where v_s is the volume fraction of the solvent in the ternary system, given by

$$v_s = x_s n_s/(x_s n_s + x_c n_c + x_{\mathrm{Bh}} n_{\mathrm{h}})$$

Then, total polymer concentration at the critical point, C_c, is given by

$$C_c = 1 - (v_s)_{\mathrm{crit}} = (1 + 1/\sqrt{r})^2/(2\chi\psi_{\mathrm{A}}) \qquad (7)$$

Equation 7 may predict the compatibility of the A–B-type block copolymer with the B polymer in a solution of common solvent as a function of the ratio of the degrees of polymerization, r, the composition of the block copolymer, ψ_{A}, and the copolymer–homopolymer interaction parameter, χ.

Consequently, one may judge roughly whether the solubilization occurs or not, from the following condition.

$$2\chi\psi_{\mathrm{A}}C^* \gtrless (1 + 1/\sqrt{r})^2 \qquad (8)$$

These results may be applicable for the system involving multiblock copolymers, such as ABA, BAB, ABAB or $(\mathrm{AB})_i$, as well as the graft copolymers, so far as the following condition is held.

$$\Delta H_{\mathrm{M}} = z\Delta w_{\mathrm{AB}} v_{\mathrm{B}} \sum_i (x_{\mathrm{A}})_i \qquad (9)$$

Acknowledgments. The authors are deeply indebted to Dr. K. Kato and Mr. M. Nishimura, Central Research Laboratory, Toyo Rayon Co., Ltd., for kindly arranging for preparation of the electron micrographs, and to Professor M. Kurata, Institute for Chemical Research, Kyoto University, for his valuable comments and discussions. A part of this work was supported by scientific research grant from the Japan Synthetic Rubber Co., Ltd.

Dynamic Properties of a Model Reinforced Elastomer. Styrene–Butadiene Reinforced with Polystyrene

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Received October 16, 1969

ABSTRACT: The dynamic storage and loss moduli of SBR 1503 reinforced with 400-Å polystyrene particles were measured at 110 cps over a 200° temperature range. The effect of the polystyrene filler on the rubber was to raise the storage modulus dramatically in the rubbery zone, but only slightly in the glassy region of viscoelastic response. As a result the transition zone appeared broadened and shifted toward higher temperature. Corresponding changes were observed in the loss maximum with a shift of 4° at the highest filler content (46%) investigated. The height of the loss maximum was nearly unaffected. The loss tangent of the filled and unfilled polymers showed no systematic shift with temperature and the dilatometric glass transition was raised only 2° at the highest filler content. All the essential features of the dynamic behavior could be described in terms of the properties of the component polymers by the phenomenological equivalent mechanical model treatment of Takayanagi. It is concluded that the effects of the polystyrene filler, which resemble those of other fillers as well, need not be caused by restriction of segmental motion in the rubber resulting from elastomer–filler interactions.

In an earlier paper it was shown that the free volume of a carbon black reinforced polymer in the rubbery region of viscoelastic response is only slightly affected by the presence of the filler.[1] It appears, therefore, that the adsorption of polymer segments on the filler surface cannot cause a major loss in segmental mobility in the bulk of the rubber. Nuclear magnetic resonance measurements have confirmed this conclusion.[2] On the other hand, dynamic mechanical measurements usually reveal much larger filler effects. These are a substantial broadening of the transition region, an increase in the loss tangent in the rubbery zone, and an apparent shift of the relaxation spectrum toward longer times or, in experiments at fixed frequency, toward higher temperatures.[3,4]

A filler-reinforced rubber may be regarded as a two-phase blend of materials of widely different viscoelastic properties. The physical properties of such a composite must depend on the properties of the components and on the morphology of the blend regardless of possible interactions between the phases. Various expressions have been developed for calculating properties of composites from those of the components and all predict the intuitively obvious fact that a high modulus material will stiffen a low modulus material proportionally more than it will stiffen a material of moderately high modulus. This is always observed when the properties of a filler-loaded rubber are studied over a temperature range which includes the glass transition and is illustrated schematically in Figure 1. Here the modulus might typically be the dynamic storage modulus (at fixed frequency) and the filler carbon black or an inorganic pigment, whose properties change little over the temperature range of the experiment. It is clear that, as the result of the larger relative contributions of the filler at higher temperatures, the entire modulus curve for the filled rubber appears shifted to the right. Obviously, any analysis which fails to take

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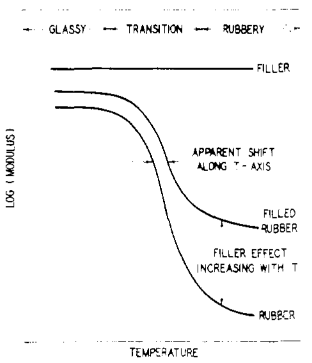

Figure 1. Schematic representation of the effect of a filler on the modulus of an elastomer.

into account the properties of the filler may result in the unwarranted conclusion that the relaxation spectrum of the *polymer* (not merely that of the *composite*) is broadened and shifted.

It would be interesting to test the composite idea on carbon black reinforced rubbers. Unfortunately, the viscoelastic properties of carbon black proper cannot be measured. However, glassy polymers of small particle size also reinforce rubber[5] and their bulk properties can easily be measured by the same techniques used to study the rubber. In this study we have investigated the dynamic behavior of polystyrene reinforced styrene–butadiene copolymer (SBR) with the objective of determining if the properties of the filled stocks can be described by some mixture rule, without invoking a change in the relaxation spectrum or the segmental mobility of the rubber phase.

Experimental Section

Materials. A polystyrene latex was prepared by emulsion polymerization at 5° in a Redox recipe. An electron microscope analysis of the latex gave D_n (number average particle diameter) = 390 Å, D_s (area average diameter) = 430 Å, and S (specific surface area per unit volume) = 140 m²/cc. By comparison, typical values for FEF carbon black are D_n = 410 Å, D_a = 510 Å, S = 118 m²/cc.

The polystyrene latex was masterbatched with commercial SBR 1503 latex and the mixed latices were coagulated with methanol. The crumb was washed thoroughly with alcohol, then water, and vacuum dried at 50°. Portions of each of the component latices were worked up in similar fashion. The polystyrene content of the blends was determined by the method of Kolthoff, Lee, and Carr[6] and agreed closely with the compositions calculated from the blending data (Table I). The molecular weight averages of the polystyrene filler, determined by gel permeation chromatography, were M_w = 660,000 and M_n = 110,000.

Vulcanization. To prevent the polystyrene particles from becoming fused during vulcanization, a special low-temperature cure recipe was employed: SBR 1503, 100; polystyrene filler, variable: zinc oxide, 5: sulfur, 2; zinc diethyldithiocarbamate, 2; dibutylxanthogen disulfide, 4; dibenzylamine, 4. Compounds were mixed on a warm mill (50°), sheeted off, and immediately cured for 18 hr at 70°. The resulting vulcanizates displayed typical properties of reinforced rubbers (Table II).

TABLE I

Wt % polystyrene	Sample number 1	2	3	4	5	6
As blended	0	11.8	23.3	34.6	45.6	100
Analytical		11.7	23.7	34.0	45.9	

TABLE II

	Vulcanizate number 1	2	3	4	5
Polystyrene, %	0	11.7	23.7	34.0	45.9
Stress at 200% elongation, kg/cm²	27	50	78	129	152
Tensile strength, kg/cm²	30	92	147	144	158
Elongation at break, %	235	350	370	240	220

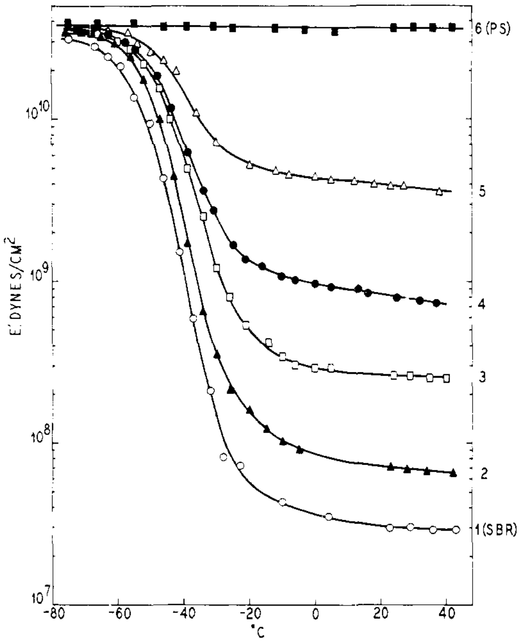

Figure 2. Storage moduli of polystyrene reinforced SBR 1503 (polystyrene contents: 2–11.7%, 3–23.7%, 4–34.0%, 5–45.9%).

Dynamic Measurements. All dynamic measurements were made at 110 cps on a Vibron direct reading viscoelastometer, Toyo Measuring Instruments Co., Ltd., Tokyo, Japan. This apparatus has been described in detail by Takayanagi and Yoshino.[7,8] The only significant modification made to the commercial unit was the installation of a nitrogen system to allow measurements to be made in an inert atmosphere. At the very small strains employed in the Vibron all samples were linearly viscoelastic.

Dilatometry. To complement the dynamic data, dilatometric determinations of T_g and of the glassy and rubbery coefficients of expansion were made. The technique was the same as described earlier,[1] except that ethanol was used as the displacement fluid.

Results

Figure 2 displays the storage moduli at 110 cps, as a function of temperature, for an interval covering the transition and rubbery zones of viscoelastic response.

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Table III

Transition Temperatures and Coefficients of Expansion[a]

Sample	Weight fraction polystyrene	T_{max}(SBR), °C E''	T_{max}(SBR), °C Tan δ	T_g(SBR), °C	$\beta \times 10^4$, cc/g °C PS(g)	$\beta \times 10^4$, cc/g °C SBR(g)	$\beta \times 10^4$, cc/g °C SBR(r)
1	0	−47	−32	−59.2		3.9	7.1
2	0.117	−46	−33	−57.9		3.6	6.9
3	0.237	−44	−31	−58.1		3.4	7.0
4	0.340	−44	−34	−58.3		3.6	6.7
5	0.459	−41	−34	−56.8		3.8	7.0
6	1.000				2.25		

[a] T_g and β on unvulcanized samples. PS(g) = polystyrene, glassy; SBR(g) = SBR, glassy; SBR(r) = SBR, rubbery. Additivity of β_{PS} and β_{SBR} assumed for samples 2–5.

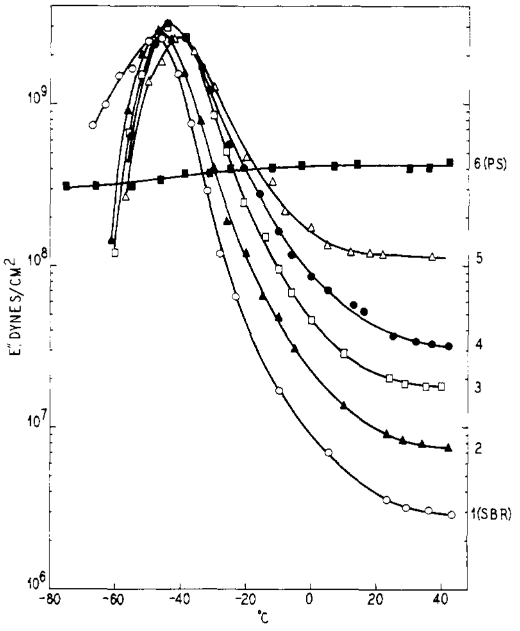

Figure 3. Loss moduli of polystyrene reinforced SBR 1503 (polystyrene contents: 2–11.7%, 3–23.7%, 4–34.0%, 5–45.9%).

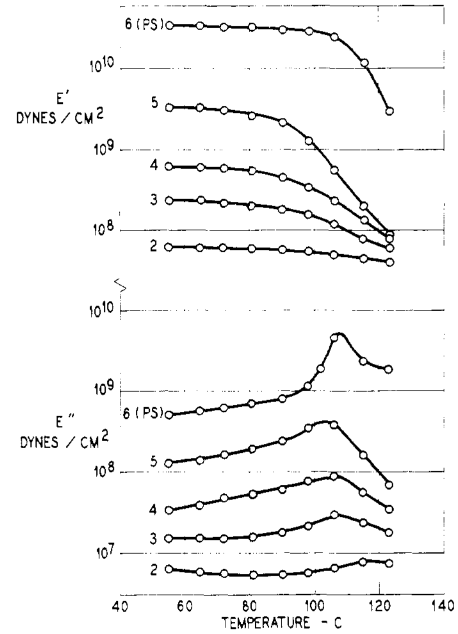

Figure 4. The polystyrene dispersion region (sytrene contents as in Figure 2).

The behavior is exactly as set forth in Figure 1. In the glassy state the curves come together, as both rubber and filler have approximately the same modulus. The corresponding loss modulus curves are shown in Figure 3. Again the polystyrene filler appears to broaden the transition zone. It is interesting, however, that the height of the loss maximum is scarcely affected by the filler even though E'' of polystyrene is substantially lower than that of SBR at this temperature. Because of the corresponding effects on E' and E'' in the transition zone, the loss tangent is not broadened (data not shown) and the maximum in tan δ is not shifted. The maximum is, however, lowered by the filler. The positions of the maxima in tan δ and E'' are compared with the dilatometric T_g values on the unvulcanized blends in Table III, which also lists the coefficients of thermal expansion. The coefficients of expansion shown (β) are simply the temperature derivative of specific volume, not $(dv/dT)/v$. The values of β(SBR) in the blends were calculated on the assumption of additivity.

Although not directly relevant to the question of the influence of the filler on segmental motion of the rubber, the effect of the rubber on the polystyrene dispersion region is shown in Figure 4. This is of interest in view of recent observations on block copolymers of styrene with other monomers.[9,10]

Discussion

It is noted from Table III that T_g of SBR is changed very little by the incorporation of polystyrene, nor is there any systematic effect on the rubbery coefficient of expansion. These observations are the same as reported for carbon black.[1] In contrast to the behavior of carbon black, the glassy coefficient of expansion of the filled polymer does not decrease much with filler loading. (The apparent minimum at 23.7% polystyrene is not considered real.) The lowering of β_g of the polymer by carbon black was explained as being due to dilatation resulting from stresses around the black particles, originating from the difference in thermal expansion of the polymer and filler.[1] This difference is much smaller in the system SBR–PS and the bulk modulus of PS is smaller than that of carbon black. Accordingly the dilatation effect should be much smaller. The results of the present study thus

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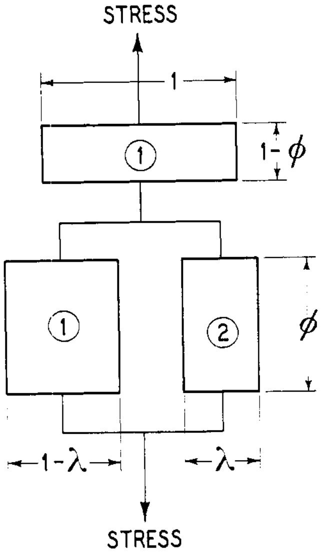

Figure 5. The Takayanagi model.

support the explanation offered for the diminished expansion coefficient of carbon black reinforced polymers in the glassy state.

The dynamic properties of polymer blends have been described with considerable success by the use of "mechanically equivalent models." In principle, these assign various amounts of parallel and series coupling to the two-phase structure of the blend. The model of Takayanagi[11] is shown in Figure 5. The two parameters ϕ and λ represent the state of mixing, but only one is independent. The product $\phi\lambda = v_2$, the volume fraction of the disperse phase. The solution for the Takayanagi model is

$$E^* = \left[\frac{\phi}{\lambda E_2^* + (1-\lambda)E_1^*} + \frac{1-\phi}{E_1^*}\right]^{-1} \qquad (1)$$

where E^* is the complex modulus of the blend and E_1^*, and E_2^* are the complex moduli of the components. To obtain separate mixture rules for E' and E'', one substitutes the complex moduli into eq 1 and separates E^* into its real and imaginary parts.

An attempt to fit the data of Figures 2 and 3 by the Takayanagi model is shown in Figures 6 and 7. While an exact fit of both E' and E'' could not be obtained, the model is obviously capable of reproducing all the essential features of the data. The storage modulus curves of the filled rubbers are raised and appear shifted toward higher temperature. The loss modulus curves are also shifted and are broadened. The model actually exaggerates these trends in E''. As in the experimental data, the height of the E'' maximum is essentially constant. The values of ϕ and λ used to fit the data are shown in Table IV. They were obtained by trial and error, seeking to minimize deviations from both the log E' and log E'' *vs.* temperature curves. They do not necessarily represent the best fit attainable. The special parameters[11] for spherical inclusions, $\lambda = (2 + 3v_2)/5$ and $\phi = 5v_2/(2 + 3v_2)$, did not produce good agreement with the data. It is interesting that ϕ, which determines the amount of parallel coupling, approaches unity with increasing filler loading.

TABLE IV
THE TAKAYANAGI PARAMETERS

Sample	v_2	λ	ϕ
2	0.105	0.175	0.600
3	0.217	0.246	0.880
4	0.315	0.330	0.955
5	0.430	0.434	0.990

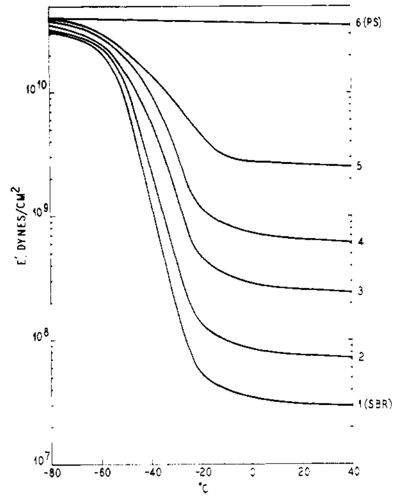

Figure 6. Representation of the storage modulus by eq 1.

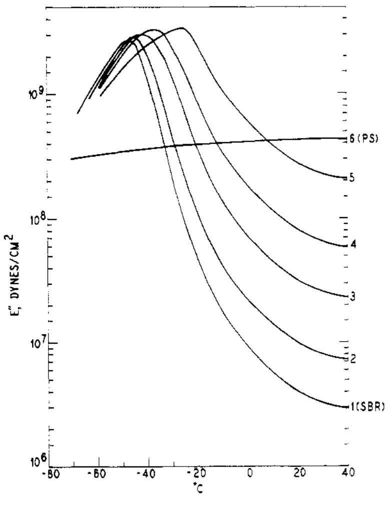

Figure 7. Representation of the loss modulus by eq 1.

The separate expressions obtained from eq 1 for E' and E'' are functions of both the storage and loss moduli of the components. This explains how some of the values of E'' can lie outside the limits set by the loss moduli of the components and how the loss maximum can be broadened and shifted, even though the E'' (PS) shows little variation over the range of temperature covered by the data.

Equation 1 with the ϕ and λ of Table IV does not produce a good fit to the data in the vicinity of the polystyrene dispersion shown in Figure 4. The reason is that the presence of the rubber apparently softens the polystyrene particles as the latter approach their T_g. This is particularly clear from the storage modulus

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data on samples 5 and 6. Similar shifts are observed in the polystyrene dispersions of two-phase block polymers of styrene with butadiene[8] and may be due to partial compatibility of the phases at these high temperatures. Such an effect would, of course, not be predictable by the mechanical equivalent model. It has, however, no bearing on the filler–rubber interaction at lower temperatures and would obviously not be present in elastomers reinforced with carbon black and other conventional fillers.

Conclusions

The dynamic behavior observed for polystyrene reinforced SBR is typical of other rubber-filled systems as well.[3] It can be described in all its essential features by a series–parallel coupled equivalent model. Thus it is not necessary to invoke an effect of the filler on the segmental motion of the rubber to explain the dynamic behavior. Since nuclear magnetic resonance and volume expansion measurements do not reveal a *substantial* effect of this nature, it must be concluded that the broadening of the relaxation spectrum of the *composite* is due primarily to other causes. The success of the equivalent model suggests that it may arise simply from mechanical coupling between the phases. Admittedly, the model is not a theory and only furnishes a phenomenological description. It is of interest, however, that theoretical stress analyses of rigid inclusions in viscoelastic media predict a broadening of the dispersion zone, even if the inclusions are perfectly elastic.[12]

Acknowledgment. The authors are indebted to C. A. Uraneck and J. E. Burleigh for the preparation of the polystyrene latex.

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Notes

Huggins Constant k_Θ' for Chain Polymers at the Theta Point

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Received August 5, 1969

The Huggins constant k' in the expression for the viscosity η of dilute solutions of nonelectrolytic chain polymers has been studied by many investigators over

$$\eta = \eta_0(1 + [\eta]C + k'[\eta]^2C^2 + \ldots) \qquad (1)$$

the years.[1,2] Experiments show that near and in particular below the Θ point k' depends critically on the solvent power.[3,4] This characteristic, among others, has made unequivocal determination of k_Θ' for chain polymers at the Θ point rather difficult. Moreover, as pointed out in a previous work,[5] theories for k_Θ' differ markedly, and there has been no generally accepted value for k_Θ'. The above facts, in turn, suggest that once k_Θ' is established it may become a very sensitive criterion for the Θ point; that is, it may be possible to use k' in estimating the Θ point.

We present in this note some additional remarks which favor our previous estimate of k_Θ'. The present models for chain polymers under the Θ condition are freely interpenetrable spheres and hydrodynamically equivalent ellipsoids which are rigid and isolated. Although the models are quite different, values predicted for k_Θ' from either of them show good agreement.

In a previous work,[5] we have set bounds for k_Θ' on the basis of k' for the equivalent particles and also obtained the value $k_\Theta' = 0.523$ from the refined Peterson–Fixman theory. The latter theory uses soft spheres,[6] which become freely permeable under the Θ condition. From a different approach, but without noting that the model they employed corresponds closely to polymers at the Θ point, Weissberg and Prager have obtained the lower bound on the relative viscosity η/η_0 for suspensions of freely interpenetrable spheres.[7] Their results are

$$\eta/\eta_0 > 1/(1 - \phi)[1 - (^3/_2) \ln (1 - \phi)] \qquad (2a)$$

$$= 1 + 2.5\phi + 3.25\phi^2 + \ldots \qquad (2b)$$

where ϕ denotes volume fraction of the suspended spheres. Replacing 2.5ϕ with $[\eta]C$, we have

$$\eta/\eta_0 > 1 + [\eta]C + 0.520[\eta]^2C^2 + \ldots \qquad (3)$$

We may, therefore, postulate that the lower bound for k_Θ' should be

$$k_\Theta' > 0.520 \qquad (4)$$

Thus, the value $k_\Theta' = 0.523$ which was obtained without the use of a parametric pair distribution for interpenetrating polymer molecules, in contrast to the minimum k' calculated from the extended Peterson–Fixman theory for polymers in good solvents,[5] is seen to be very close to the lower bound.

Polymers at the Θ point should remain constant in size independently of concentration due to the absence

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