

The Effect of Rubber Particle Size on the Mechanical Properties of High-Impact Polystyrene

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Synopsis

Resins having different rubber particle sizes were prepared by polymerizing impact polystyrene using different agitation rates but keeping all other parameters constant. Also, samples were made varying the amount and type of rubber and type of agitation. The impact and tensile properties of the prepared resins are studied in relation to existing theories of rubber particle reinforcement. The particle size dependence of energy absorption in impact (high intensity) and tensile (low intensity) testing appear to be opposite in nature. Energy absorption increases with increasing particle size in the high-intensity mode and decreases in low-intensity testing. Different mechanisms are, therefore, postulated to be operative in each of these two test methods.

INTRODUCTION

Today, it is well known that an impact-grade polystyrene is formed by dissolving rubber in a styrene monomer and then polymerizing. The graft copolymer thus formed results in a manyfold increase in rubber toughening efficiency when compared to mechanical blending.¹ Microscopic studies show the morphology of this impact-grade polystyrene to be that of a two-phase system consisting of small particles of rubber in a matrix of polystyrene.

In a typical industrial reaction, 5%–10% of styrene–butadiene or polybutadiene rubber is dissolved in styrene monomer, and the solution is polymerized in an agitated reactor to 35%–40% conversion. As the polymerization proceeds, the polystyrene in the styrene phase grows at the expense of the rubber–styrene phase until the latter becomes too small to be the continuous phase. At this point, a phase inversion occurs and the polystyrene in styrene phase becomes continuous, with rubber-in-styrene droplets making up the discontinuous phase. As the polymerization reaches its final stages, the rubber-phase droplets shrink as they continue losing styrene to the continuous phase, resulting in the final product of rubber particles in a polystyrene matrix.²

The necessity of agitation during the first 35%–40% conversion in the polymerization of impact polystyrene was recognized early in the patent literature,³ although its precise function was not understood. Keskkula and co-workers,^{2,4} who did much work and published many papers on the subject, explained that agitation acted as a catalyst to help the system achieve proper phase equilibrium. At the point where phase inversion is favored, the system is too viscous at normal polymerization temperatures for the equilibrium forces to achieve inversion on their own. If the polymerization is carried out without inversion, the rubber-in-styrene phase remains the continuous phase, and an inferior, brittle product results.⁵

Phase-contrast microscopy has been used extensively in research involving

rubber-modified polymers.⁶ In dark phase-contrast microscopy, the rubber phase is light while the polystyrene phase is dark. Thus, the morphology, size, shape, and distribution of rubber particles in polystyrene can be studied. In recent work, electron microscopy has been used to look at the inside of rubber particles.⁴ It was found that large amounts of mechanically occluded polystyrene existed as a separate phase within these particles, which increased the size of the rubber phase 10%–40%.⁷

Merz et al.⁸ proposed a mechanism of rubber reinforcement in which rubber particles absorb energy as an elastomeric phase and, in spanning across developing cracks, they hold together the fracture surfaces of the glassy polymer matrix, thus acting to stop the cracks. Newman and Strella⁹ proposed that the rubber particles generate a hydrostatic tensile stress state in the adjacent matrix polymer owing to the different Poisson ratios of the rubber and the matrix. This results in an increase in the free volume, which facilitates yielding rather than brittle fracture.

Schmitt¹⁰ theorized that the polystyrene matrix is under circumferential compression due to the difference in thermal expansion between the two phases. A highly popular theory was that of Schmitt and Keskkula,¹¹ which states that the rubber particles act as sites of stress concentration which cause a large number of small cracks to form, radiating out from the particles. These small cracks absorb more energy than the large cracks that form in the absence of rubber particles. Electron photomicrographs have actually shown cracks radiating from rubber particles. Also, since the cracks generally form perpendicular to the applied force, the area between small cracks will act as long, thin beams which can be bent and thus cause even greater elongation.

A related theory by Bucknall and Smith¹² holds that the lines radiating from the particles are actually craze bands. According to Sauer et al.,¹³ crazes are composed of oriented polymer interspersed by voids, so that the total polymer content of the crazed area is only 50%–60%. When stress is applied to high-impact polystyrene, the rubber relaxes first, creating a nonuniform stress field. The crazes are then initiated at points of maximum stress concentration. Kambour¹⁴ modifies the theory of Bucknall and Smith¹² to state that the rubber particles initiate crazes and then, by blocking them, prevent them from developing into cracks.

As far as particle size and its relation to impact strength is concerned, all authors seem to agree that there is a minimum size of particle below which impact improvement occurs only to a minimal extent. Merz et al.⁸ refer to this size as the "domain" size of the continuous glassy phase. Rosen¹⁵ indicates that the requirement is that the particle size not be at or near molecular level. He puts this minimum at 0.01 micron, so that the particles are large enough to exhibit typical rubbery properties. Based on most of the theories of rubber reinforcement presented above, once this minimum is exceeded, impact strength should decrease as particle size increases. By whatever mechanism the reinforcing particles act, having smaller particles means more sites for reinforcement for the same amount of rubber.

Boyer and Keskkula¹⁶ state that the "recognized" optimum particle size is 2 to 5 microns. They also note that according to the Schmitt mechanism,¹¹ the stresses will increase as the cube of the particle diameter. This would indicate that at least within some range of particle sizes, the reinforcement should increase

with increasing particle size. Bragaw¹⁷ maintains that, based on his theory of reinforcement due to branching, impact strength should increase geometrically with the number of particles, and hence with decreasing particle size, for constant rubber content.

In studying the high-impact polystyrene polymerization reaction, Bender¹⁸ found that shearing due to agitation had an effect on ultimate particle size up to about 25%–30% conversion. After this point, the rubber droplets became very viscous due to loss of styrene and were not broken up by further agitation. In order to make resins with different rubber particle sizes, he used a series of SBR rubbers having different viscosities and found that the higher the viscosity of the rubber, the greater the particle size in the resultant high-impact polystyrene resin. He found a general increase in impact strength with increasing particle size.

In the present study, a series of high-impact polystyrenes were prepared, of different rubber particle sizes but similar in every other respect. The method by which we have sought to accomplish this is by carrying out the polymerization of these resins under the same time-temperature conditions, using the same type and amount of rubber and other ingredients, varying only the rate of agitation during the prepolymerization step. In this manner, molecular weight, graft copolymer level, and other resin parameters are kept constant making it possible to more easily assess the effect of particle size on resin toughness. An attempt has been made to draw some conclusions on the general subject of rubber reinforcement of polystyrene.

EXPERIMENTAL

Polymerization of Samples

The prepolymerization was carried out in a jacketed 2-l. resin reactor fitted with a variable speed agitator consisting of two four-bladed turbine-type impellers. All reaction parameters were kept constant except for the rate of agitation, which was varied from run to run.

A large number of trial polymerization runs were made to achieve the proper balance of ingredients and reactor conditions. Both low- and high-temperature catalysts (benzoyl peroxide and *t*-butyl peroxide) were used to assure elimination of volatiles during the latter stages of polymerization. The prepolymerizations were carried out at 78°–80°C and lasted about 7 hr, which corresponded to 26%–31% styrene conversion. The reaction mixture consisted of a 5% solution

TABLE I
Experimental Conditions Used in the Polymerization Runs

Sample no.	Agitation rate, rpm	Type of agitator	Type of rubber	Rubber content, %
1	50	turbine	SBR	5
2	100	turbine	SBR	5
3	200	turbine	SBR	5
4	400	turbine	SBR	5
5	100	turbine	SBR	6
6	100	turbine	Polybutadiene	5
7	100	propeller	SBR	5

of Goodyear RPF 1288 SBR rubber in freshly distilled styrene. As soon as this solution was brought to temperature, the first catalyst addition was made. Table I gives a summary of the experimental runs carried out. Samples for determination of percent conversion were taken all along the prepolymerization and analyzed by first dissolving in toluene and then precipitating the polymer from warm methanol and filtering.

Relative viscosity measurements were taken along the course of the reaction using a Cannon-Fenske viscometer at constant temperature. This was done to note the reaction progress and to find the phase-inversion point. This point was also confirmed by visual observation of the solution behavior and by testing dried prepolymer films for solubility in methyl ethyl ketone. Before phase inversion, the dried films are insoluble due to the insolubility of the continuous rubber phase in methyl ethyl ketone.

When the reaction had run for the proper duration, the contents of the reactor were emptied into a rectangular quart can. The can was sealed and fitted with a dial thermometer and then heated in a 125°C oven until the contents began to evolve heat. The exotherm was controlled by placing the can in a cold water bath, thereby not allowing the polymerization temperature to exceed the 180°–200°C level. After the temperature began to fall, the can was heated for 2 hr at 125°C and then for 3 hr at 180°C.

The resulting resin was then ground, milled on a hot two-roll mill for 10 min, and reground. Mastication does not affect the mechanical properties of impact polystyrene if phase inversion was achieved.

An indication of the volatile content of the resins was obtained by the commercially utilized technique described by Bishop¹⁹ of finding the weight loss of 10 g ground resin upon heating for 2 hr in a circulating-air oven at 285°F. Also, melt flow values (ASTM 1238, Condition I) were obtained for the resins. The volatile content and melt flow values for the resins prepared at different agitation rates (run nos. 1–4 of Table I) were in the ranges of 0.45–1.01% and 19–29 g/10 min, respectively. The corresponding ranges for commercial resins used as controls were 0.10–0.12% and 22–26 g/10 min. The volatile content readings were taken before milling the resins.

In addition to the four runs made at different rates of agitation (run nos. 1, 2, 3, and 4 in Table I), several polymerizations were done while varying other single parameters but keeping the agitation rate constant at 100 rpm, designated as run nos. 5, 6, and 7 in Table I.

Microscopy and Mechanical Testing

The method of sample preparation for phase-contrast microscopy was that described by Hannah and Bond.²⁰ This consists of slicing off a small piece of sample and placing it on a microscope slide. A small drop of cinnamaldehyde is placed on the piece and the slide heated until the resin breaks up. Hot cinnamaldehyde dissolves the polystyrene phase but leaves the rubber droplets intact. A slide cover is applied, and the slide is ready for microscope viewing. An older method by Traylor,⁶ in which a microtome is used to slide the specimen, was abandoned because of difficulty encountered in slicing a sufficiently thin sample.

The slides were viewed on a Nikon phase-contrast microscope with inverted

optics fitted with a Nikon 35-mm camera at 400 \times magnification. The size scale for the photomicrographs was established by photographing a micro-inscribed scale slide.

Bars for Izod impact testing were injection molded at 400 $^{\circ}$ F. The $\frac{1}{4}$ -in.-wide bars complied with ASTM D256-73 except that the notches were molded in, rather than machined. The impact readings were made on a 2-ft lb scale.

Bars for tensile testing were injection molded and had a cross section of $\frac{1}{8}$ by $\frac{1}{4}$ in. They were tested on an Instron tensile testing machine. The initial gauge length of the bars was 1 in. The cross-head speed was 0.2 in./min. The unusually small bar size and gauge length used were necessitated by the limited amount of sample resin available. The resulting stress-versus-strain curves were used to calculate tensile stress at yield and at break, modulus of elasticity, percent elongation at break, and the total energy required to break.

RESULTS AND DISCUSSION

Factors Affecting Particle Size

Varying the agitation rate during prepolymerization proved highly successful in creating resins having different rubber particle sizes. Varying the type of agitation and type and amount of rubber, likewise, had a significant effect on particle size and its distribution.

Figure 1 gives photomicrographs of typical rubber particles in resin samples no. 1-4. The decrease in particle size with increasing agitation, although expected, is clearly seen. The particle size distribution, especially in the resins with larger particles, is extremely broad. It is also interesting to note, in Figure

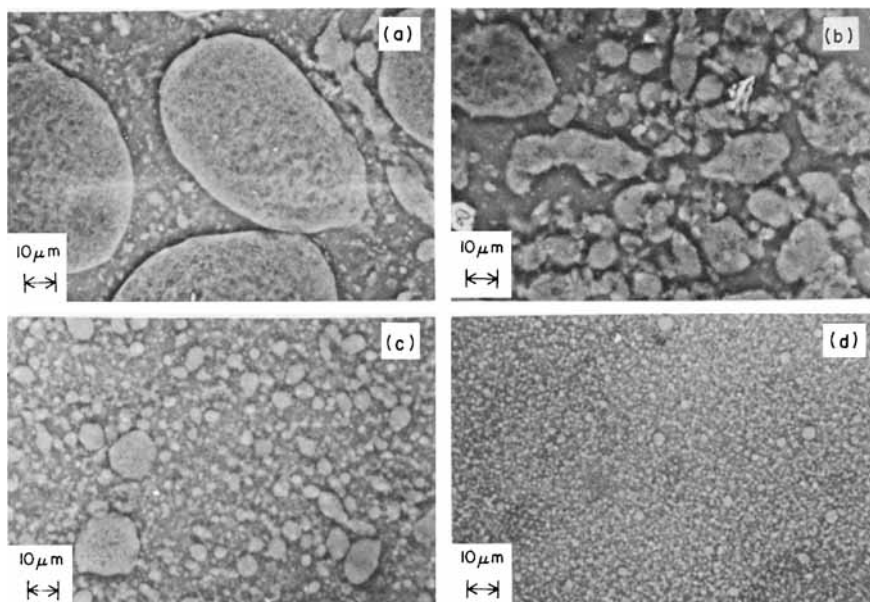


Fig. 1. Phase-contrast photomicrographs of the rubber particles: (a) sample no. 1; (b) sample no. 2; (c) sample no. 3; (d) sample no. 4.

TABLE II
Variations of Rubber Particle Size With Intensity of Agitation

Sample no.	Agitation rate, rpm	Range of particle size, microns
1	50	50-100
2	100	15-40
3	200	5-20
4	400	less than 1-5

1(a), that even in sample no. 1 there are a large number of very small ($1\ \mu\text{m}$ or less) particles distributed among the very large particles. It may be that these particles are formed by two separate mechanisms. The large particles are equilibrium suspension droplets formed during phase inversion, and the much smaller droplets are formed as a result of continued shearing after phase inversion is complete. In any event, it is the large droplets that are mainly responsible for reinforcement, since they collectively contain by far the larger amount of rubber. They contain an even higher percentage than is apparent from their larger diameter, since the amount of rubber present is a function of the cube of the diameter.

In sample no. 4 [see Fig. 1(d)], where the shearing was the most intense, most of the particles are of the very small variety, both because of the originally small equilibrium droplets and their further breakdown as a result of high-intensity shearing. The size ranges of the reinforcing particles for samples no. 1-4 are given in Table II. Visible in the photomicrographs, especially Figure 1(a), are the polystyrene occlusions within the rubber particles, which appear as small black spots.

Figure 2 shows a photomicrograph of sample no. 5, which was made with 6% SBR rubber but is otherwise similar to sample no. 2 [see Fig. 1(b)], which contains only 5% rubber. The particles in Figure 2 are much larger, even though the agitation rates are the same, since the viscosity of the 6% rubber solution is considerably higher, resulting in larger equilibrium droplets. Also, due to the higher viscosity, the phase inversion process is slower and more difficult to accomplish, hence the lack of any appreciable postinversion breakup of particles.

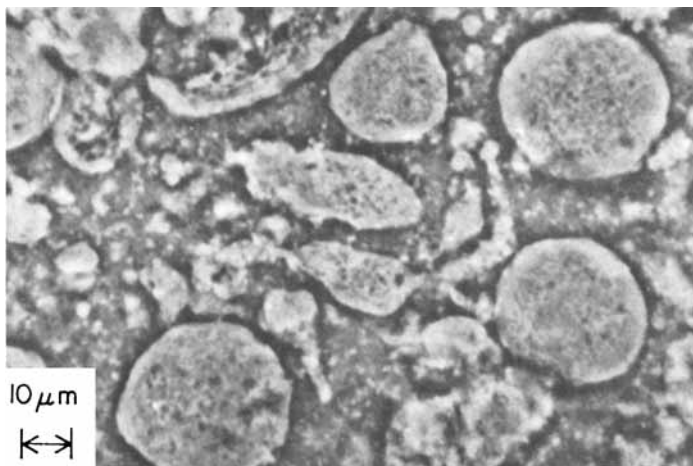


Fig. 2. Phase-contrast photomicrograph of sample no. 5.

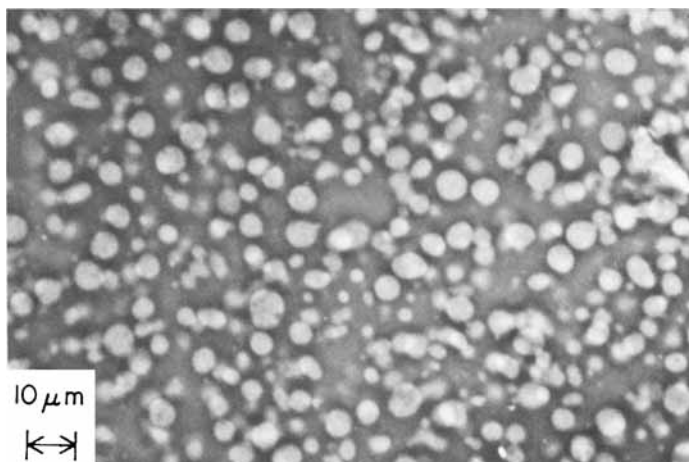


Fig. 3. Phase-contrast photomicrograph of sample no. 6.

Figure 3 gives a photomicrograph showing the particles of sample no. 6, which was prepared with 5% polybutadiene rubber. The much narrower particle size distribution of this sample than that of sample no. 2 [see Fig. 1(b)], its analog in SBR, is quite obvious.

It was noticed during the prepolymerization of sample no. 6 that the viscosity during the entire course of the reaction was much lower than with the SBR rubbers. Also, the phase inversion occurred sooner and was less abrupt. These factors may account for the smaller reinforcing particle size and the narrower distribution. The more even, spherical shape of the polybutadiene particles is a characteristic of the particular rubber type.

The final photomicrograph of the series, Figure 4, shows the particles of sample no. 7, in which the agitator blades were of the propeller rather than the turbine type. The average particle size is smaller than that of sample no. 2 [see Fig. 1(b)], which was made with a turbine-type blade at the same rpm. The particle size distribution, however, is narrower. The propeller-type blade places less shear on the system than the turbine-type blade for the same rpm. Consistent with

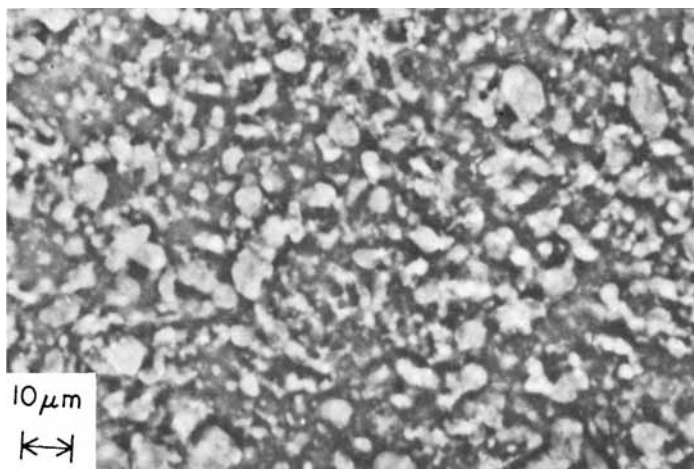


Fig. 4. Phase-contrast photomicrograph of sample no. 7.

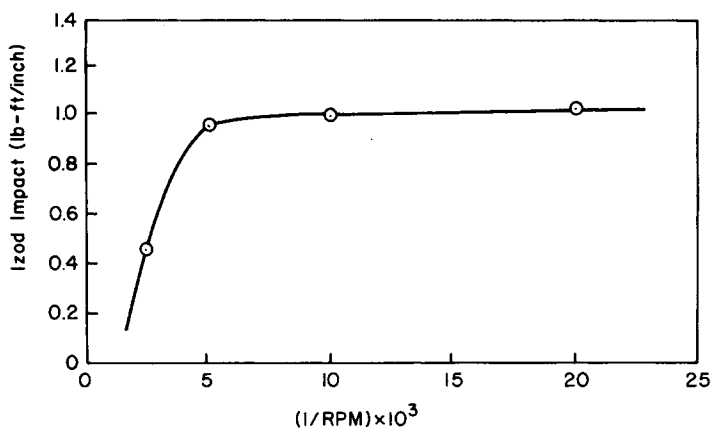


Fig. 5. Plot of Izod impact strength vs reciprocal of agitation rate (rpm).

the previous discussion, it is possible that because of the lower shear, less cleavage of rubber particles occurs, which results in a narrower distribution of particle sizes.

High-Intensity Fracture—Izod Impact Test

Table III lists the average Izod impact strength values found for bars injection molded out of the seven sample resins prepared. When the impact values are plotted against the reciprocal of agitation rate (since particle size and agitation rate are inversely related), Figure 5 is obtained. As the shape of the curve indicates, when particle size is very small, impact reinforcement is almost negligible and the impact strength approaches that of unmodified polystyrene homopolymer. Once a certain threshold level of particle size is reached, impact reinforcement has achieved most of its full potential, and after this, the curve levels off and increases with increasing particle size only to a minor degree.

The threshold level for reinforcement found in our experiment was about 1 micron. This is two orders of magnitude higher than the 0.01- μ m size predicted by Rosen.¹⁵ The 2-5- μ m optimum level for commercial resin quoted by Boyer and Keskkula¹⁶ is, however, quite consistent with our result. Although the impact strength seems to improve with increasing particle size even past the 2-5- μ m level, this slight improvement is offset by the poorer surface qualities.

TABLE III
Experimentally Determined Values of Izod Impact Strength

Sample no.	Izod impact strength, lb-ft/in. notch	Area under stress-strain curve, psi
1	1.02	480
2	1.00	553
3	0.95	688
4	0.44	612
5	0.84	338
6	1.20	530
7	0.97	400

The higher impact strength of sample no. 6 (see Table III), the resin containing polybutadiene rubber, is attributed to the rubber type.¹⁶ Also, the narrow particle size distribution (see Fig. 3) may contribute to its superior impact strength. The impact value of sample no. 5, containing 6% SBR, is rather anomalous. An increase in rubber level should, of course, increase rather than decrease impact strength. The only possible explanation is that the phase inversion was incomplete to the extent that enough rubber was tied up in the un-inverted parts of the resin to seriously reduce the level of reinforcing rubber. Sample no. 7, made with a propeller blade, has a somewhat higher impact value than sample no. 3 made with a turbine blade. This may be accounted for by the narrower particle size distribution of sample no. 7 (see Fig. 4), as previously indicated.

Low-Intensity Fracture—Instron Tensile Test

It is well known that the tensile curve for unmodified polystyrene rises steeply up to the yield point and then shows little elongation before breaking. It is also well known that an elastomer has a low-sloped tensile curve before yield and has a high degree of elongation the extent of which depends on the toughness of the rubber. The shape of the curves of samples no. 1-7 were, predictably, somewhere between these two extremes. Table IV gives the tensile data derived from the curves of samples no. 1-7.

Except for some deviation by sample no. 4, the series of samples no. 1-4 shows a decrease of tensile stress both at yield and at break, as well as a decrease in modulus with increasing particle size. This is consistent with the generally more "rubbery" behavior accompanying increasing particle size that was apparent from the impact results. Also notable is that sample no. 4, with the smallest particle size, is the only one where the tensile stress at yield exceeds its value at break. This further emphasizes the close relation this sample has to unmodified polystyrene.

Following a similar line of thought, sample no. 5 (6% SBR) and sample no. 6 (butadiene rubber) show low tensile stress values due to the higher level of SBR in the former and the higher efficiency rubber type used in the latter.

TABLE IV
Experimentally Determined Values of the Tensile Properties

Sample no.	Tensile stress at yield, ^a psi	Tensile stress at break, ^a psi	Per cent elongation at break	Tensile modulus, psi
1	900	1100	48	110,500
2	1025	1100	52	115,000
3	1064	1152	62	144,000
4	1034	980	61	126,000
5	784	824	42	104,000
6	830	975	59	106,000
7	945	1005	41	112,000

^a Due to the unusual sample bar size and gauge length used in obtaining these values, they are not indicative of standard tensile strength and are used here only in comparing relative strengths of the samples.

When we examine the percent elongation data, we find a trend opposite to that indicated by the tensile stress values. Although high elongation is usually indicative of "rubberiness," the elongation values of Table IV show a decrease in elongation with increasing particle size and increasing impact reinforcement.

A possible explanation for the elongation values is that in the samples with larger particle size, the rubber particles form large enough holes in the cross section of the tensile bar to cause serious weakening of the continuous matrix structure. The adhesion of the rubber particles to the polystyrene is not sufficient to withstand the applied stress. The premature fracture of the tensile bar thus results.

Comparison of Impact and Tensile Results and Their Implications

The areas under the stress-strain curves of samples no. 1-7 were estimated (see Table III) by multiplying the average of the stress at yield and the stress at break by the elongation at break. In Table III, the impact values, which are proportional to energy to break, are placed beside the energy-to-break values from the tensile results.

The trends in the two sets of results seem to be of opposite nature. Although the impact values and the levels of crazing on impact indicate a decrease in reinforcement with decreasing particle size, the uniform whitening observed in all samples in the tensile tests and the tensile results themselves do not bear this out.

The findings of the present study appear to indicate that although various theories⁸⁻¹⁴ may hold true for low-intensity fracture, they fail to explain the decrease in reinforcement with decreasing particle size in high-intensity testing. Such theories predict that, since with a decrease in particle size the number of reinforcing particles increases, the level of reinforcement should also increase. For instance, the craze branching theory of Bragaw,¹⁷ which predicts that the increase in reinforcement varies exponentially with the increase in the number of reinforcing particles, certainly is not supported by our findings.

The results of the present study as well as that of Bender¹⁸ indicate that a special mechanism is operative in high-intensity tests which is able to assure ductile fracture in some resins while failing to do so in others, although both resins may undergo ductile fracture in low-intensity tests.

The Schmitt mechanism¹⁰ fulfills the requirements of being rapidly operative and of being specific to impact or high-intensity testing. As mentioned previously, the reinforcing effects attributable to this mechanism should increase with increasing particle size.

The following conclusions may then be reached from our results: (1) In low-intensity fracture, reinforcement is due to the presence of discrete rubber particles which cause energy absorption by any of several possible mechanisms. Smaller particle size, for the same amount of rubber, increases reinforcement due to the larger number of particles present. (2) High-intensity testings will result in brittle fracture, even of rubber-modified polystyrene, unless there is a rapidly operating mechanism of energy absorption available to convert the potentially brittle fracture to a ductile one. The increase in impact strength with increasing particle size, found in this study, indicates a large contribution by the Schmitt mechanism¹⁰ in impact reinforcement.

References

1. D. J. Angier and E. M. Fettes, *Rubber Chem. Technol.*, **38**, 1164 (1965).
2. G. E. Molau and H. Keskkula, *J. Polym. Sci. A1*, **4**, 1595 (1966).
3. J. L. Amos, J. L. McCurdy, and O. R. McIntire, U.S. Pat. 2,694,692 (1959).
4. H. Keskkula and P. A. Traylor, *J. Appl. Polym. Sci.*, **44**, 2631 (1967).
5. H. Keskkula, *Appl. Polym. Symp.*, **No. 15**, 51 (1970).
6. P. A. Traylor, *Anal. Chem.*, **33**, 162 (1961).
7. D. A. Walker, in *Modern Plastics Encyclopedia*, Vol. 45, No. 14A, McGraw-Hill, New York, 1968-1969, p. 334.
8. E. H. Merz, G. C. Claver, and M. Baer, *J. Polym. Sci.*, **22**, 325 (1956).
9. S. Newman and S. Strella, *J. Appl. Polym. Sci.*, **9**, 2297 (1965).
10. J. A. Schmitt, *J. Appl. Polym. Sci.*, **12**, 533 (1968).
11. J. A. Schmitt and H. Keskkula, *J. Appl. Polym. Sci.*, **3**, 132 (1960).
12. C. B. Bucknall and R. R. Smith, *Polymer*, **6**, 437 (1965).
13. J. A. Sauer, J. Marin, and C. C. Hsiao, *J. Appl. Phys.*, **20**, 507 (1949).
14. R. P. Kambour, *Appl. Polym. Symp.*, **No. 7**, 215 (1968).
15. S. L. Rosen, *Polym. Eng. Sci.*, **7**, 115 (1967).
16. R. F. Boyer and H. Keskkula, in *Encyclopedia of Polymer Science and Technology*, Vol. 13, N. Bikales, Ed., Interscience, New York, 1970, p. 375.
17. C. G. Bragaw, *Adv. Chem. Ser.*, **No. 99**, 86 (1971).
18. B. W. Bender, *J. Appl. Polym. Sci.*, **9**, 2887 (1965).
19. R. B. Bishop, *Practical Polymerization of Polystyrene*, Cahners Publishing, Boston, 1971, p. 209.
20. R. E. Hannah and R. H. Bond, *J. Appl. Polym. Sci.*, **13**, 337 (1969).

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