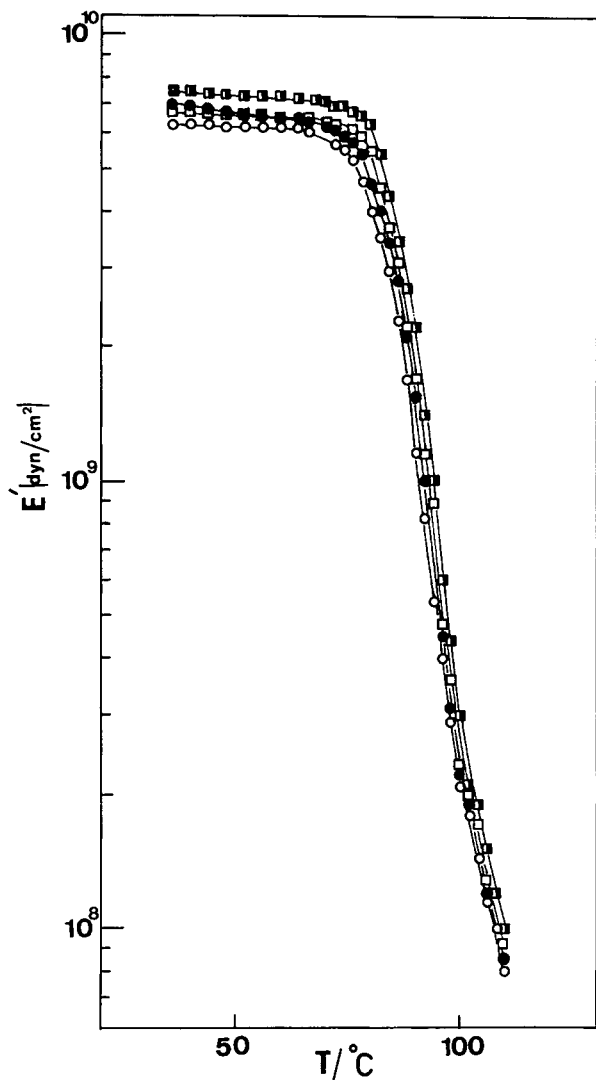

Figure 4   Temperature dependence of tan δ for PVC films with different thermal histories; Symbols as in Figure 3.

Figure 3   Temperature dependence of the storage modulus E' for PVC films with different thermal histories: (O) quenched; (●) annealed at 66°C for 66 h; (□) annealed at 132°C for 300 min; (■) annealed at 132°C (300 min) and at 66°C (66 h).
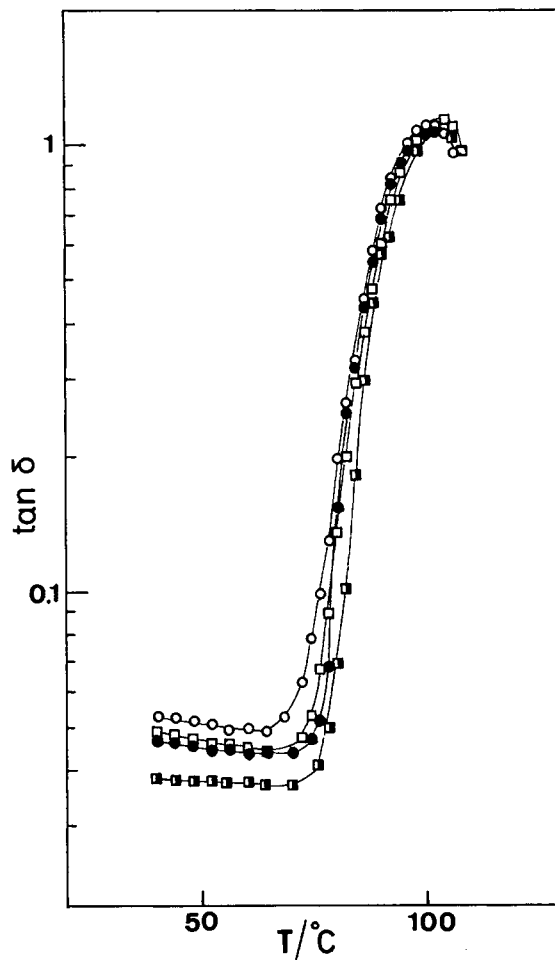
To explain the above peculiar result, the model of Struik concerning the semicrystalline polymers had been considered. According to this model, the crystals disturb the amorphous phase and reduce segmental mobility. This reduction is more pronounced in the vicinity of the crystals

Table I   Storage Modulus E' for Samples with Different Thermal Histories Measured at 80°C

Crystallized At 132°C (t_c[min])	$10^{-8} \times E'$ dyn/cm^2		10^{-8} $\Delta E'$ (dyn/cm^2)
	Quenched	Annealed At 66°C For 66 h	
10	4.62	5.46	0.84
300	5.3	6.6	1.3
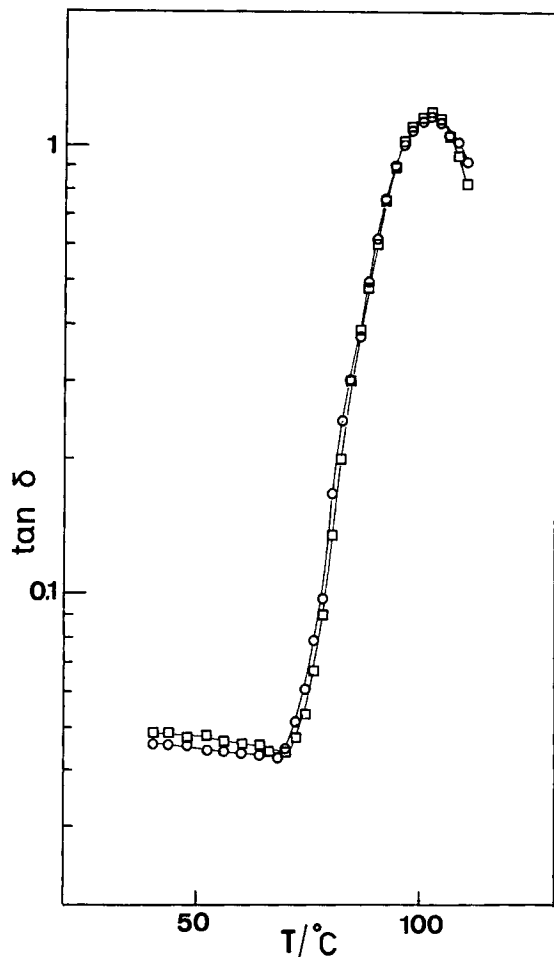
Figure 5 Temperature dependence of tan δ for PVC films crystallized at 132°C for (O) 10 min and ($\square$) 300 min.

One of the reasons for the above-mentioned behavior was that the lower crystallinity sample should present more disturbed regions (reduced mobility), implying more extension of the tan δ peak toward the higher temperatures. From Figure 5 it can be seen that the high-temperature side of the tan δ peak related to the sample with t_c = 10 min tends to shift to higher temperatures than that of the sample with t_c = 300 min, partially satisfying the above assumption. Therefore, the second reason concerning the kind of segments bound in the crystallites should be adopted. As has been reported based on the DSC results, the crystallites of the PVC (t_c = 10 min) are formed from segments of larger mobility (as they melt at lower T_m), disposing fewer parts of large mobility that are able to undergo physical aging than those of the PVC (t_c = 300 min). The final result is that the regions of PVC (T_c = 300 min) presenting high segmental mobility available to physical aging are more extensive than are those of PVC (t_c = 10 min).

References

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and is eliminated at large distances from them. The main consequence of this immobilization is that the glass transition will be extended toward the high-temperature side.