Cooperative Molecular Motion in Blends of Poly(vinyl chloride) with Ethylene–Vinyl Acetate Copolymers

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Received July 23, 1970

ABSTRACT: Torsion pendulum studies of blends of poly(vinyl chloride) (PVC) and ethylene–vinyl acetate (E–VA) copolymers show peaks in the curves of internal friction over the temperature range −180–100°. The results show a two-phase blend for E–VA polymers below 50% in VA, and a single-phase blend when the VA level is 65–70%. The latter blends produce an internal friction peak which obeys the conventional reciprocal temperature law for the effect of plasticizers on T_g. The low-temperature (−150°) (γ) peak for the E–VA resins is unaffected by the blend formulation. The results show (1) that the single-phase blends are compatible down to the scale of chain segments, (2) that cooperative intermolecular segmental motion of both types of molecules is required for the relaxation motion associated with the new blend peak, (3) that the γ peak for E–VA is intramolecular, not requiring cooperative motion of neighboring chains, and thus that (4) there are two types of main chain segmental motion in these blends.

A number of authors and speakers have discussed the configurational changes and molecular motions associated with the glassy transitions of high polymers. The qualitative descriptions are generally that of a jump of a segment of 10–30 carbon atoms, plus associated movement of neighboring atoms in the same polymer chain. As our work progressed, we found that it enables us to draw more specific conclusions regarding the nature of the various molecular motions.

The work reported herein became possible as a result of a discovery of McDonald,[1] a fellow worker. He found that apparently homogeneous blends can be made from poly(vinyl chloride) (PVC) and high molecular weight ethylene–vinyl acetate (E–VA) copolymers if the level of VAc in the latter resins is in the range of 60–75% by weight. Blends of 50/50 wt % are clear and flexible and appear to be completely compatible. Thus, the system [PVC–EVA] appeared to be a good one to study since previous work had shown the transition temperatures of these polymers to be widely separated.

The experimental approach to this work was also stimulated by the work of Hughes and Brown.[2] They showed that two polymers can be blended to give clear films, but that clarity is not definite proof of compatibility on a molecular scale. The lack of such compatibility was demonstrated by the appearance of specific loss peaks taken from curves of dynamic loss *vs.* temperature obtained by use of a torsion pendulum.

Experimental Section

A torsion pendulum similar to that of Heijboer[3] was used to determine the torsion modulus and internal friction of the samples. The measurements were made at intervals of 20° unless otherwise noted from −180 to 100°. The mass of the moment arm was adjusted to give a period of about 1 cps over the entire temperature range.

The temperature at which the loss reaches a maximum can be judged to within about 5°. These temperatures are designated as α, β, and γ to correspond to the nomenclature of previous workers.

The blends described herein were made by milling the resins for about 15 min on a two-roll mill at about 190°. The same results were obtained from solution blending, using 10% of the polymer in tetrahydrofuran, followed by compression molding of the sample bars. The blends used are listed in Table I.

Results and Discussion

The choice of the torsion pendulum depends upon the fact that theories of molecular motion are related to the dynamic mechanical measurements. It is generally accepted that the loss peaks obtained from 1-cps torsion modulus measurements are related to molecular motions of chain segments or side chains. In the case of linear polymers such as poly(vinyl chloride) the loss peak associated with T_g is believed to be related to the motion of chain segments from 10 to 30 carbon atoms long. This theory, then, determines the scale at which we determine compatibility. This point is so important that it is restated in a slightly different form. The T_g loss peak depends upon there being a domain of pure PVC large enough to contain a 10–30 carbon atom segment of PVC, and large enough for the relaxation jump to take place. When blending causes that characteristic T_g peak to disappear, we conclude that no such domain of pure PVC of that size remains, that the chains are intermixed to a finer degree than a 10–30-Å scale.

Figure 1 shows the internal friction curve for poly(vinyl chloride) from Schmieder and Wolf[4] plotted from −180° to above the glass transition temperature. There are two small peaks and the α peak at about 92° which is associated with T_g. In Figure 2 is shown the internal friction curve for an ethylene–vinyl acetate copolymer containing 40% vinyl acetate from Nielsen.[5] This shows two loss peaks—a γ peak at about −150° and a β peak at about −30°. The blend of these two

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(1) J. W. McDonald, private communication.

(2) L. J. Hughes and G. L. Brown, *J. Appl. Polym. Sci.*, **5** (17), 580 (1961).

(3) J. Heijboer, P. Dekking, and A. J. Staverman, *Proc. Ind. Int. Congr. Rheol. 1953*, 123 (1954).

(4) K. Schmieder and K. Wolf, *Kolloid-Z., Z. Polym.*, **127**, 65 (1952).

(5) L. E. Nielsen, *J. Polym. Sci.*, **42**, 357 (1960).

TABLE I
SAMPLES USED

Sample	Blend
A	PVC[a]
B	50/50 PVC/E-VA[b] (82–18) (by weight)
C	50/50 PVC/E-VA[c] (75–25) (by weight)
D	50/50 PVC/E-VA[d] (67–33) (by weight)
E	50/50 PVC/E-VA[e] (60–40) (by weight)
F	50/50 PVC/PVAc[f]
G	50/50 PVC/E-VA (35–65, experimental resin) M_n = 40,000
H	80/20 PVC/E-VA (35–65, experimental resin)
I	65/35 PVC/E-VA (35–65, experimental resin)
J	25/75 PVC/E-VA (35–65, experimental resin)
K	80/20 PVC/E-VA (30–70, experimental resin)
L	65/35 PVC/E-VA (30–70, experimental resin)
M	50/50 PVC/E-VA (30–70, experimental resin)
N	25/75 PVC/E-VA (30–70, experimental resin)

[a] Vygen 110 (General Tire Co.) was used for the PVC in all cases and contained 1% Thermolite 31, a heat stabilizer supplied by M&T Chemicals, Inc., Rahway, N. J. [b] Elvax 420 vinyl resin. [c] Elvax 360 vinyl resin. [d] Elvax 150 vinyl resin. [e] Elvax 40 vinyl resin. [f] Gelva V-7 poly(vinyl acetate).

polymers in a 50/50 blend ratio enables us to obtain the curve shown in Figure 3. This shows the characteristic bands of the poly(vinyl chloride) and the E–VA copolymer. This result demonstrates that this blend is incompatible. No matter how much effort is put into mixing these polymers, they separate into domains big enough so that the loss curves are additive.

In the next case (blend G) an E–VA copolymer with about 65% VAc was used. This polymer has the same curve for dynamic loss *vs.* temperature as did the previous E–VA (40% VA) resin. The blend of this with PVC, however, gives the loss curve shown in Figure 4.

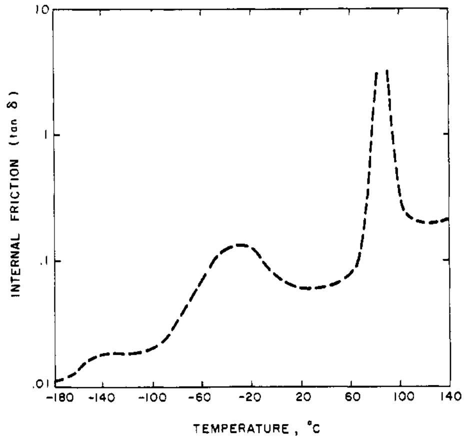

Figure 1. Internal friction from −180 to 100° for PVC.

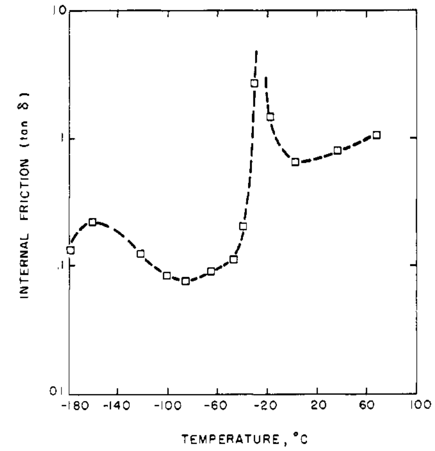

Figure 2. Internal friction from −180 to 100° for an E–VA (60–40) polymer.

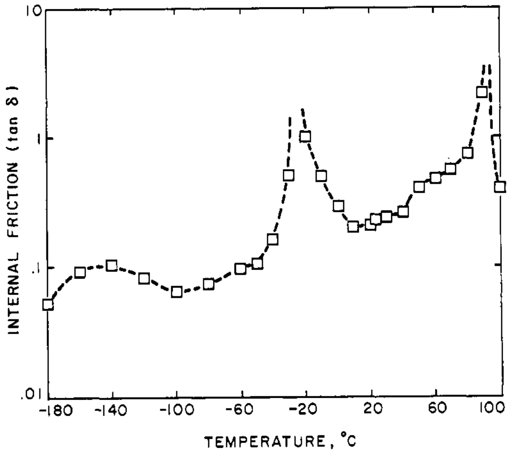

Figure 3. Internal friction from −180 to 100° for a two-phase blend of PVC with an E–VA copolymer (blend E).

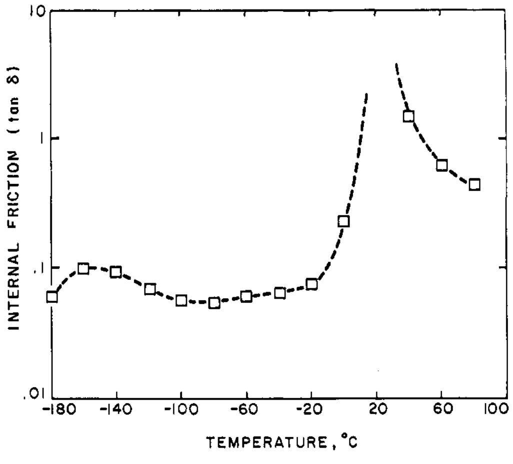

Figure 4. Internal friction from −180 to 100° for a single-phase blend of PVC with an E–VA copolymer (blend G).

In this figure there is one new band at about 25°, and one peak at −150°. There is no α peak due to the poly(vinyl chloride). There is no β peak at −30° associated with the E–VA polymer. From this, we conclude that there is no domain present in this blend large enough to allow the poly(vinyl chloride) characteristic relaxation mechanism to take place. Similarly, there is no domain of ethylene vinyl acetate polymer present large enough to support the characteristic E–VA

β transition. Furthermore there is no relaxation occurring in which just PVC chain moves by itself, and there is no relaxation in which just the E–VA moves by itself as far as the relaxation that has been previously found at $-30°$. This new peak must be a relaxation which consists of the common or cooperative motion of both E–VA chain segments and poly(vinyl chloride) chain segments.

In Figure 5 is shown the temperature at which the loss maximum occurs when the content of the PVC in the compatible blend (65% VA) is changed from 25 to 85%. This shows that the temperature corresponding to the α peak for PVC and the temperature corresponding to the β peak for the E–VA resin can be used to calculate the temperature for the peak of the blend according to the expression

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}$$

This shows that when two polymers are compatible down to the scale of segmental chain motion, the glass transition temperature obeys, approximately, the same law as that for a polymer and a monomeric plasticizer.

In Figure 6 the temperatures of the relaxation peaks are *mapped* for all of the blends made with 50% PVC. The variation is provided by using polymers containing different levels of vinyl acetate (blends B, C, D, E, F, G, and M). The upper half of the curve shows a relatively abrupt change in the temperature of the loss peaks as the blends change from two phase to single phase.

In the lower half of Figure 6, we see the behavior of the γ loss peak for the E–VA copolymer. This peak shows no detectable change, as the blends change from a compatible to a noncompatible system. That is, the the E–VA copolymers relax in the same manner whether they are surrounded by other E–VA segments or by poly(vinyl chloride) segments. They persist in moving all by themselves in this mode of motion. This γ peak has been ascribed by Schatzki[6] as due to a more limited type of rotational motion of a few CH_2 groups. This viewpoint is borne out by our results, from which we conclude that the methylene motion is short range and entirely unaffected by the presence of nearby C–Cl groups. Thus we note that in the 50/50 compatible blend with PVC we have two types of main chain segmental motion occurring. One type is the short segment motion of the CH_2 groups just described. The other type is the cooperative segmental motion of PVC chains along with E–VA chains as discussed previously.

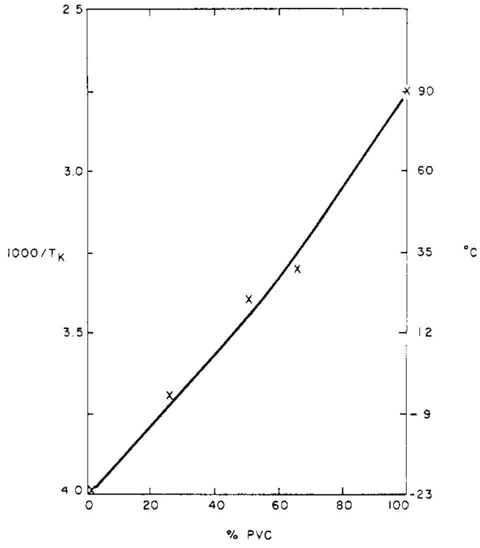

Figure 5. Temperatures of internal friction peaks for blends of PVC with an E–VA (35–65) resin as the polymer ratios change.

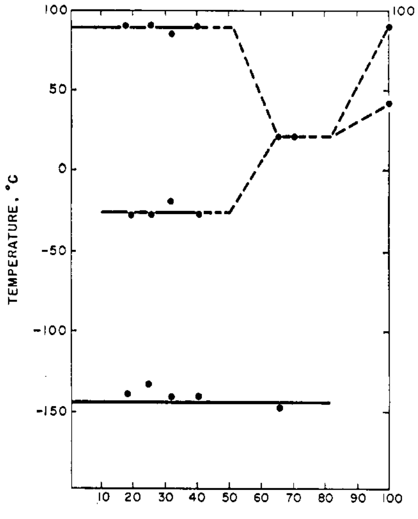

Figure 6. Temperatures of internal friction peaks for 50/50 blends of PVC with a series of E–VA resins.

Summary

From the results given we conclude (1) that the blends made with the E–VA resins containing 60–75% VA are compatible down to the scale of short segments of molecules, and do obey the additive law for low molecular weight plasticizers; (2) that for the relaxation characterized by the internal friction peak near 25°, the segments of both kinds of molecules move simultaneously and cooperatively (this seems to be direct evidence for cooperative motion of neighboring segments for the amorphous transition for identical polymer molecules which, in the past, was supported only by geometrical considerations); (3) that the motion of short segments of CH_2 groups associated with the γ peak is independent of the environment and does not require extensive cooperative motion of neighboring chains; (4) that, in accordance with Rabold's[7] spin-probe studies of polyethylene, there are two types of chain backbone relaxation mechanisms occurring in the compatible blends. One mechanism is short range, intramolecular, and does not require cooperative motion of neighboring chains, the other is longer range, intermolecular, and does require cooperative motion of chains.

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(6) T. F. Schatzki, *J. Polym. Sci.*, **57**, 496 (1962); T. F. Schatzki, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., 1965; *Polym. Prepn., Amer. Chem. Soc., Div. Polym. Chem.*, **6**, 646 (1965).

(7) G. P. Rabold, *J. Polym. Sci., Part A-1*, **7** (5), 1203 (1969).