Miscibility of chlorinated polymers with epoxidized poly(hydrocarbons): 1. Epoxidized natural rubber/poly(vinyl chloride) blends

Antonis G. Margaritis and Nikos K. Kalfoglou*
Department of Chemistry, University of Patras, 26110 Patra, Greece
(Received 23 May 1986; revised 22 July 1986)

The compatibility of poly(vinyl chloride) (PVC) with epoxidized natural rubber containing 25 and 50 mol% oxirane groups (ENR 25 and ENR 50) was studied in the complete composition range. The techniques used were phase-contrast microscopy, dynamic mechanical analysis (d.m.a.), differential scanning calorimetry (d.s.c.) and tensile testing. The results obtained indicate that ENR 50 is miscible at the segmental level throughout the composition range, while ENR 25 is only partially so. Also the d.m.a. technique is more sensitive in distinguishing segment–segment interactions in the blends than is d.s.c. Of practical consequence is the realization that the introduction of oxirane groups gives a stiffer polymeric plasticizer compared to other macromolecules plasticizing PVC with pendant active groups. This is mainly reflected in the tensile behaviour of the two sets of blends.

INTRODUCTION

Extensive experimental work on the compatibility of polymer blends supports the view[1,2] that for miscibility to take place a negative or near-zero enthalpy of mixing is required. In most cases this is ensured by the interplay of such intermolecular forces as, for example, donor–acceptor[3], dipole–dipole[4], ion–dipole[5]. Thus it has been proposed that the existence of an acidic hydrogen in poly(vinyl chloride) (PVC) is responsible for its miscibility with polyesters[6] and poly(ε-caprolactone)[7].

In this paper the compatibility behaviour of PVC with epoxidized natural rubber (ENR) is examined. ENR forms a new class of modified elastomers[8,9] with special properties, e.g. increased oil resistance and wet traction, decreased air permeability and the ability to be highly reinforced by silica fillers without coupling agents. Various considerations led to this choice. It is well known that epoxidized oils (mainly esters) are used as PVC plasticizers[10-12] and certain advantages (less thermal oxidation and better light stability) were reported for these particular systems. It is also known[13] that ethers, especially cyclic ethers (e.g. tetrahydrofuran), have strong solvating power for PVC and other chlorinated hydrocarbons. Though the nature of this interaction between these ethers and the halogenated compounds has not been elucidated, it most probably involves the chlorine atom. One could also consider the oxirane group as a proton acceptor while polar forces can also be important. Therefore, it was of interest to examine the compatibility of ENR with PVC and the effect of changing the degree of epoxidation on its compatibility. Aside from theoretical considerations related to polymer–

polymer miscibility, PVC modification is of special technical importance. In this context its compatibility with polymer is gaining acceptance since polymeric plasticizers, though difficult to incorporate, have definite advantages (no migration, low volatility and extractability) as compared to low molecular weight plasticizers[10,14]. Also since epoxidation is a relatively straightforward polymer modification reaction, epoxidized polymers may form a versatile new class of polar polymeric plasticizers.

Blends were studied in the complete composition range. The techniques used to determine the degree of compatibility were phase-contrast microscopy and dynamic mechanical analysis (d.m.a.) supplemented by differential scanning calorimetry (d.s.c.). Tensile testing was also applied to examine ultimate properties.

EXPERIMENTAL

PVC used in this study was an unplasticized commercial product. G.p.c. measurements in tetrahydrofuran gave $\bar{M}_n = 27\,000\,\mathrm{g\,mol^{-1}}$ and $\bar{M}_w/\bar{M}_n = 1.9$. Epoxidized natural rubber used had an epoxidation of 50 mol% (ENR 50) and 25 mol% (ENR 25). It was reported[15] that epoxidation proceeds in a random manner and that the cis configuration is maintained. ENR was donated by the Malaysian Rubber Producers' Research Association Laboratory, Hertford, UK.

Blends were prepared by using a common solvent, butanone-2, and heating the solution. Considerable difficulty was encountered in bringing ENR into solution. A PVC stabilizer (dibutyltin dilaurate, 4 wt% calculated on PVC) was added to the blend solution and subsequently solvent was removed in a rotary

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* Author to whom correspondence should be addressed.

evaporator. This was followed by drying to constant weight at 60°C in a vacuum oven. Blends were compression moulded into films at 150–190°C (depending on composition) and ~15 MPa and quenched at 0°C. For the microscopic examination, films were deposited on slides from blend solutions.

The following compositions were studied using ENR 50: 0/100P, 5/95P, 10/90P, 15/85P, 20/80P, 25/75P, 50/50P, 75/25P, 90/10P and 100/0P, where the first and second numerals denote the percentage by weight of the ENR and PVC, respectively. Using the ENR 25, compositions studied were: 10/90P, 25/75P and 100/0P.

Thin films were examined under a phase-contrast microscope (Orthoplan Leitz) with oil immersion ($n_c^{23} = 1.5180$) in bright field.

D.s.c. measurements were carried out in a nitrogen atmosphere using a DuPont 910 calorimeter system coupled with a 990 programmer recorder. Calibration was made with indium standard. Sample weight was 15 mg. Initially samples were heated to 150°C at 20°C min^{-1}, held for 30 s, quenched within ~3 min to −100°C and heated at 10°C min^{-1} to 130°C to determine T_g.

Dynamic mechanical data, loss tangent tan δ and complex modulus $|E^*|$ were obtained between −100 and 110°C at 110 Hz, using a direct-reading viscoelastometer (Rheovibron model DDV II-C, Toyo-Baldwin). A slow stream of precooled argon reduced moisture content in the measuring chamber. The correction due to clamp extension was applied at all temperatures. Specimen dimensions were $2.8 \times 0.25 \times 0.03$ cm^3.

Tensile tests were performed according to ASTM D882 at room temperature (~17°C), using a J.J. Tensile Tester type T5001 and film strips with dimensions $6.0 \times 1.20 \times 0.05$ cm^3.

RESULTS

Morphology

Phase-contrast micrographs of representative compositions are given in *Figure 1*. No gross phase discontinuity is evident for the two sets of blends. Given the refractive index value of PVC reported to be $n = 1.539$ and of ENR 50 calculated[16] to be $n = 1.507$ at positive phase contrast, the dark areas should represent the chlorine-containing component. A qualitative difference is discernible between blends containing ENR 50 and ENR 25, the latter exhibiting a finely dispersed PVC phase.

Dynamic mechanical properties

The results are summarized in *Figures 2* and *3* and in *Table 1* where d.s.c. results have also been included. Both the PVC α and β relaxations are in agreement with literature values[17].

For the pure ENR component our T_g data using both techniques show a shift to higher temperatures compared to literature values[9,15]. This difference may be explained partly by the higher frequency used in our work. It is also possible[15] that during film preparation some epoxide rings open and this may give structures with an increased T_g value. This difference in T_g value for ENR is of no consequence since in this type of work comparative values are of interest.

Inspection of the dynamic moduli spectra in *Figure 2*

shows the plasticizing action of ENR 50. The spectra indicate also that blends are 'divided' into two groups: those with less and those with more than 50 wt% ENR. This is also reflected on the tan δ_{max} vs. composition behaviour (see *Table 1*). Associated with this is an irregularly stiffer 90/10P blend compared to the 75/25P composition. Modulus data do not suggest antiplasticization[18]; however, ultimate tensile properties are more revealing (see below). The loss moduli spectra are typical of a miscible system and there is only a moderate broadening of the main T_g relaxation. This suggests that the blends are homogeneous.

The broad PVC β relaxation at *ca.* −40°C is suppressed. This is of practical consequence since it was reported to be associated with stress-activated processes[19]. The tan δ_{max} values are systematically higher than E''_{max} values (see *Table 1*) and this is expected whenever structural factors (crystallinity, polarity) affect the dynamic modulus. The polarity is the cause here.

Figure 3 gives the thermomechanical spectra for the ENR 25/PVC blends at low rubber values. The results indicate very limited miscibility, the two main relaxations persisting but shifting towards each other. Increasing the rubbery component increases the width of the spectrum (incomplete miscibility). Further addition of ENR 25 would not improve miscibility since both the E' and the E''_{max} do not change when ENR 25 is increased from the 10 wt% to the 25 wt% level.

Tensile properties

Stress–strain properties reported as nominal stress vs. elongation are given in *Figure 4*. At small ENR 50 contents, stiffness does not drop and ultimate strength is reduced. This is attributed to segment–segment interactions which effectively crosslink the solid. Increased flexibility is apparent above ~50/50 composition, a not unusual ratio for polymer-plasticized systems[14].

DISCUSSION

The morphology examination is in essential agreement with the d.m.a. and d.s.c. results, indicating miscibility and limited miscibility for the ENR 50/PVC and ENR 25/PVC blends, respectively. Phenomenologically this can be attributed to the solubility parameter δ increase of the natural rubber caused by the oxirane groups, which at the same time introduce the element of complementary dissimilarity[20] to the non-polar component. Use of Hoy's data[21] gives an increase in δ of 1 compared to pure NR. A slightly higher estimate is obtained using Schneier's relationship[22] and assuming ENR to be a copolymer consisting of isoprene and epoxidized isoprene comonomers. The density value for ENR 50 was calculated[23] to be 1.06 g cm^{-3}. As to the molecular origin of miscibility, both components have the possibility of polar–polar and/or donor–acceptor interactions among the acidic α hydrogens of PVC and the 'exposed' oxirane group which imparts such a high solvating power to analogous small molecule systems[13]. It is probable that both types of forces are active depending on blend constituents. Recently, we observed[24] miscibility in chlorinated polypropylene (PP)/ENR 50 blends in the complete composition range. In this case the amount of α hydrogen available is greatly
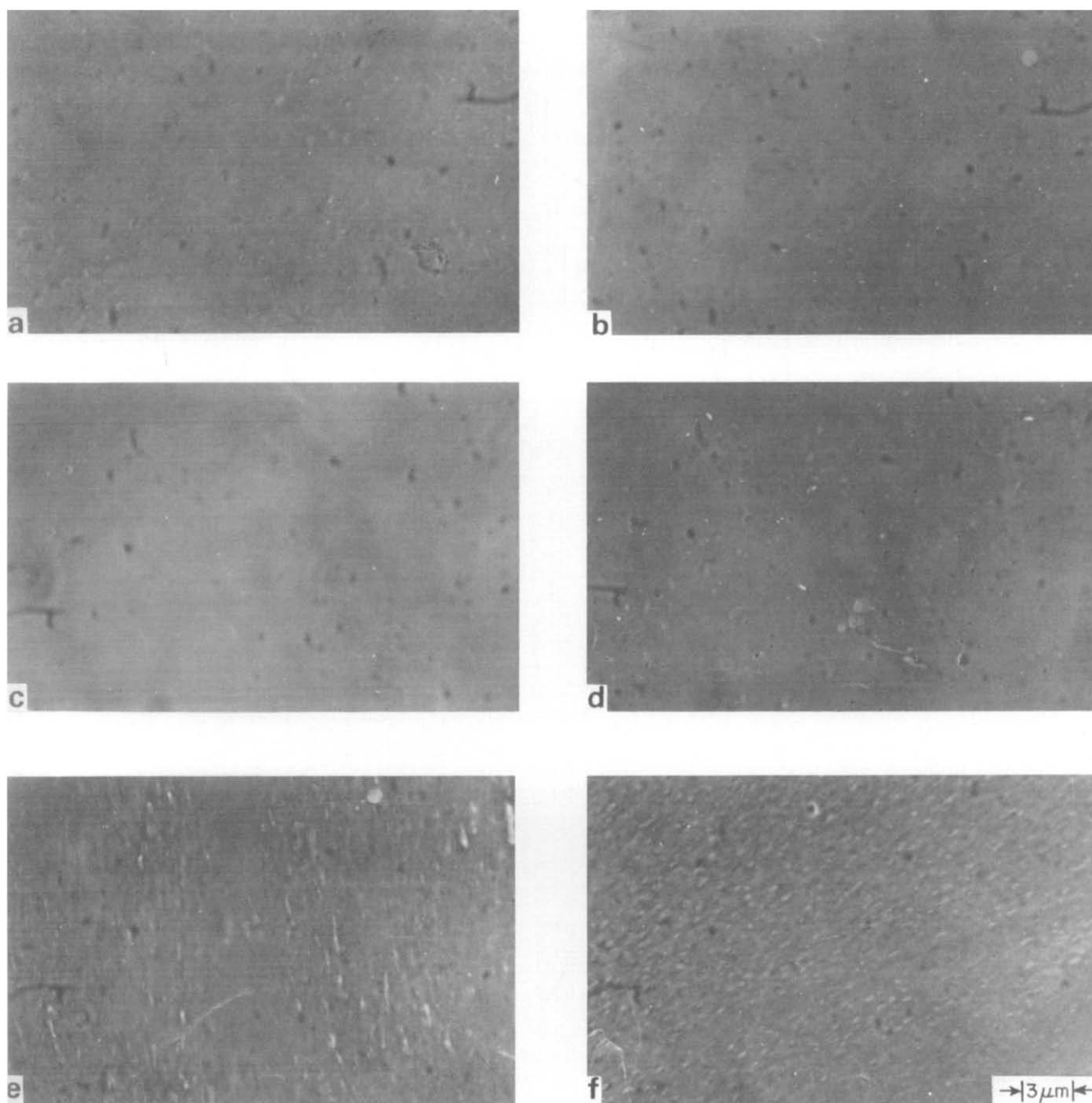
Figure 1 Phase-contrast micrographs of ENR 50 blends: (a) 5/95P; (b) 10/90P; (c) 25/75P; (d) 50/50P. Blends with ENR 25: (e) 10/90P; (f) 25/75P

diminished because of preferred chlorine substitution at the α position of PP. In this connection the particular configuration of the cyclic ether structure is of importance since we have found[24] very limited miscibility between PVC and linear poly(alkylene oxides).

The variation of T_{gb} with blend composition for the ENR 50/PVC system is of interest (see *Figure 5*). T_{gb} values determined by the d.s.c. technique (except at the rubber-rich extreme) give the usual functional dependence on composition; concave upwards towards the weight-average line. Various equations based on volume or entropy additivity of mixtures have been proposed to explain it. Two commonly used expressions are the Gordon–Taylor[25] and the Couchman[26] equations

written in the same order below:

$$T_{gb} = T_{g1} + k\frac{W_2}{W_1}(T_{g2} - T_{g1}) \tag{1}$$

$$T_{gb} \simeq (\Phi_1 \Delta\alpha_1 T_{g1} + \Phi_2 \Delta\alpha_2 T_{g2})/(\Phi_1 \Delta\alpha_1 + \Phi_2 \Delta\alpha_2) \tag{2}$$

where indices b, 1 and 2 refer to the blend, the rubbery and PVC phase, respectively, W_i and Φ_i are the weight and volume fractions of component i, and $k = \Delta\alpha_2/\Delta\alpha_1$ is the ratio of thermal expansion coefficient differences in the rubbery and glassy states of the two constituents. Recently we have applied these and other relations to
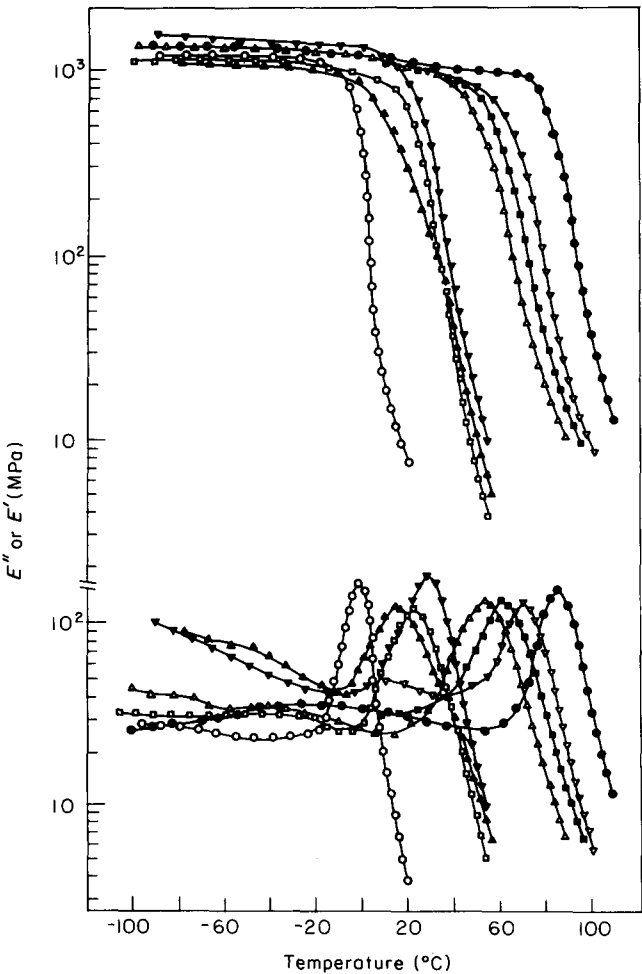
Figure 2 Thermomechanical spectra of ENR 50/PVC blends: (●) 0/100P; (▽) 5/95P; (■) 10/90P; (△) 25/75P; (▼) 50/50P; (□) 75/25P; (▲) 90/10P; (○) 100/0P
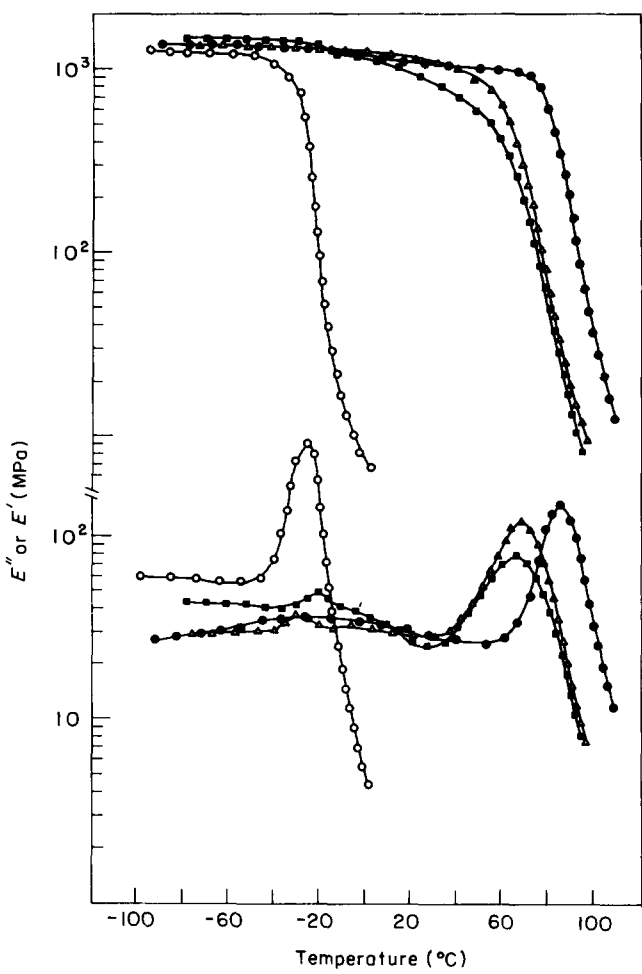

Figure 3 Thermomechanical spectra of ENR 25/PVC blends: (●) 0/100P; (△) 10/90P; (■) 25/75P; (○) 100/0P

Table 1 Glass transitions of blends (°C)

ENR 50/PVC	E''_{max}	tan δ_{max}	d.s.c.
0/100P	84(α)	98(α)	71
5/95P	70	86	45
10/90P	65	84	33
25/75P	54	75	19
50/50P	28	47	7
75/25P	22	49	−7
90/10P	14	−^{a}	−8
100/0P	−2(β)	7(β)	−15

ENR 25/PVC	α	β	α	β	α	β
0/100P	84	–	98		71	
10/90P	68	−26	85	−26	44	
25/75P	66	−20	89	−18	44	10
100/0P	–	−26		−17		−40

^{a} No maximum detected

miscible blends of PVC and other chlorinated polymers with an acrylic rubber[27,28].

In the same figure, the T_{gb} determined by the d.m.a. technique shows an S-shaped dependence on composition. Such a dependence had been observed by other workers[29] in miscible blends where the existence of hydrogen bonding was independently established. It was proposed that this type of dependence can be represented
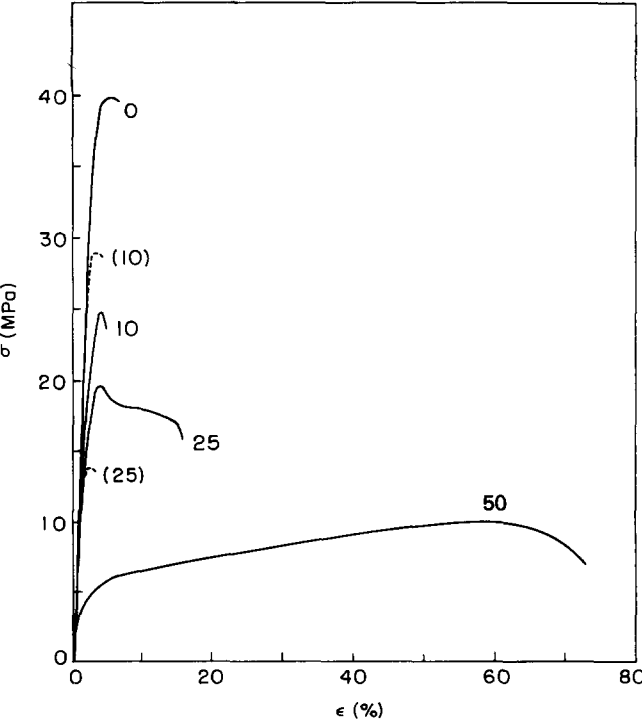

Figure 4 Stress–strain properties of blends. Numbers next to curves indicate ENR 50 percentage. The broken curves are for ENR 25 blends
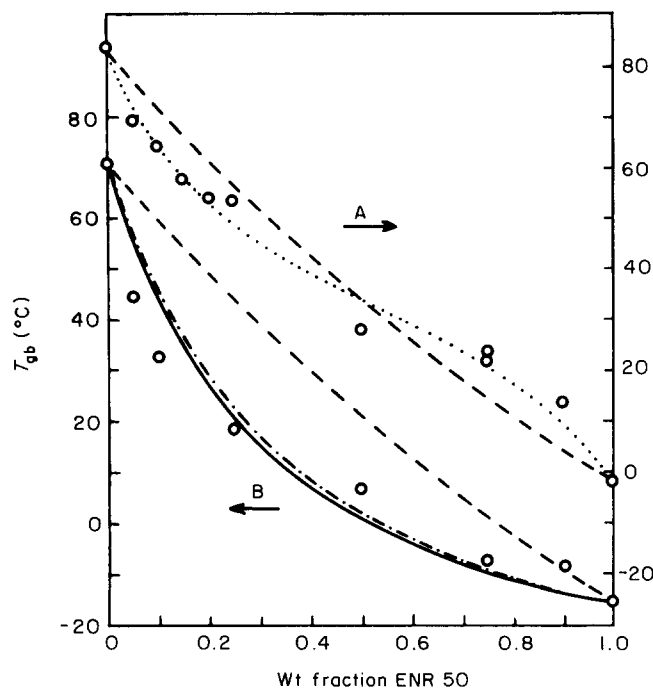
Figure 5 T_{gb} dependence on epoxidized rubber weight fraction (curves A, d.m.a. results; curves B, d.s.c. results): (O) experimental points; (———) Fox equation; (—·—·—) Gordon–Taylor equation; (————) Couchman equation; (· · · ·) Kwei equation. Additional experimental points are reported that are not included in *Table 1*

by the relationship:

$$T_{gb} = (W_1 T_{g1} + k W_2 T_{g2})/(W_1 + k W_2) + q W_1 W_2 \qquad (3)$$

where the first term is the usual expression for polymeric mixtures[25,26] and the second quadratic term is proportional to the number of specific interactions and gives the positive deviation (concave downwards) from the weight-average line. The quantity q has been cited[29] as a measure of the efficacy of specific interactions. In past work[30] a value $k \geqslant 0.2$ and a Cl content $\geqslant 30$ wt% was used as a criterion of miscibility of various polyesters with chlorinated polymers. In this study, using the d.s.c. results, $k = 0.25$ and 0.35 from equations (1) and (2), respectively. A suitable treatment of d.m.a. data using equation (3) gave for the k and q parameters the values of 0.25 and 80, respectively. Referring to *Figure 5*, at high ENR contents increased segment–segment interactions to give a positive deviation. No estimate of the effect of oxirane concentration on the degree of bonding can, however, be made since it was reported[15] that ENR itself may also be hydrogen bonded. As to the reason why d.s.c. does not indicate so clearly the S-shaped dependence of T_{gb} on composition, it is suggested that d.m.a. is more sensitive to motions of chain segments. In a previous paper[28] we tested with some success an empirical equation predicting blend modulus E_b in a miscible blend. It was assumed that a parallel connectivity allowing for maximum reinforcement is applicable because segment–segment interactions can in principle align chains in parallel. The relationship has the form:

$$E_b = E_1 \Phi_1 + E_{2,\text{eff}} \Phi_2 \qquad (4)$$

where the effective modulus of the stiffer phase 2 (PVC) is modified by plasticization by ENR and is related to the

pure PVC value by:

$$E_{2,\text{eff}} = E_2 [1 - (T_{g2} - T_{gb})(T_{g2} - T_{g1})] \qquad (5)$$

It was found that agreement with the experimental results was best (see *Figure 6*) when pure component data were obtained by extrapolation of blend data (at each temperature), to $\Phi(\text{ENR }50) \to 0$ for E_{PVC} and to $\Phi(\text{ENR }50) \to 1.0$ for $E_{\text{ENR }50}$. The test indicates that, once the pure component values are corrected to take into account their modified mechanical behaviour in the blend, the parallel model is adequate in most cases. Another possibility is the interpenetrating model[31] given by the relationship:

$$\log E_b = \Phi_1 \log E_1 + \Phi_2 \log E_2 \qquad (6)$$

also tested in *Figure 6*. No essential improvement is seen when tested in the complete composition and temperature range.

With regard to tensile behaviour, though the tests were not optimized with respect to recipe formulation (use of additives etc.), they indicate that ENR has a plasticizing
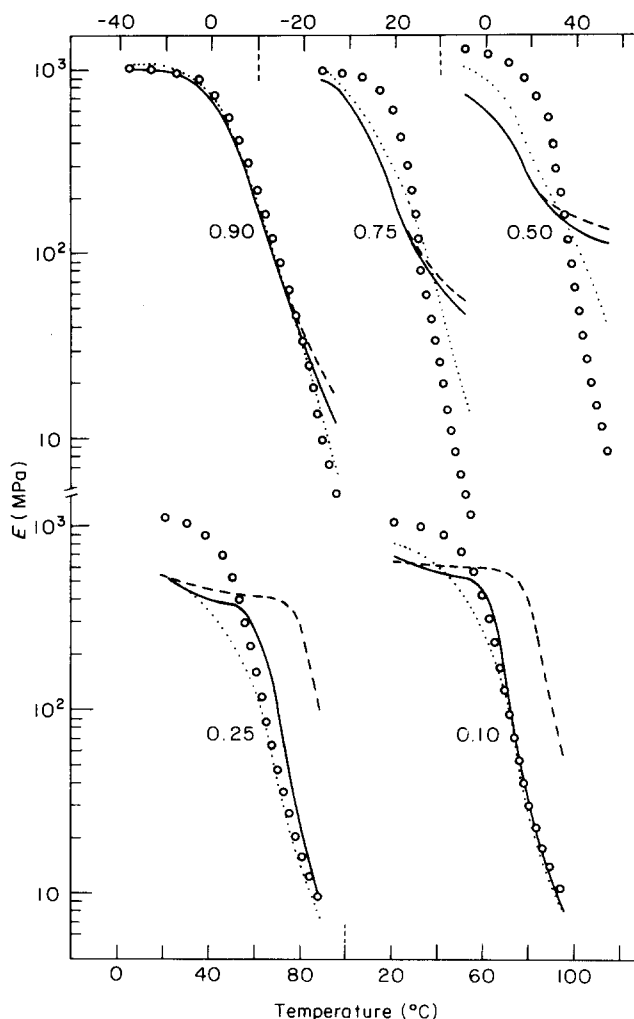

Figure 6 Comparison of experimental and calculated E (blend) values: (O) experimental values; (———) equation (4) using bulk properties of pure components; (————) equation (4) and (· · · ·) equation (6) using pure component data obtained by extrapolation (see text). Numbers next to curves indicate rubber weight fraction in ENR 50/PVC blends. Upper temperaure scale refers to blends with weight fraction of ENR $\geqslant 0.50$

action. A recent report by Gelling[32] described improved tensile properties of polyester-reinforced PVC/ENR laminated composites and of blends of ENR with other rubbers. These results are a consequence of mutual miscibility at the interface ensuring strong bonding in these laminated products.

It is of interest to contrast the qualitative difference in tensile behaviour between ENR 50/PVC and of an acrylic rubber/PVC blend shown also[27] to be miscible. Both these hydrocarbon rubbers contain groups interacting with PVC. However, as shown below,
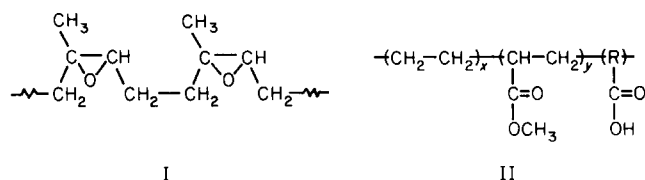
in I the oxirane groups form part of the main chain of the 'polymeric plasticizer' while in polymer II the ester group is a pendant interacting unit. This allows a less tight intertwining of chains in blends with II and explains the higher plasticizing efficiency of the acrylic rubber compared to ENR.

To conclude, the oxirane group when introduced into a macromolecule in substantial amounts can promote its miscibility with other 'complementary dissimilar' polymers.

Work in progress aims at optimizing the amount of oxirane content and the choice of the parent macromolecule so as to increase the polymeric plasticizer's efficiency.

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