Dynamic Mechanical Properties, Structure, and Composition of Impact Polystyrene

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Synopsis

Two series of impact polystyrene were studied; they had been obtained by grafting and by mechanical mixing, at two different known polybutadiene levels. Their biphasic structure had been characterized by optical microscopy and physicochemical separation. The following factors were investigated: morphology and content of the dispersed phase and continuous phase, composition of the dispersed phase, and molecular weight of the continuous phase. The elastic shear modulus and mechanical damping were measured. It was found that the elastic shear modulus of the two series of materials does not depend on the total polybutadiene content, as is often suggested in the literature, but on the rubbery dispersed phase content. The polybutadiene concentration of this phase, although varying between 100% for the mechanical mixes and 34% for one of the grafted polymers, does not influence the mentioned correlation. The particle size of the dispersed phase and the molecular weight the continuous phase have very little or no influence. The found correlation agrees with the theories for the moduli of models consisting of dispersions of spheres or particles in a matrix, like those of Kerner,[13] Hashin,[14,15] and Mackenzie.[18]

INTRODUCTION

Impact polystyrene in general consists of a two-phase system: PS-(polystyrene) matrix and rubbery dispersed phase.

Its properties are considered to be strongly dependent on its composition, the relative amount of the two phases, the number and character of the dispersed particles, and the molecular weight of the continuous phase.

These factors were measured on some samples, aiming at correlations between these factors and dynamic properties.

EXPERIMENTAL

Materials

The materials investigated were:

(a) One series of nine impact polystyrenes (A–I), obtained by graft polymerization of a solution of 10% PBD (polybutadiene) in styrene, in a mass suspension process. The stirring speed in the mass prepolymerization and the initiator and chain transfer concentrations were varied.

TABLE I
Summary of Experimental Results

Properties	Unit						Samples					
		PS'	A	B	B'	C	C'	D	D'	E	F	F'
Initiator concn	%	—	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Chain-transfer concn	%	—	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.02	0.05	0.05
Stirring speed	rpm	—	12	33	33	60	118	118	60	60	60	60
Polybutadiene (PBD)	%	0	10	10	10	10	10	10	10	10	10	10
Soluble part	%	100	73.1	71.2	71.1	67.9	67.6	71.2	71.2	75.5	71.4	71.8
Dispersed phase gel	%	0	25.6	27.8	27.0	30.6	30.2	27.4	27.1	22.5	26.7	26.4
Av. mol wt of PS, $\times 10^{-3}$	—	182	171	163	165	175	164	176	175	261	210	195
Polybutadiene in gel	%		36.3	34.3	35.7	32.5	34.4	34.5	41.0	44.3	38.0	39.3
Volume fraction, V_f	%		46.0	56.4	48.0	57.2	51.6	61.1	61.4	59.5	52.8	58.0
Ratio of particle surface to total volume, S_o	mm²/mm³		568	524	440	497	424	730	715	1565	688	689
Mean cord (or segment), $\bar{c}$	μm		1.66	2.16	2.24	2.35	2.46	1.60	1.65	0.74	1.48	1.72
Mean free distance between particles, MFD	μm	124	2.06	1.67	2.36	1.72	2.28	1.02	1.09	0.55	1.39	1.22
Shear modulus G' 20°C	$N/m^2 \times 10^7$	124	65.8	64.2	61.9	57.0	55.1	64.8	64.2	74.9	65.5	67.7
$\Delta G'$ 20°C (G' of PS = 124)	$N/m^2 \times 10^7$	0	59.2	60.8	63.1	68.0	69.9	60.2	60.8	50.1	59.5	57.3

Properties	Unit						Samples					
		G	H	H'	I	B''	C''	D''	F''	H''	I	II	III
Initiator concn	%	0.05	0.05	0.05	0.07	0.05	0.05	0.05	0.05	0.05			
Chain transfer concn	%	0.12	0.12	0.12	0.08	0.08	0.08	0.08	0.05	0.12			
Stirring speed	rpm	60	118	118	60	33	60	118	60	118			
Polybutadiene (PBD)	%	10	10	10	10	5	5	5	5	5			
Soluble part	%	68.1	69.3	69.4	68.1	84.7	83.3	84.3	84.7	83.6	10	20	30
Dispersed phase gel	%	29.2	28.8	28.5	30.3	13.7	15.3	13.6	13.8	14.1	90	80	70
Average mol. weight of PS, $\times 10^{-3}$	—	136	138	135	136	180	187	193	193	165	10	20	30
Polybutadiene in gel	%	34.3	34.6	39.3	33.5	38.4	36.2	39.0	38.3	36.7	182	182	182
Volume fraction, V_f	%	52.5	47.9	49.0	54.3	34.2	35.2	40.7	42.8	35.5	100	100	100
Ratio particles surface to total volume, S_o	mm²/mm³	465	422	377	376	398	364	515	574	324			
Mean cord (or segment), $\bar{c}$	μm	2.24	2.37	2.58	2.87	1.69	1.93	1.57	1.44	2.02			
Mean free distance between particles, MFD	μm	2.05	2.47	2.70	2.38	3.32	3.62	2.29	1.84	4.17			
Shear modulus G' 20°C	$N/m^2 \times 10^7$	59.4	55.1	55.1	54.7	89.8	86.2	92.2	94.1	86.1	103	77	56.5
$\Delta G'$ 20°C (G' of PS = 124)	$N/m^2 \times 10^7$	65.6	69.9	69.9	70.3	35.2	38.3	32.8	30.9	38.4	21	47	67.5

(b) One series of five impact PS, obtained from the previous samples by extrusion (B', C', D', F', H').

(c) The samples of (b) diluted by extrusion with 50% PS homopolymer (B", C", D", F", H").

(d) One PS homopolymer sample.

(e) Three mechanical mixes obtained by direct extrusion of PS and PBD rubber and containing 10%, 20%, and 30%, respectively (I, II, III).

The description of these materials and their characteristics are summarized in Table I.

Phase Separation and Phase Characterization

Each sample was dissolved in a mixture of 57% toluene and 43% methyl ethyl ketone; partial solubilization occurred. After centrifugation[1] at 5800 × G (6000 rpm), the insoluble part was separated as a swollen gel from the overlying solution. At least two washings of the separated gel with fresh solvent followed by centrifugation were necessary in order to eliminate completely the soluble part contained in the solvent swelling the gel. The washing solvent must not cloud the methanol by polymer precipitation.

From the toluene/methyl ethyl ketone solutions, the soluble part was obtained by precipitation with methyl alcohol. Separately, also the swollen gel was determined after coagulation with methanol.

The precision of the analysis is about ±0.5% in absolute value. In the grafted products investigated (A, B, and C), the obtained values of the gel were between 13.6% and 30.6%, and those of the soluble parts, between 84.7% and 67.4%. The rest consisted of low molecular weight polymer and remainders of additives, soluble in methyl alcohol. The rubbery parts of gels have PBD contents between 34% and 41%, measured by infrared spectroscopy. The soluble parts have in general a PBD content less than 1%. On these parts, measurements of intrinsic viscosity in toluene at 30°C were made.

The average molecular weights were calculated according to the following equation:[2]

$$[\eta]_{l/g} = 1.10 \cdot 10^{-5} \cdot M^{0.725}.$$

The resulting values of $\bar{M}_v$ were between 135,000 and 261,000. The molecular weight of sample 2 was 182,000. Upon treatment of the mechanical mixes (I, II, III) with the mentioned mix of solvents, they (mechanical mixes) dissolved completely.
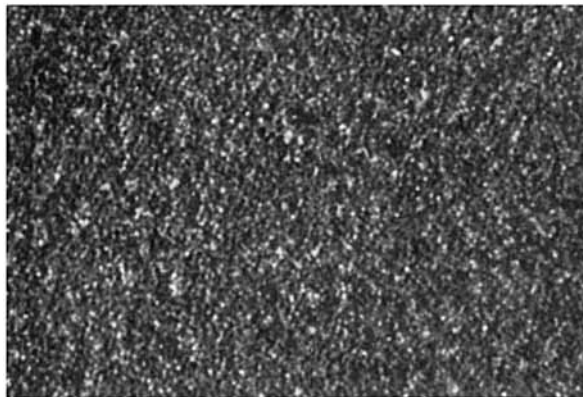
Thus it was impossible to separate the rubbery phases from the rest. The two phases exist in the solid state, but they are not separable in this way. The dispersed phase equals the PBD in amount (100% of PBD). The continuous part is PS of molecular weight 182,000. All the mentioned results are reported in Table I.
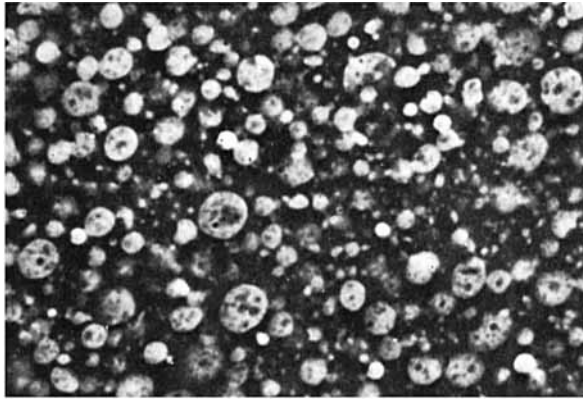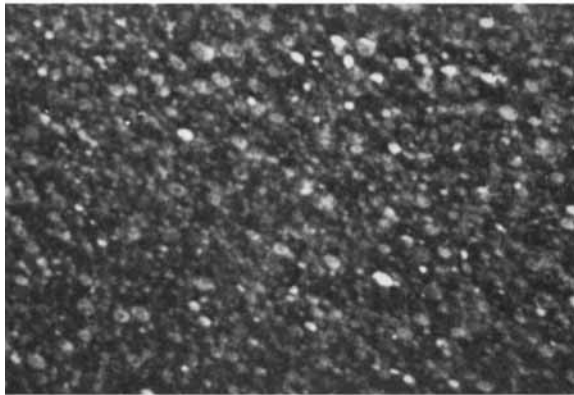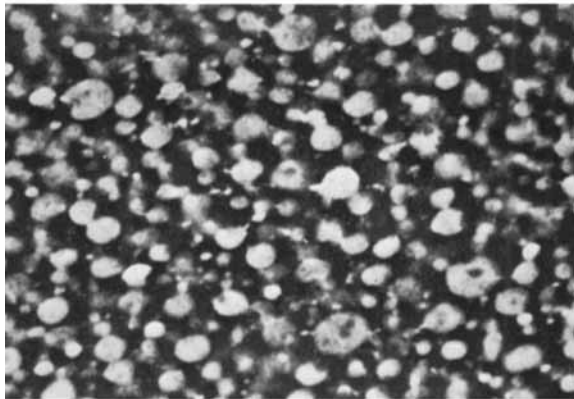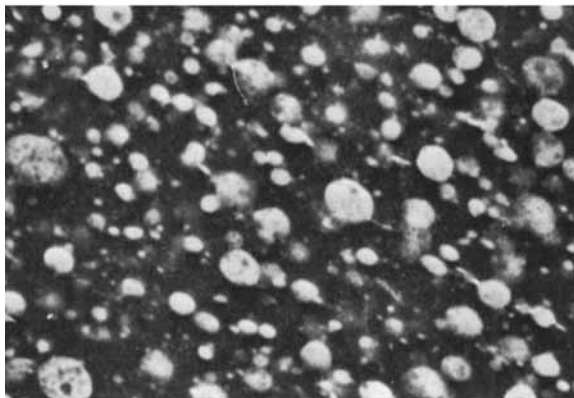
(a)
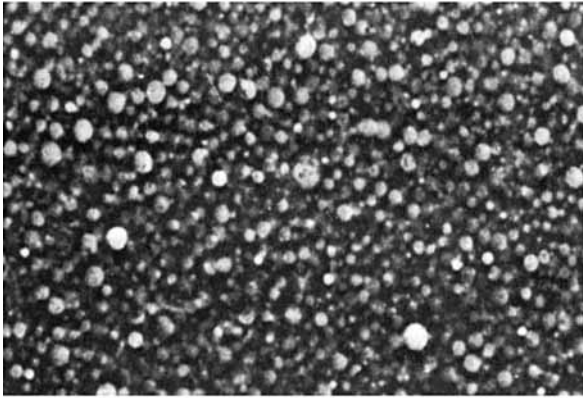
(b)

(c)

(d)

(e)

(f)

Fig. 1. Phase contrast micrographs at 1620× of some representative samples having different particle sizes: (a, b, c, d, e) samples C, D, E, F, and H, having 10% polybutadiene; (f) sample C″, obtained by extrusion of a mix of 50% sample C and 50% PS homopolymer.

Microscopic Measurements

Micrographs in phase contrast at 1620x were made on sections obtained from specimens of compression-molded graft-impact PS. Slices of about $2\,\mu$ thickness were prepared by the method of Traylor.[3] In order to get good results, 2 to 5 micrographs were made of one sample.

The method of evaluation of the micrographs used in this work is an adaptation of methods used in metallography.[4-7] It consists of the following procedure: On every micrograph, 12 lines were drawn through the center of the picture, at angles of 15° with respect to each other. On each line, the following quantities were measured: L_s, the length of the line on the micrographs; L_p, sum of the lengths of the cords through the particles; N_a, the number of sectioned particles along L_s.

From the average of 12 values for L_s, L_p, and N_a, the following parameters were calculated:

(1) Volume fraction of the dispersed phase, V_f (dispersed phase per mm³ matrix), defined as

$$V_f = \frac{L_p}{L_s} \text{ mm}^3.$$

(2) Particles surface per unit of volume of the sample, S_v, defined as

$$S_v = \frac{2N_a}{L_s} \text{ mm}^2/\text{mm}^3.$$

(3) Mean cord $\bar{c}$ (for spheres or mean segment for particles of different form) defined as

$$\bar{c} = \frac{L_p}{N_a} \text{ mm}.$$

(4) Mean free distance MFD among the particles, defined as

$$MFD = \frac{L_s - L_p}{N_a} \text{ mm}.$$

The obtained values, reported in Table I, for the investigated samples lie between 34.2% and 61.4% for V_f; between 324 and 1565 mm²/mm³ for S_v; between 0.74 and 2.87 for $\bar{c}$ and between 0.55 and 5.17 for MFD. For example, the micrographs of samples C, D, E, F, H, and C″ are given in Figures 1a, b, c, d, e, f.

Shear Modulus and Dynamic Mechanical Damping

Shear modulus and damping, tan δ, were measured for all the samples as a function of temperature in the range of $-170°C$ to $+90°C$. The measurements were performed on bars of $3.0 \times 7.0 \times 185$ mm³, using a Nonius torsional pendulum. In Table I only the modulus values G' and the differences ΔG (10^7 N/m²) at 20°C between the modulus of PS and those of the several composite materials are reported. The modulus and

tan δ were also measured on specimens of gel phase and PS continuous phase that had been obtained by previous separation of sample C. The G' values at 20°C of the soluble part and of the gel phase of this sample are, respectively, ca. $120 \times 10^7 \, N/m^2$ and $3.1 \times 10^7 \, N/m^2$.

In Figures 2 and 3 one can, for example, observe the diagrams of G' and tan δ as a function of the temperature for some of the samples and, par-
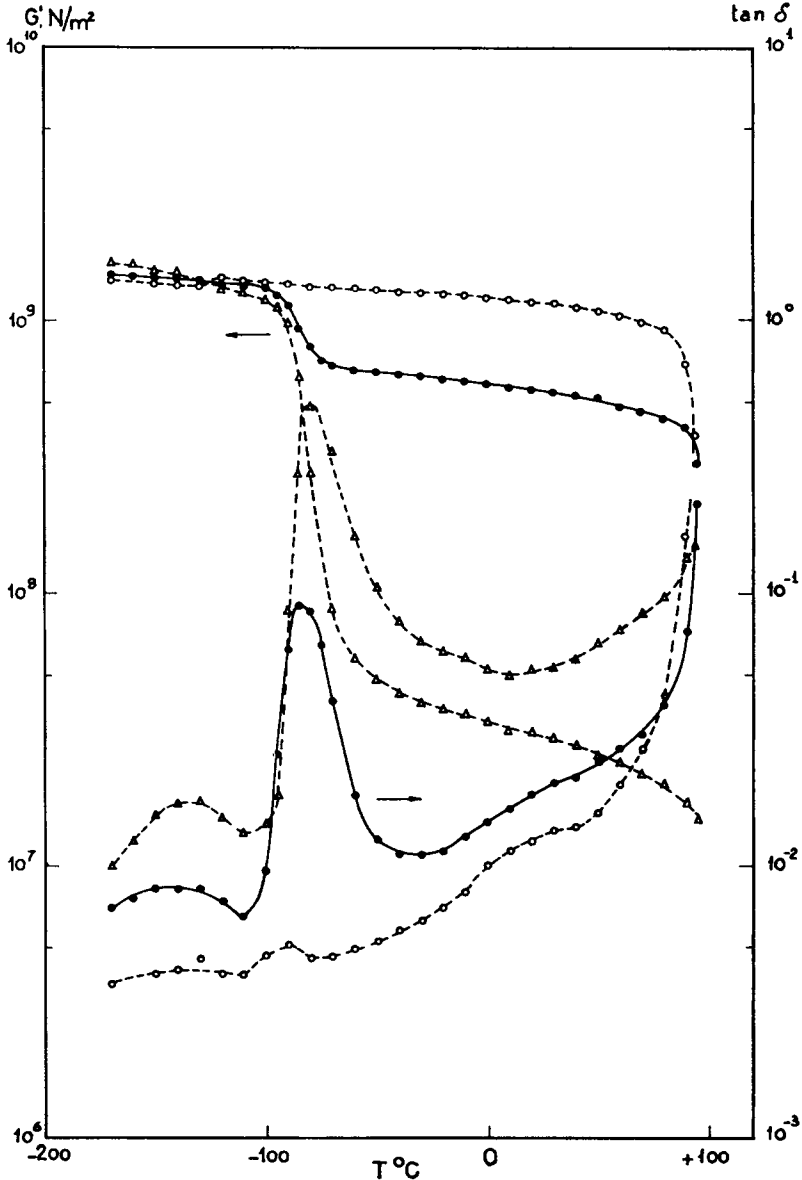

Fig. 2. Shear modulus and mechanical damping versus temperature of sample C and its separated phases: (●) sample C; (○) soluble part; (△) insoluble part "gel".
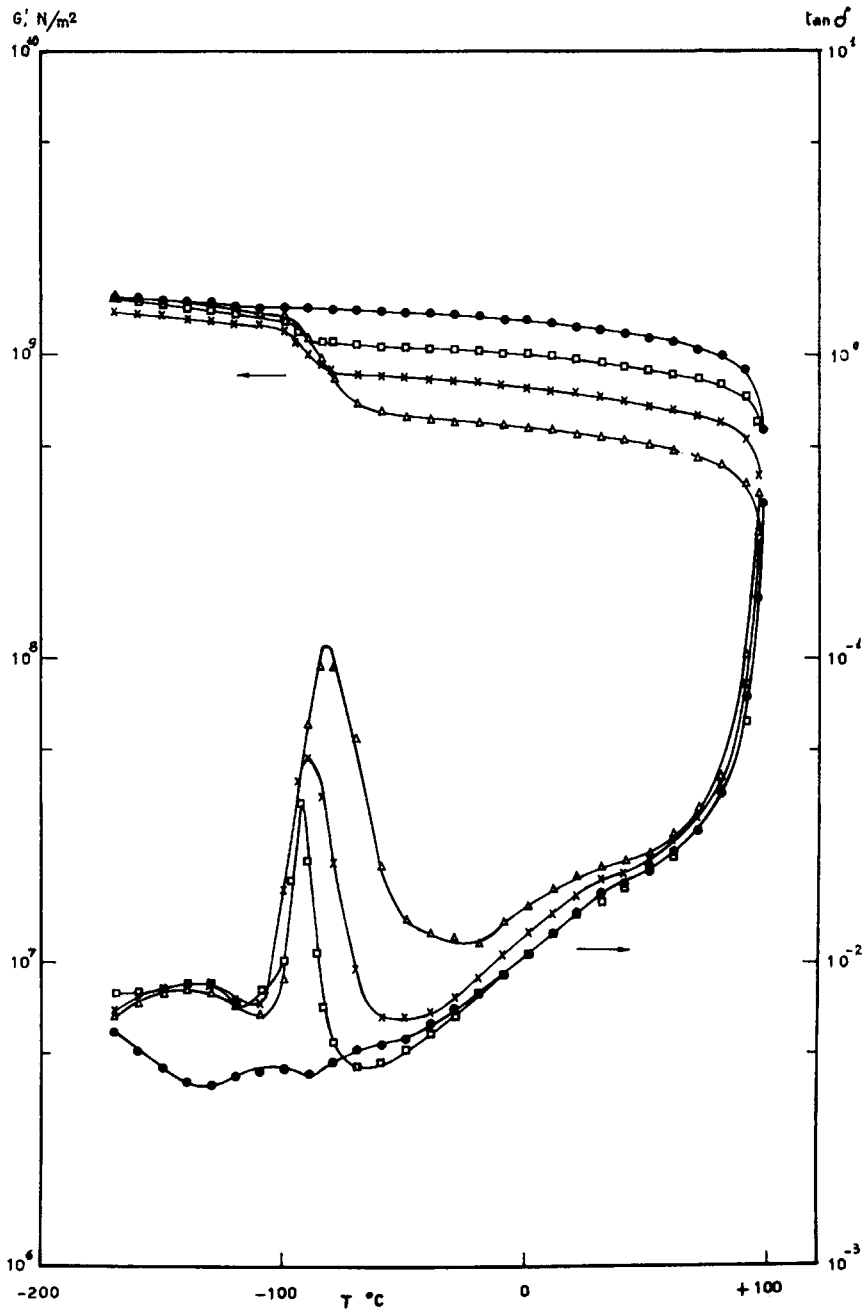
Fig. 3. Shear modulus and mechanical damping versus temperature of some representative samples: (●) PS; (×) sample E; (△) sample C''; (□) mechanical mix PS–PBD.

ticularly in Figure 2, for sample C and its separated phases. Figure 3 shows sample PS, mechanical mix I (10% PBD), and samples C″ and E.

DISCUSSION OF RESULTS

Correspondence Between Separated Fractions and Existing Phases

In the previous sections it has been supposed that the gel and the soluble separated parts represent the phases existing in the composite materials. In support of this hypothesis, the following facts were established:

The soluble part contains very little residual PBD. The part separated from sample C has a modulus G' at 20°C nearly identical with that of PS, and the T_g peak in its damping curve (Fig. 2) has almost disappeared.

The insoluble part behaves like an ensemble of crosslinked microgels. Three different solvents good for PS were used to dissolve a few samples. For each sample, the insoluble part was more or less swollen and its percentage was almost the same in the three solvents.

One micrograph taken of the gel part of sample C shows the presence of inclusions similar to those contained in the original dispersed particles.

The hypothesis would be further confirmed by a correspondence between the values of the gel volume fraction (density gel $\cong 1$) and the values of V_f measured by microscopy. The agreement, however, was not good: the V_f values were systematically higher. This may be due to the impossibility of a good V_f measurement. Although the thickness of the specimen is about 2 μ, it is still too thick. Too many planes of particles are in focus at the same time. This results in L_p values greater than real.* The best indirect confirmation of the hypothesis mentioned comes from the following.

Dependence of Modulus of Grafted Samples and of Mechanical Mixes from Gel, Content or PBD Content

Figure 4 gives the values of moduli G' measured at 20°C as a function of the gel content or PBD content (for the mechanical mixes). A modulus decrease is noted which is directly dependent on the gel content for the grafted samples and on the PBD content for the mixes. The correlation is the same for all the materials: mixes, grafted, and extruded or diluted grafted, although they are different in particle size and molecular weight or rubber content of the phases.

A similar correlation exists between the $\Delta G'$ (difference between the modulus at 20°C of the PS and that of each sample) and the gel or PBD content.

These correlations hold in a large temperature range down to the glass transition T_g of the PBD as lowest limit. At temperatures lower than T_g, the correlation does no longer hold.

* Parameters S_v, $\bar{c}$, and MFD are more precise because of a certain compensation of the errors of L_p and N_a.
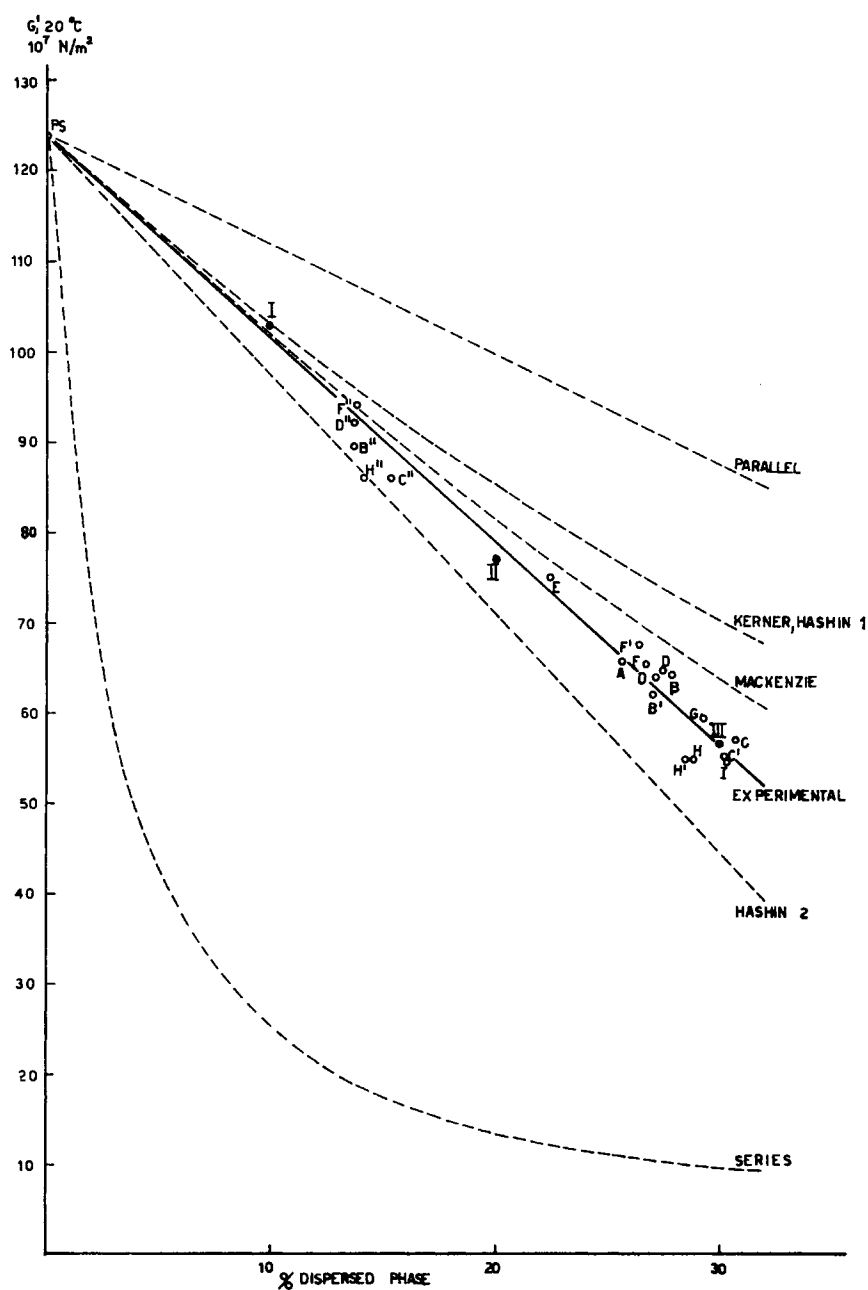
Fig. 4. Experimental points of shear modulus versus dispersed phase content of all the samples examined: (O) dispersed phase "gel" in the grafted samples; (●) dispersed phase PBD in the mechanical mixes. Dashed lines represent theoretical calculated models.

The experimental results reported in the literature[8-10] show a relation between G' modulus and rubber content in the ABS polymers or in the impact PS from ethylene–propylene rubber, in agreement with the theoretical models for composite materials of Kerner[13] and Hashin.[14,15] The amount of rubber is by these authors considered the dispersed phase. Probably in these cases the rubber is almost the exclusive component of the dispersed phase itself.

Our results show correlation with the mentioned theories if gel content and not PBD content is chosen as the dispersed phase (except for the cases of the mechanical mixes, in which the dispersed phase is the same as the PBD component). The separated gel part functions as a phase of low modulus in spite of the fact that the dispersed particles[11,12] (Fig. 1) contain large quantities of bonded or included PS. (The glass transition at low temperature is very close to that of PBD, but the modulus decrease is proportional to the phase amount and not to the amount of PBD.)

It is probable that the inclusions themselves, although rigid, can follow the local movements of the rubbery matrix, without contributing to the rigidity and the modulus very much. At temperatures lower than T_g, the rubbery matrix of the dispersed particles also becomes rigid and elastic like the inclusions. Therefore the modulus of the composite material is determined by other factors.

Agreement with Theoretical Models

Among the several theories for calculation of the moduli of composite materials from the moduli of their phases and their fractions, the following are noteworthy:

$$\text{series } G = \frac{G_0 G_r}{G_0(1 - V_0) + G_r V_0}$$

and the parallel model

$$G = G_0 V_0 + G_r(1 - V_0)$$

which are rather approximate.

The Kerner model[13] applies to systems consisting of a suspension of grains, perfectly bonded to the suspending medium and in form of spheres.

One of the Hashin models[14] describes the effect in a system with rigid spherical inclusions in an infinite medium. This model can be applied only at low concentrations of the dispersed phase. The application of this theory at large volume fraction fixes a lowest limit for the modulus of the real system.[7]

One other Hashin model[15] can be applied also at high concentration of the dispersed phase, in systems consisting of elastic, homogeneous, isotropic materials embedded in an elastic, homogeneous, isotropic matrix. This model predicts values very close to those resulting from the Kerner model.

The above models apply to systems with combinations of elastic phases. The perturbation method of Fröhlich and Sack[16] takes into account both the combined elastic and viscous properties of a dispersed system. This method has been applied by Oldroyd[17] to a system with small viscous inclusions in an elastic solid and by Mackenzie[18] to a system containing empty holes in an elastic matrix. Its mathematical expression is

$$1 - \frac{G}{G_0} = \frac{5(3K_0 + 4G_0)}{9K_0 + 8G_0} (V_r + AV_r^2).$$

In all these methods, the G' modulus can be calculated as a function of G_0, modulus of the continuous phase; G_r, modulus of the dispersed phase; V_0, volume fraction of the continuous phase; V_r, volume fraction of the dispersed phase; ν_0, Poisson's ratio of the continuous phase; $K_0 = f$ (ν_0, G_0), compression modulus of the continuous phase.

The moduli of the composite materials have been calculated by all the models described, assuming that $G_0 = 124.10^7$ N/m²; $G_r = 3.10^7$N/m² or 3.10^7 N/m² (values close to these measured on the separated phases of sample C); $\nu_0 = 0.325$[19]; $K_0 = 2.60G_0$; and $A = -0.467$ as obtained after Coble and Kingery[20] with $G/G_0 = 0$ and $V_r = 1$. In Table II are reported the values obtained with $V_r = 0.1, 0.2,$ and 0.3. Figure 4 shows the curves obtained with these values. It will be observed that the experimental values lie between those calculated from the two different Hashin models. They lie very close to the values calculated from the Mackenzie model.

TABLE II
G' Values of Composite Materials (10^7 N/m²)
Predicted by Several Models

V_r	Series model	Parallel model	Kerner[13] model	Hashin[14] model 1	Hashin[15] model 2	Mackenzie[18] model
0.1	25	112	103.5	97.5	102	101.7
0.2	13.5	99.8	85.7	71.0	85.4	81.8
0.3	9.5	87.5	70.5	44.5	70.7	63.9

The result is satisfactory if one considers that the gel and the PBD have a very low modulus (2 or 3 decades less) with respect to the elastic matrix. Therefore, the agreement is most likely with the model of dispersed empty holes, in which factor G_r does not appear.

References

1. I. A. Blanchette and L. E. Nielsen, *J. Polym. Sci.*, **20**, 317 (1956).
2. F. Danusso and C. Moraglio, *J. Polym. Sci.*, **24**, 161 (1957).
3. P. A. Traylor, *Anal. Chem.*, **33**, 1629 (1961).
4. C. S. Smith and L. Guttmann, *I. Metals*, **1**, 81 (1953).
5. E. Underwood, *Amer. Soc. Metals Eng. Quart.*, **11**, 62, 70 (1962).

6. L. Holliday and G. Thackray, *Nature*, **201**, 270 (1964).

7. L. Holliday, *Composite Materials*, Elsevier, Amsterdam, 1966, pp. 16, 211, 236.

8. L. Holliday and I. Mann, *Advances in Materials*, Pergamon Press, Oxford, 1965.

9. K. Flechter, R. M. Haward, and I. Mann, *Chem. Ind.*, 1854 6 November (1965).

10. G. Natta, M. Pegoraro, F. Severini, and S. Dabhade, *Chim. Ind.*, **47**, 384 (1965); *ibid. Rubber Chem. Technol.*, **39**, 1667 (1966).

11. B. I. Spit, *Polymer*, **4**, 109 (1963).

12. G. E. Molau and H. Keskkula, *J. Polym. Sci. A-1*, 1595, Vol. IV (1966).

13. E. H. Kerner, *Proc. Phys. Soc. (London)*, **69B**, 808 (1966).

14. Z. Hashin, *Bull. Res. Counc. Israel*, **5c**, 46 (1955).

15. Z. Hashin, *J. Appl. Mechanics*, 143, March 1962.

16. H. Fröhlich and R. Sack, *Proc. Roy. Soc. (London)*, **185A**, 415 (1946).

17. J. G. Oldroyd, *Verformung und Fliessen des Festkörpers*, R. Grammel, 1956, p., 304.

18. J. K. Mackenzie, *Proc. Phys. Soc.*, **63B**, 2 (1950).

19. J. Brandrup and E. H. Immergut, *Polymer Handbook*, Interscience, New York, 1966, p. VI–76.

20. R. L. Coble and W. D. Kingery, *J. Amer. Ceram. Soc.*, **39**, 377 (1956).