The Effect of Additives on Impact Poly(Vinyl Chloride)

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Synopsis

The two-phase nature of a graft copolymer of ethylenepropylene-1:4 hexadiene (EPDM) and poly(vinyl chloride) (PVC) has been established by dynamic mechanical measurements. The interaction of different additives with the isolated graft copolymer has also been inferred from their dynamic mechanical and thermal properties. Carbon black and titanium dioxide act as inert filler, while the effect of including straight-chain hydrocarbons (e.g., n-hexadecane and n-hexatriacontane) is strongly dependent upon the melting point of the hydrocarbons. Sunflex 110 plasticizes the rubber phase of the graft copolymer while dioctyl (di-2-ethyl hexyl) phthalate (DOP) plasticizes the PVC phase and reduces T_g. At lower temperatures, however, the elastic modulus is increased by an "antiplasticization" effect. The local environment of PVC chains in the graft copolymer is modified by the presence of the rubber and PVC chains are less mobile.

INTRODUCTION

The toughening of a brittle polymer to yield an impact resistant thermoplastic can be effected by dispersing rubber particles in the original glassy matrix.[1-3] The presence of rubber averts brittle failure and permits enhanced energy absorption by facilitating the orientation and cold drawing of the glassy phase to form crazes.[4,5] The size[6,7] and spatial distribution[8] of the rubber are critical to impact behavior. Because of entropic considerations, polymeric materials are usually incompatible and blends are thermodynamically unstable. Accordingly, blend morphology is often altered by processing. In order to stabilize a rubber in glass dispersion, block or graft[9] copolymers are frequently used as emulsifiers. A common technique is to polymerize a solution of rubber in a monomer.[10] The initially homogeneous solution is ultimately converted to a two-phase system consisting of rubber dispersed in glass. The stabilizing ingredient in this polymer composite is a graft copolymer composed of glassy chains attached to a rubber backbone.

The efficacy of the graft copolymer as an emulsifier depends on structure. Consequently, the processability and the retention of impact properties are also structure sensitive. Processing the composite polymer is often facilitated by the inclusion of processing aids, lubricants, and plasticizers. Morphology and impact stability can also be affected by the presence of such additives.

The two-phase nature of the isolated graft copolymer is readily established by measuring dynamic mechanical or calorimetric properties. The graft copolymer may therefore be used as a model for studying the effect of an additive on the glass and/or rubber phases. Structural information about the graft is also

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inferred by comparing the behavior of the graft copolymer and analogous ho-
mopolymers.   In these studies we have examined the effect of additives on the
glass transition phenomenon by dynamic mechanical and calorimetric mea-
surements.

EXPERIMENTAL

The graft copolymerization of PVC with the rubber ethylenepropylene-1:4
hexadiene has been described.[11]   Isolation of the graft portion of the reinforced
PVC was effected by sequential removal of free PVC and rubber using the pro-
cedure described below.

Two hundred grams of the rubber-modified PVC was added to 200 ml of 75/25
wt.% acetone/DMF mixture.   The mixture was shaken for 60 min at 65°C after
which it was centrifuged 10 min and decanted.   The procedure was repeated
successively with 200 ml DMF, 2 × 100 ml acetone followed by similar shaking,
centrifugation, and decantation.   The remaining acetone was removed by purging
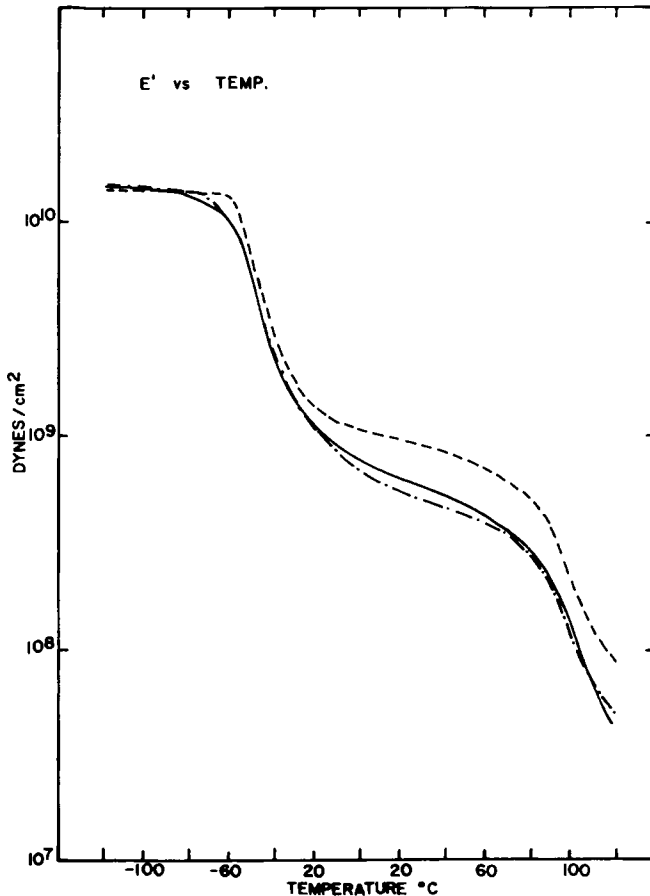with nitrogen.

Fig. 1. Temperature dependence of dynamic storage modulus E' for the isolated EPDM/PVC
graft copolymer: (- -) control; (- - -) sample containing 40% carbon black; (- --) 40% titanium
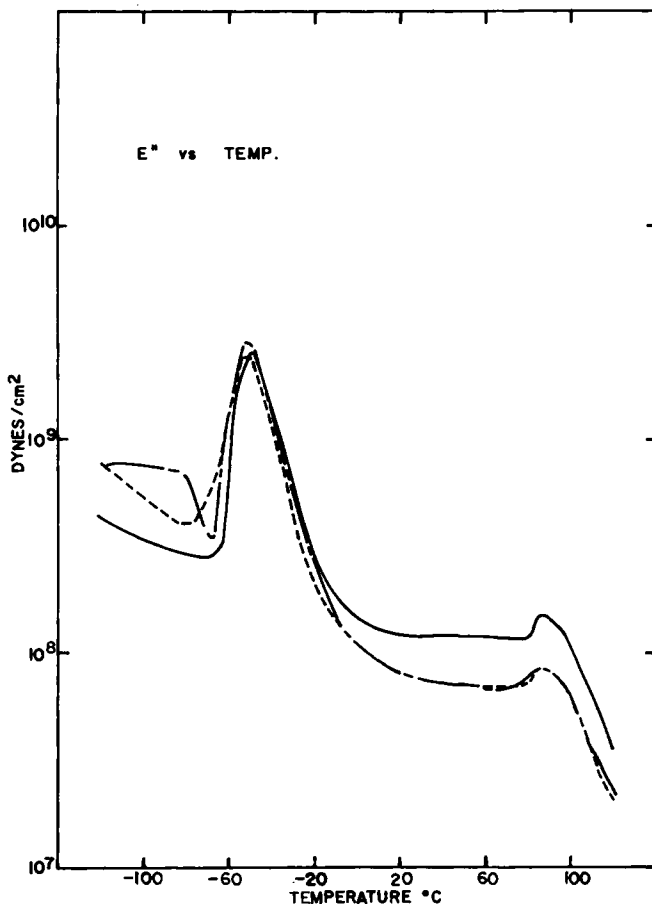dioxide.

Fig. 2. Temperature dependence of dynamic loss modulus E″ for the isolated EPDM/PVC graft copolymer: (- - -) control; (——) sample containing 40% carbon black (- ·· -) 40% titanium dioxide.

Removal of free rubber was then effected by adding the above portion to 2 × 200 ml heptane after which it was allowed to stand at room temperature for 2 hr with frequent agitation. The subsequent suspension was centrifuged and decanted. Residual heptane was purged with nitrogen.

Precipitation of the graft copolymer was subsequently carried out by dissolving the homopolymer-free sample in ~50 ml THF, followed by dropwise addition of ~500 ml MeOH. The precipitate was then filtered and dried in a vacuum oven at 60°C until constant weight was obtained.

The graft copolymer contains 50:50 wt.% PVC and ethylenepropylene-1:4 hexadiene rubber. The dioctyl (di-2-ethylhexyl) phthalate (DOP) used is from the Union Carbide Company; the n-hexadecane, $CH_3(CH_2)_{14}CH_3$, mp 17–18°C, from Humphrey Chemicals; the n-hexatriacontane, $CH_3(CH_2)_{34}CH_3$, mp 74–76°C, from Eastman Chemicals; the carbon black of MT grade from R. T. Vanderbilt Company; the titanium dioxide is of R-900 grade from du Pont Chemicals; and the Sunflex 110 paraffin oil is from the Sunoco Company. The weight percent of the additives in the graft copolymer is relative to the weight of PVC (for DOP) and rubber (for Sunflex 110, n-hexadecane and n-hexatriacontane) in the copolymer.
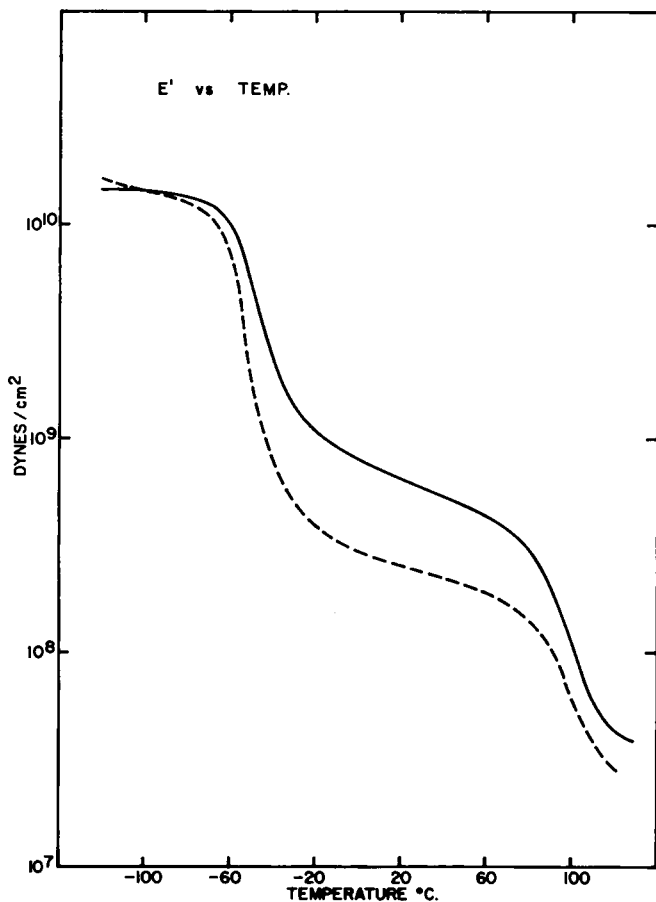
Fig. 3. Temperature dependence of dynamic storage modulus E' for the isolated EPDM/PVC graft copolymer containing 0% (– –) and 20% (- - -) Sunflex 110.

Dynamic mechanical measurements were carried out at 110 Hz with a Rheo-Vibron Viscoelastometer (Toyo Company Model DDV-11) over the temperature range of $-120°C$ to $120°C$. The temperature of the sample was monitored by a precalibrated iron–constantan thermocouple placed near the sample. Sample dimensions used in these measurements are $0.010 \times 0.05 \times 1.5$ in. The heating rate during the measurement was about $1°C/min$.

RESULTS

Successive Vibron scans on films of an isolated and additive filled graft copolymer of EPDM/PVC produced reproducible values of storage and loss moduli, E' and E''.

The temperature dependence of the dynamic modulus E' for an isolated EPDM/PVC graft copolymer and the effect of including 40% carbon black and titanium dioxide are shown in Figure 1. Corresponding loss moduli E'' plots are shown in Figure 2.

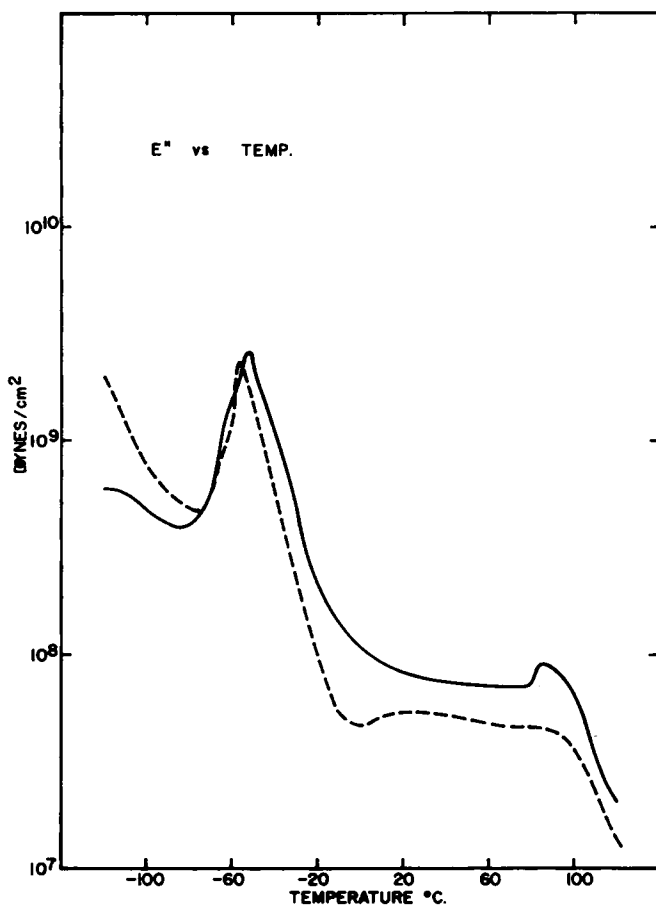Similar temperature dependence of E' and E'' for the isolated EPDM/PVC

Fig. 4. Temperature dependence of dynamic loss modulus E'' for the isolated EPDM/PVC graft copolymer containing 0% (– –) and 20% (- - -) Sunflex 110.

graft copolymer and the effect of including 20% Sunflex are shown in Figures 3 and 4, respectively.

The temperature dependence of E' and E'' before and after including 5% and 10% DOP is shown and compared in Figures 5 and 6. Similar plots of E' and E'' versus temperature and the effect of including 20% hexatriacontane and n-hexadecane are shown in Figures 7 and 8. The dependence of the temperature of the E''_{max}, associated with the glass transition (T_g) on DOP content in PVC copolymer is listed in Table I and compared with PVC homopolymer. Corresponding calorimetric results are also included and compared.

DISCUSSION

The modulus E'' shows two main transitions with maxima at $-50°$ and $88°$C corresponding to the glass transitions of the rubber and poly(vinyl chloride) (PVC) phases in the isolated graft copolymer (Fig. 2). Sequences of the rubber and PVC, composing the graft copolymer, segregate into discrete domains. Since toughening a glassy polymer requires a discrete rubbery phase, the graft co-
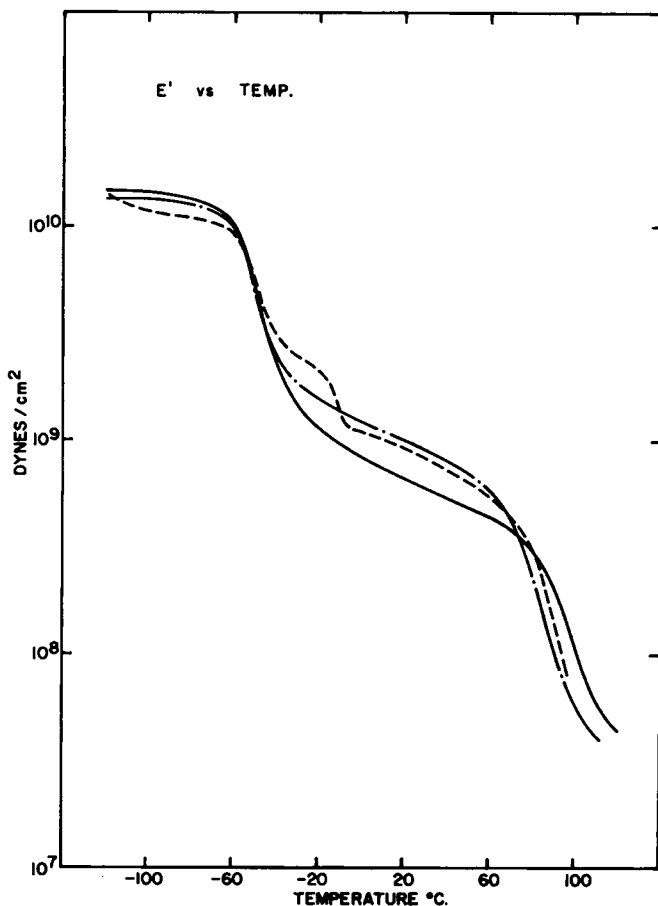
Fig. 5. Temperature dependence of dynamic storage modulus E' for the isolated EPDM/PVC graft copolymer containing 0% ($--$), 5% ($---$), and 10% ($-\cdot-$) DOP.

TABLE I
Effect of DOP on T_g of PVC and EPDM/PVC Copolymer

| % DOP (based on PVC weight fraction) | T_g of PVC, °C | | | |
| | Homopolymer | | Copolymer EPDM/PVC | |
	E''_{max}	DSC	E''_{max}	DSC
0	88	86	88	87.5
5	78	71	82	81.0
10	64	58	78	74.0

polymer functions as an impact resin within the temperature range between E'' maxima. The isolated graft copolymer is used as an emulsifier to stabilize a rubber dispersion in PVC. The identification of discrete domains suggests that the copolymer can disperse the rubber and couple the rubber and glass phases. The graft copolymer, composed of approximately equal weights of rubber and PVC, is utilized in this study as a model for an impact system.

The effect of including 40% of a reinforced filler (carbon black) and white pigment (titanium dioxide) upon the storage and loss moduli is shown in Figures
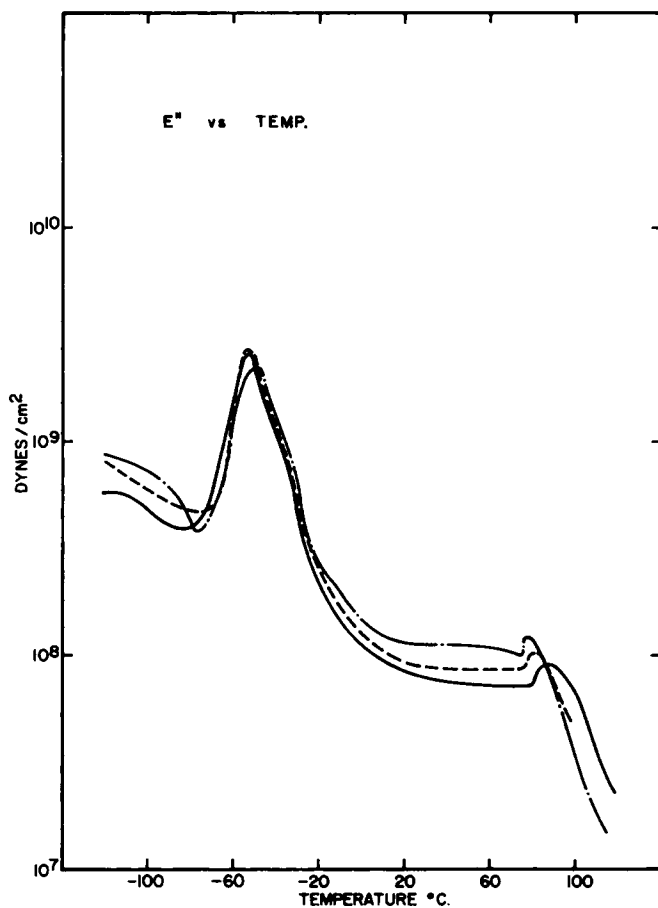
Fig. 6. Temperature dependence of dynamic loss modulus E'' for the isolated EPDM/PVC Graft Copolymer containing 0% (– –), 5% (- - -), and 10% (–·–) DOP.

1 and 2, respectively. It can be seen that carbon black raises the E' from -80 to 120°C. There is however hardly any significant reinforcing effect imparted by the titanium dioxide. The glass transition temperature of the rubber and PVC phases in the graft copolymer is however not shifted, indicative of the absence of the interaction of the additives with the two phases.

The effect of incorporating 20% Sunflex oil upon the storage modulus E' of the isolated graft copolymer is evident in Figure 3. At all temperatures above $-80°C$, the storage modulus E' of the graft copolymer is reduced by the addition of 20% Sunflex oil. This is attributed to plasticizing the rubbery EPDM phase by the additive which reduces the overall stiffness of the backbone. The temperature of the E''_{max} corresponding to the T_g of the EPDM phase is lowered from -53 to $-59°C$ by Sunflex 110 (Fig. 4). The glass transition of the PVC phase is however unaffected. Between 0 and 90°C, the reduction in storage modulus E' exceeds that in loss modulus E''. However, both moduli decrease because polymer chain deformation is facilitated by the oil.

The storage modulus E' of the graft copolymer is changed in a complex way by DOP inclusion (Fig. 5). The reduction in elastic modulus in the vicinity of
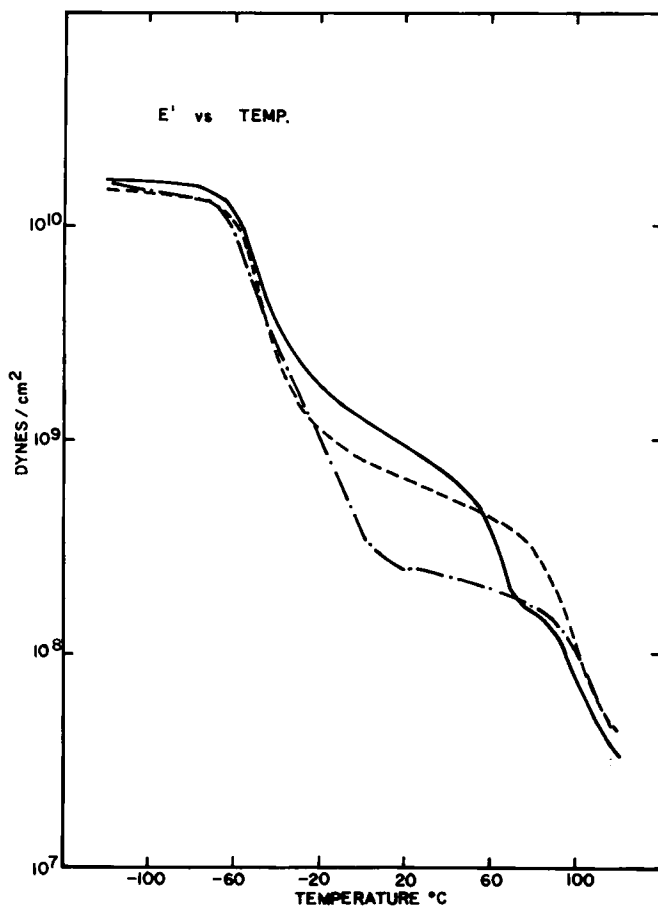
Fig. 7. Temperature dependence of dynamic storage modulus E' for the isolated EPDM/PVC graft copolymer: (- - -) control; (- · -) sample containing 20% n-hexadecane; (——) 20% n-hexatriacontane.

100°C is due to the decrease in T_g of the PVC phase. Between −20 and 70°C, the storage modulus of the graft copolymer is increased by the addition of DOP. The increase in modulus can be described by the "antiplasticization" phenomenon which is a consequence of an increase in molecular interaction (cohesive energy density) produced by the addition of small quantities of DOP. Dipolar interaction between DOP molecules and PVC segments restrains motion of the PVC chain.[12] At very low temperatures, the elastic modulus is about the same in control and 10% DOP samples.

The dependence of the loss modulus E'' on temperature (Fig. 6) also indicates a DOP induced reduction in T_g for the PVC phase and "antiplasticization" between −20 and 70°C. In the region of the glass transition of the rubber, the loss modulus is essentially unaffected by DOP, which is apparently excluded from the rubber phase. Incorporation of DOP into PVC effectively consumes the plasticizer, and it is absent from the rubber phase. This is reflected by the reduction in the temperature of the E'' maximum associated with the PVC phase. As expected, DOP internally lubricates the PVC molecules facilitating the onset of large-scale segmental motion producing the glass-to-rubber transition.
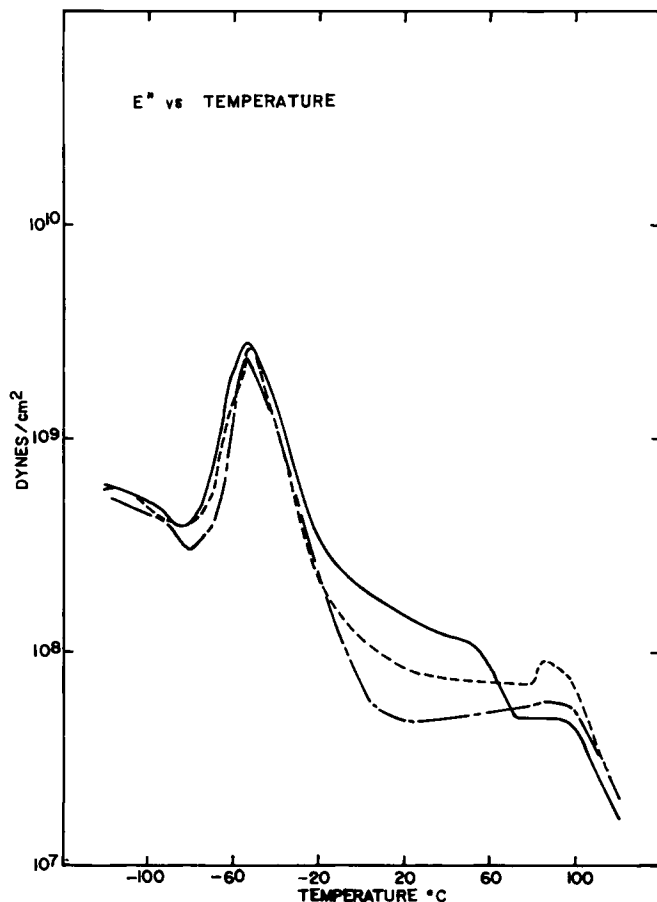
Fig. 8. Temperature dependence of dynamic loss modulus E'' for the isolated EPDM/PVC graft copolymer: (- - -) control; (-·-) sample containing 20% n-hexadecane; (——) 20% n-hexatriacontane.

The effect of including 20% of two hydrocarbons, n-hexatriacontane and n-hexadecane, upon the E' and E'' is shown in Figures 7 and 8, respectively. The lower molecular weight n-hexadecane does not affect the E' of the graft copolymer at temperatures below $-20°C$. However, above $-20°C$, the onset of softening and eventually the melting of this hydrocarbon lowers dramatically the modulus of the copolymer (Fig. 7). The glass transition temperature of the rubber phase is depressed slightly ($\sim4°C$), but the T_g of the PVC phase is hardly affected because of incompatibility (Fig. 8). Slight reinforcement is imparted by the higher molecular weight n-hexatriacontane on the copolymer at temperatures up to about 55°C, and this is reflected by the increase in E' in Figure 7. Above 60°C, the gradual melting of the hydrocarbon exhibits similar softening effect on the copolymer as described in the case of n-hexadecane. Again, slight depression in T_g of the rubber phase is observed but there is hardly any shift in the glass transition temperature of the PVC phase. Also, an additional shoulder assignable to the melting of the n-hexatriacontane is observed at $\sim55°C$. The absence of such a corresponding shoulder in the case of n-hexadecane is due to the overshadowing of the T_g peak of the rubber phase.

Comparing the glass transition temperatures obtained by DSC (midpoint of endotherm) and Vibron (E''_{max}), the latter always gives a higher value due most probably to the higher frequency (110 Hz) of the measurement. The lower depression in T_g by the inclusion of DOP in the graft copolymer compared with that in the PVC homopolymer suggests incomplete localization of the DOP in the PVC phase of the copolymer and reduced mobility of the PVC chains in the presence of the rubber.

CONCLUSIONS

A graft copolymer of EPDM and PVC forms discrete rubber and PVC phases. Carbon black and titanium dioxide act as inert filler, while the effect of including straight chain hydrocarbons on the dynamic mechanical properties of the graft copolymer is strongly dependent upon the melting point of the hydrocarbons. Sunflex 110 plasticizes the rubber phase of the graft copolymer, while DOP plasticizes the PVC phase and reduces T_g. At lower temperatures, however, the elastic modulus is increased by an "antiplasticization" effect. The local environment of PVC chains in the graft copolymer is modified by the presence of the rubber and PVC chains are less mobile.

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