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Modulus Reinforcement in Elastomer Composites. II. Polymeric Fillers

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Synopsis

Blends were prepared with high-modulus "filler polymers," polystyrene, polyamide, and poly(methyl methacrylate) dispersed in a low modulus matrix of ethylene/vinyl acetate copolymer. The modified Kerner equation was applied to dynamic mechanical data obtained on these blends, which may be considered to be model systems for thermoplastic elastomer block polymers. The implication of the interaction parameter, B, in terms of the reinforcing capability of each polymer as well as its optimum volume fraction in the blend, is discussed.

INTRODUCTION

In the forefront of today's polymer technology is the developing discipline of polymer composites, multiple-component, multiple-phase materials whose combination of physical properties and processing flexibility render them of great commercial importance. These composites can be prepared by copolymerization, by simple blending, or by a combination of these two techniques to provide stabilized polymeric "alloys."

The enormous variety of polymers available leads to an almost infinite number of combinations for possible composites. To simplify this choice of components, certain restrictions must be imposed, most logically those which result in final composites which posess superior properties. The interaction between the two (or more) polymers very likely plays an extremely important role in the ultimate performance profile of a multiphase system. This interaction might be gauged from a simple solubility standpoint, for instance, by comparing solubility parameters obtained from viscosity or swelling measurements. This approach implies that polymers of similar polar and hydrogen bond character will lead to stable blends. While this is probably quite true, the desirable physical and rheological properties of composites are achieved when one phase is rigid, that is, exhibits a higher modulus, compared to the second phase; hence the chemical characteristics of the "filler" phase are usually significantly different from the

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"matrix" in order to maintain a rigidity/flexibility combination over a relatively broad-use temperature span. Thus, the need for a different sort of polymer/polymer interaction parameter becomes apparent, one that would apply to the region of temperature and/or frequency where one phase is of significantly higher modulus than the other.

In an accompanying contribution[1] it was demonstrated that the modulus reinforcement of elastomer by solid inorganic fillers (at 30°C) can be described by the Kerner equation[2] modified to include an interaction parameter B, which represents the relative increase in effective volume of the filler due to the presence of a tightly adhering "interphase." We report here the mechanical response over a wide temperature range of two-phase systems where both phases are polymeric materials. The extent to which the Kerner equation describes the observed response is examined and the significance of the interaction parameters is discussed.

EXPERIMENTAL

Materials

The matrix elastomer used was a commercial copolymer of ethylene and vinyl acetate, trade name Levapren 450 P, produced by Výskumný Ústav Káblov a Izolantov, Bratislava, ČSSR. The ethylene content was approximately 45% by weight, and M_n was 4.7×10^4.

The filler polymers were: (1) polystyrene (PS), trade name Vestyron N, $M_n = 180{,}000$; (2) polyamide (PA), product of Považské chemické závody n.p. Žilina; (3) poly(methyl methacrylate) (PMMA).

Preparation of Blends

Physical mixtures of matrix and filler polymers were accomplished using a plasticizer mill designed and constructed at the Polymer Institute of the Slovak Academy of Sciences, Bratislava, ČSSR. A mixture of shredded elastomer and finely powdered polymeric filler was blended in shear using a spiral-cut faced disc rotating at 300 rpm against a stationary face containing a spiral cut in the opposite direction. Pressure was applied and maintained by a threaded ring. Heat was applied up to 120°C, using an oil circulation system.

Powdered specimens of polystyrene and polyamide were prepared by flocculation from a 1% solution. Benzene solvent and methanol precipitant were used for the polstyrene, while formic acid solvent and water precipitant were used for the polyamide. Powdered PMMA was obtained using a solid commercial slab and abrading it with a high-speed grinding wheel.

Testing

Dynamic testing in tension was performed over the temperature range −50°C to 50°C on a Vibron Model DDV-II instrument, Toyo Measuring Instruments Co., Ltd., Tokyo, Japan. A driving frequency of 110 Hz was maintained throughout.

THEORETICAL

When polymers are blended together and the composite produced is tested under temperature and frequency conditions such that each is in the "rubbery" state, the dynamic moduli E' and E'' are often observed to obey the "rule of mixtures":

$$E_c(T) = \Sigma_i \varphi_i E_i(T)$$

where φ_i is the volume fraction of the ith component and E_i its modulus at temperature T. The definition of "rubbery" state may be simply that the poisson ratio ν is approximately 0.5. The situation is different, however, when one of the components is in the glassy state or is in a crystalline form. No longer are both phases characterized by $\nu = 0.5$. This difference in volume change upon extension gives rise to complex stress fields around the rigid inclusion, which in turn affect the composite modulus of elasticity. Kerner,[2] working from Goodier's[3] analysis of a single solid grain suspended in an extensible matrix, derived an equation describing the effect of rigid filler particles on the storage modulus E'. For elastomeric matrices, where $\nu = 0.5$, the Kerner equation can be written as

$$\frac{E'_c}{E'_0} = \frac{1.5\,\varphi_F(G_F/G_0 - 1) + 1.5 + (G_F/G_0)}{\varphi_F(1 - G_F/G_0) + 1.5 + (G_F/G_0)} \tag{1}$$

where G is the shear modulus (real component), φ_F is the filler volume fraction; and the subscript F refers to the (polymeric or inorganic) rigid filler, and 0 to the elastomeric matrix. Attempts to use this equation to describe the E'_c versus φ_F behavior of composites using both inorganic fillers[1] and polymeric fillers (this work) have proved unsuccessful. In earlier studies[4] of energy dissipation, E''_c versus φ_F, the concept of strain magnification due to the presence of inextensible filler was discussed in terms of the ratio of average local extension in the filled systems ϵ_c versus that in an unfilled sample ϵ_0. This ratio was described as

$$\langle \epsilon_c/\epsilon_0 \rangle = [1 - \varphi_F B]^{-1} \tag{2}$$

where B, the interaction parameter, represents the increase in volume of the filler particle because of an adherent interphase of immobilized matrix polymer. The thickness of the interphase in the solid state can apparently be quite large compared to what would be predicted from simple adsorption of polymer from solution[4,5] in some cases comparable to the original filler particle diameter. We have already demonstrated that when the φ_F term in the Kerner equation is changed to $\varphi_F B$, this modified equation adequately describes modulus reinforcement by inorganic fillers; hence we apply the same approach with polymer fillers, using experimental results to obtain the interaction parameter.

RESULTS AND DISCUSSION

In preparing the blended mixtures of EVAc and rigid polymers, volume ratios of elastomer matrix/filler of 9/1, 7/3, 5/5, 3/7, and 1/9 were attempted. None of the blends could be successfully prepared in the 3/7 or 1/9 ratios; brittle, crumbling mixtures were obtained. For the system EVAc/PS, only a maximum of 50% of PS could be incorporated. Results of dynamic testing in terms of storage modulus E' are shown in comparison with the unfilled elastomer in Figures 1, 2, and 3 for each of the samples prepared.

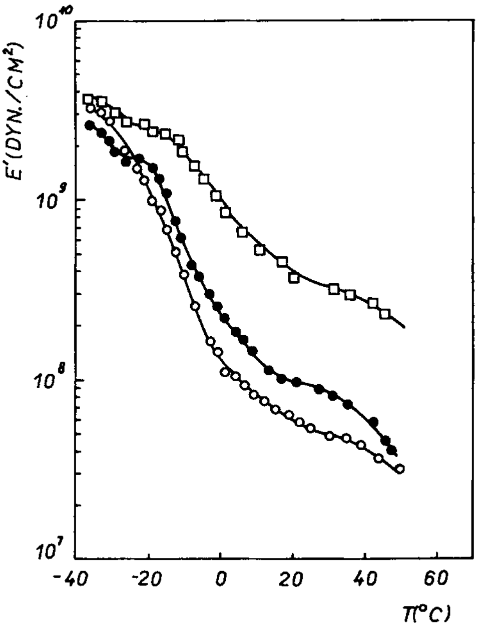

Fig. 1. Storage modulus E' vs. temperature. System: EVAc/PS volume ratios 7/3 (□), 9/1 (●), and pure EVAc (○).

From the ratios E'_c/E'_0, and the estmated ratios G_F/G_0 obtained from literature values[6,7] of G_F for the pure rigid polymers, the interaction parameter B was calculated as a function of temperature and volume fraction using eq. (1), modified and rearranged to

$$B = \left[\frac{(E'_c/E'_0)(1 + 1.5\, G_0/G_F) - 1.5\, G_0/G_F - 1}{(E'_c/E'_0)(1 - G_0/G_F) + 1.5 - 1.5\, G_0/G_F}\right] \Big/ \varphi_F. \qquad (3)$$

The results for a matrix/filler volume ratio of 7/3 are shown in Figure 4. The modified Kerner equation appears to accurately describe the observed response, as indicated by the constancy of B over a fairly broad temperature range. Values of B drop precipitously around −15°C, which is the glass transition temperature of the copolymer EVAc as measured by loss

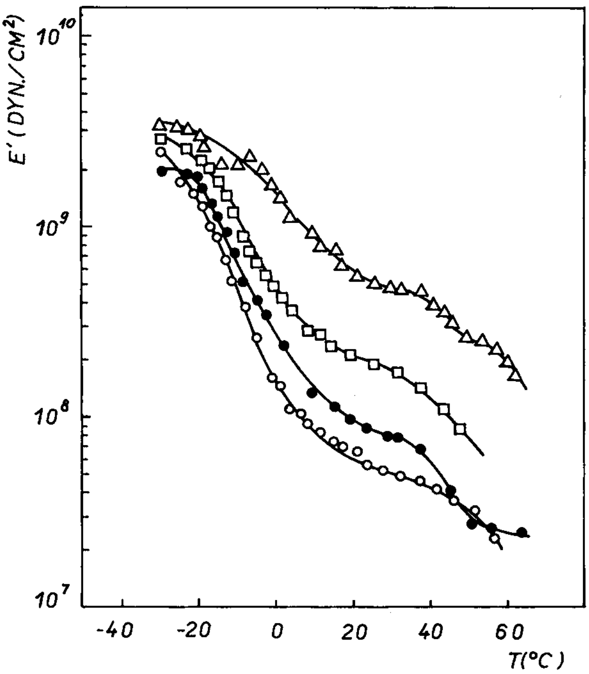

Fig. 2. Storage modulus E' vs. temperature. System: EVAc/PA volume ratios 5/5 (△), 7/3 (□), 9/1 (●), and pure EVAc (○).

tangent. Since eq. (1) is derived for $\nu = 0.5$, it cannot be expected to work in the glassy matrix region. The dropoff of B values at around +40°C may be interpreted as a "melting" of the interphase.

The interaction parameter B was found to be fairly insensitive to the concentration of the rigid phase, for example, 2.26 for EVAc/PS in the volume ratio 9/1 and 2.33 for 7/3. A comparison of the B values shows that for the matrix copolymer EVAc the effectiveness of these rigid polymers as modulus reinforcing fillers is in the order PS > PMMA > PA.

One of the outgrowths of the strain magnification theory is the concept of critical volume fraction, φ_c. This is the value of φ_F where the filler, including the immobilized interphase, can no longer be "wetted" by the matrix, or from eq. (2) where $\langle \epsilon_c/\epsilon_0 \rangle$ approaches infinity. Hence, φ_c is simply the reciprocal of B. Thus, the polystyrene as filler, with $B = 2.33$, the maximum concentration of filler is 0.43 volume fraction, whereas with the polyamide, $B = 1.64$, a φ_c of 61 vol-% is feasible. This explains why we were unable to form coherent mixtures with PS at the 5/5 volume ratio and highlights the principal practical benefit of the modified Kerner equation. An evaluation of the parameter B from blends can be useful in selecting the optimum concentration of rigid phase based on the critical volume concept.

It is not readily apparent what causes the filler polymers to "reinforce" EVAc in the order observed. As a possible clue, the effect of these filler

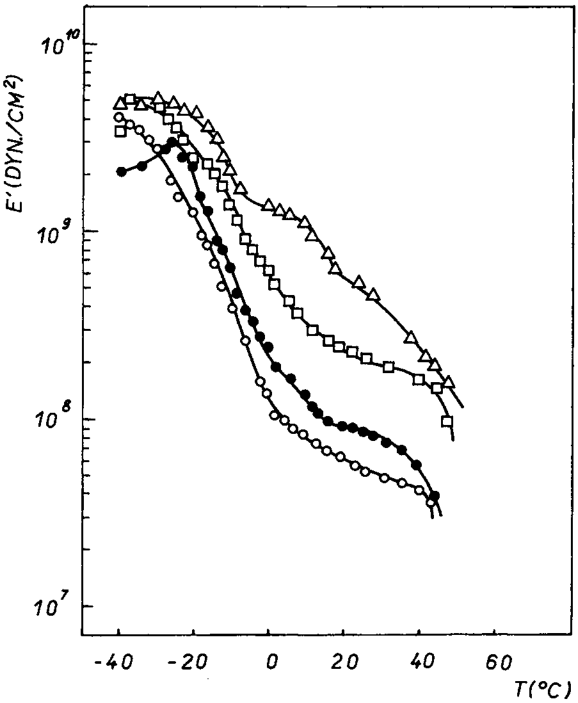

Fig. 3. Storage modulus E' vs. temperature. System: EVAc/PMMA volume ratios 5/5 (△), 7/3 (□), 9/1 (●), and pure EVAc (○).

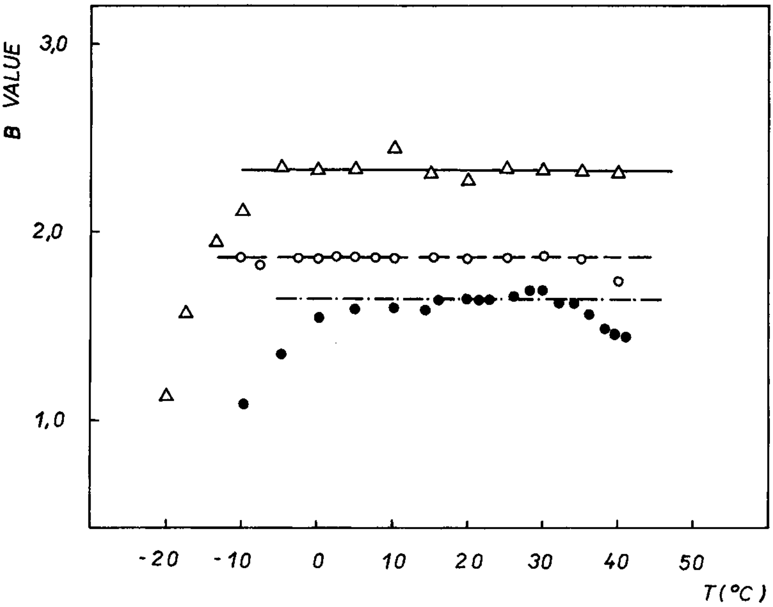

Fig. 4. Interaction parameter B vs. temperature. Systems: EVAc/PA (●), EVAc/PMMA (○), and EVAc/PS (△), all at volume ratios 7/3.

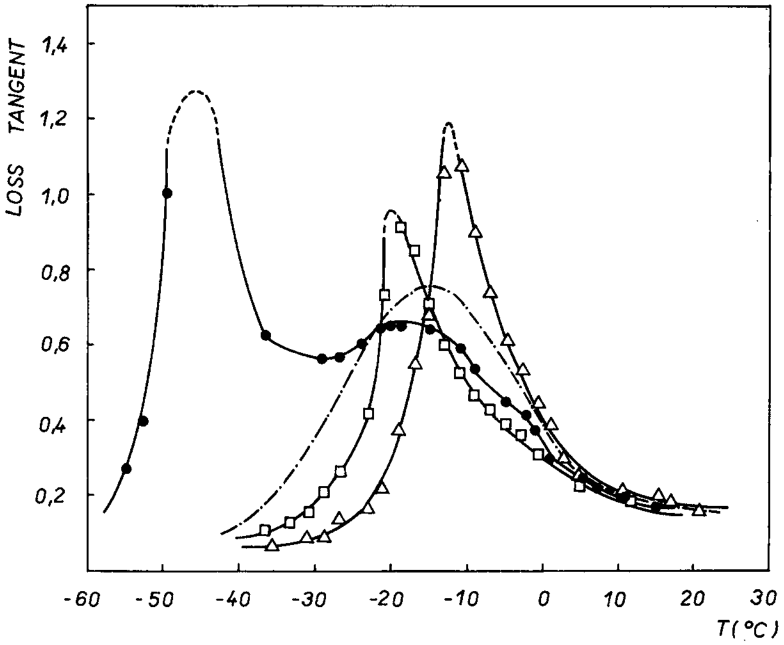

Fig. 5. Loss tangent δ vs. temperature for systems EVAc/PA (△), EVAc/PMMA (●), and EVAc/PS (□); pure EVAc shown on broken line, volume ratio of blends 7/3.

polymers on the glass transition of the copolymer was investigated. Data are presented in Figure 5. Interestingly, both the best (PS) and poorest (PA) polymers sharpen the dispersion peak while the PMMA blends exhibit two low temperature transitions. Inorganic fillers generally lower the loss tangent value and have little effect or the temperature position of the maximum. Thus, no correlation can be found between the B parameter and loss tangent data.

In order to assess the general applicability of the modified Kerner equation, we have applied it to other polymer-reinforced elastomer systems reported in the literature. First, the data of Kraus et al.[6] concerning the reinforcement of styrene–butadiene copolymers by styrene resin were studied. To convert their weight fraction data to volume ratios densities for PS of 1.05 and polybutadiene copolymer of 0.97 (at 40°C) were used. B estimates were made according to eq. (3), and also following the equation derived for energy dissipation[4]:

$$E''_c/E''_0 = [1 - \varphi_F B]^{-1}. \qquad (4)$$

Results are summarized in Table I.

As observed in the accompanying contribution,[1] application of eq. (4) results in B values which decrease as a function of concentration. An empirical form of eq. (4) with variable exponent in the $\varphi_F B$ term is found to better describe the observed response. However, eq. (3) provides a good valuation of B. The average of all four concentrations is B = 2.8, which

TABLE I
Data of Kraus[6] Arranged For Calculation of B Interaction Parameter at 40°C

	Styrene volume fraction[a]				
	0	0.109	0.223	0.223	0.439
E'_c, (dynes/cm^2) × 10^{-7}	3.0	6.5	24.0	20.0	340.0
E''_c, (dynes/cm^2) × 10^6	2.9	7.2	17.5	31.0	110.0
E'_c/E'_0	—	2.17	8.00	23.33	113.33
E''_c/E''_0	—	2.48	6.03	10.69	37.93
B (eq. (4))	—	5.47	3.74	2.81	2.22
B (eq. (3))	—	2.92	3.30	2.79	2.34

[a] Styrene polymer in polybutadiene/styrene copolymer.

would predict a φ_c of 0.352 and shows styrene, as would be expected, to highly reinforce the copolymer.

Finally, the modified Kerner equation is applied to the data of Marcinčin et al.[8] who used the same matrix elastomer as in our study but employed rigid poly(vinyl chloride) (PVC) as filler. Their data were collected on a torsion pendulum and represent the application of eq. (1) to shear data. A summary of results appears in Table II for the observed best-fit B value of 1.2. Thus, we may extend our original EVAc polymer interaction to PS > PMMA > PA > PVC.

A very interesting aspect of the data of Marcinčin is an apparent minimum in their curves of G'_c of the blended composites versus T occurring just prior to the T_g of the filler PVC phase. Such a minimum, or dip, was not observed by Kraus[6] and at first seems very difficult to explain. However, if we consider the effect of the change of the filler from the glassy state ($\nu \simeq 0.3$) to the rubbery state ($\nu \simeq 0.5$) on the behavior of

TABLE II
Data of Marcinčin: Comparison of Predicted and Observed Values of G_c for PVC in EVAc (B = 1.2)

Temp., °C	φ_F	G_c observed × 10^{-9}	G_c' predicted (eq. (1)) × 10^{-9}
	.8	5.0	5.5
0	.75	3.6	3.6
	.60	1.5	1.5
	.50	1.0	1.0
	.8	7.5	7.1
−20	.75	5.6	6.3
	.60	3.3	3.3
	.50	2.9	2.9
	.8	3.6	3.4
+30	.75	1.8	2.4
	.60	1.0	0.7
	.50	0.8	0.5

the blend, we observe that just at the region of T_g, the modulus change is quite small, although the first derivative dG/dT changes sharply, while the change in Poisson ratio is quite abrupt and essentially discontinuous. Above the T_g of the filler, the composite modulus should be predicted to a reasonable degree by the rule of mixtures, while just below T_g the modified Kerner equation would apply. Furthermore, once the rigid filler is in the rubbery state, the concept of an immobilized interphase is no longer viable, hence at the point of T_g, eq. (3) ceases to be valid and is replaced by an equation of the type

$$E'_c/E'_0 = \varphi_F[G_F/G_0 - 1] + 1. \tag{5}$$

Unless these two equations happen to coincide just at the T_g of the filler, there exists a discontinuity near the T_g which could give rise either to a "dip"

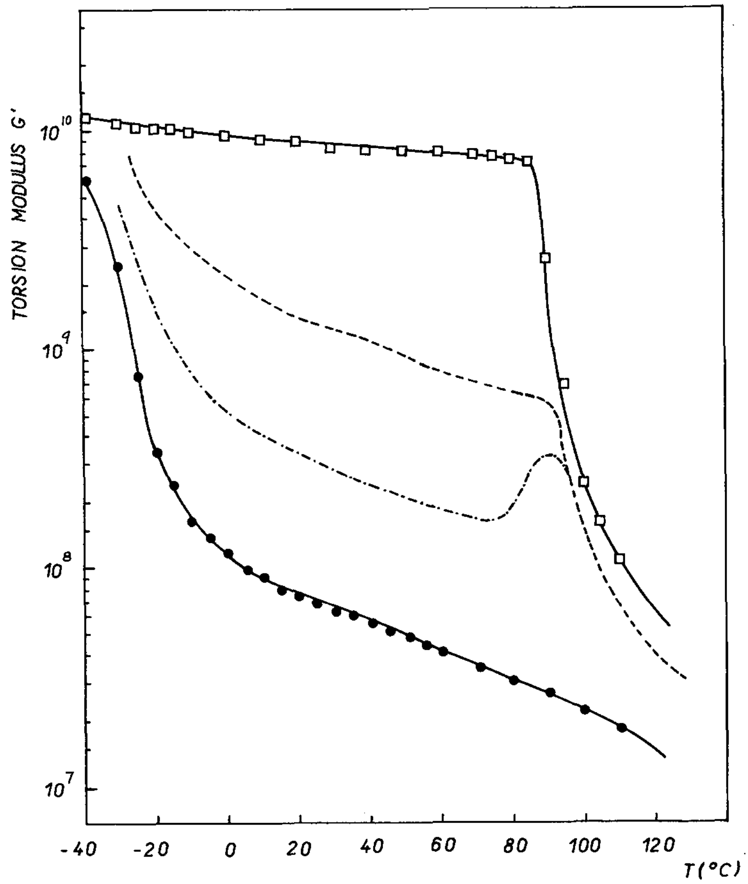

Fig. 6. Influence of B factor on torsion modulus of composites, employing eq. (3), in the region −40° to +80°C and eq. (4) in the region +95° to +125°C. Theoretical curves for $B = 1.2$ (—·—·—) and $B = 1.8$ (- - -) at $\varphi_F = 0.5$ and $G_F/G_0 = 20$. Data for PVC (□) and EVAc (●) are from ref. 8.

as observed by Marcinčin, or to a "stepped plateau." The factor which will determine the actual behavior is the interaction parameter B. We have calculated, for $\nu = 0.5$ and $G_F/G_0 = 20$, that for B values less than 1.5, the modified Kerner equation predicts E'_c/E'_0 less than eq. (5) at the point just just prior to the T_g of the filler polymer. This explains quite readily why such a dip was observed by Marcinčin working with PVC in EVAc with a B value of only 1.2. Theoretical curves based on the observed properties of filler and matrix are presented in Figure 6 for various values of B to illustrate this point.

In conclusion, we have found that a rigid polymer/elastomeric polymer interaction parameter B can be evaluated from modulus data using a modified Kerner equation, and that this parameter predicts reinforcement behavior from the T_g of the matrix to near the T_g of the filler. From it, one can estimate the critical volume fraction φ_F beyond which the reinforcement effect is below optimal effectiveness.

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