Force–Displacement Evaluation of Macromolecular Materials in Flexural Impact Tests. II. Influence of Rubber Content, Degree of Grafting, and Temperature on the Impact Behavior of ABS Resins*

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Synopsis

The impact behavior of ABS (acrylonitrile-butadiene-styrene) resins was studied by measuring the force-deflection curve generated during flexural impact tests. Each curve is characterized by a limited number of significant parameters. Their dependence on the following constitutive or ambient variables was investigated: content of butadiene rubber, degree of grafting of acrylonitrile and styrene onto polybutadiene, and temperature. The results are analyzed phenomenologically and are tentatively interpreted in the light of possible micromechanical mechanisms.

INTRODUCTION

Conventional measurement of impact strength, leading to the value of the total energy lost by a pendulum breaking a test specimen in a standardized fashion, gives only an overall characterization of the impact behavior of macromolecular materials. For more detailed information, we instrumented¹ an Izod tester in such a way as to obtain the force-deflection curve generated during the impact experiment. For a thorough qualitative and quantitative evaluation of materials, a complete stress-strain curve should in general be considered. More conveniently, we select a limited number of significant parameters on the force-deflection curve which, although not representing intrinsic material properties, provides a valuable phenomenologic characterization of the impact behavior.

The present paper deals with the impact behavior of rubber-modified glassy polymers. In order to better understand the toughening action of rubbery particles dispersed in the glassy matrix, the dependence of impact force-deflection curve parameters on the following constitutive or ambient variables was studied on ABS (acrylonitrile-butadiene-styrene) resins: content of butadiene rubber, degree of grafting of acrylonitrile and styrene onto polybutadiene, and temperature.

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EXPERIMENTAL

Materials

A series of ABS samples with varying rubber content was prepared by blending a latex of grafted rubber containing 50 wt % polybutadiene and 50 wt % poly-(styrene-acrylonitrile) with a latex of styrene-acrylonitrile copolymer (SAN resin) in different ratios. A second series of ABS samples, with varying degrees of grafting, was prepared by blending latexes of polybutadiene rubber grafted to different degrees with a latex of styrene-acrylonitrile copolymer (SAN) in such a ratio that the final ABS samples had the same basic rubber content (namely, 32.5 wt % butadiene). Each final ABS sample was then recovered from the latex mixture by coagulation.

More details on the preparation and the characterization of the latter series of samples can be found in a previous paper.² In particular, it is worth recalling that the degree of grafting, defined as the mass ratio of grafted glassy comonomers (i.e., styrene and acrylonitrile) to rubber (i.e., polybutadiene), was determined by measuring the ungrafted glassy polymer ("free" SAN resin) extractable by methyl ethyl ketone according to a suitable separation technique.³

Test Specimens

All samples were compression molded at 180°C into 0.63_5 -cm-thick plates from which standard $6.35 \times 1.27 \times 0.63_5$ -cm bars were cut and, in most cases, V-notched according to ASTM specification⁴ D256-72a.

Measurements

We measured the impact force-deflection curve at room temperature on each sample of the two series of ABS resins considered by means of the Izod-type tester instrumented by us.¹

In addition, an ABS sample of the former series, having a rubber content of 25 wt %, was tested at different temperatures ranging from -160° to $+100^{\circ}$ C. In these experiments, the test specimen was heated or cooled in air, kept at the required temperature for at least 30 min, then transferred to the testing spot as quickly as possible so as to minimize temperature changes, and tested. The actual temperature was measured by means of a thermocouple with the sensing junction embedded into a twin ABS specimen accompanying the test specimen.

Samples of the series of resins having varying rubber content were also tested at low speed in three-point flexure using an Instron tester (cross-head speed 0.5 cm/min).

Each impact or low-speed flexural test was repeated at least five times, and the results were averaged.

RESULTS AND DISCUSSION

The force-deflection curves obtained can be classified into one of the three fundamental types reported in Figure 1, where (a) illustrates brittle fracture, (c) ductile fracture, and (b) intermediate behavior. These curves are generalized



Fig. 1. Examples of typical force-deflection curves obtained on ABS samples: (a) brittle fracture; (c) ductile fracture; (b) intermediate behavior. Also, schematic representation of a force-deflection curve showing significant parameters; F indicates force, W indicates energy, d indicates deflection.

and schematically drawn in the upper right corner of Figure 1, where the selected characteristic parameters are also indicated. Each experimental force-deflection curve was analyzed by means of a suitable computer program¹ in order to obtain the values of these parameters. (By convention, the force and the energies are referred to unit initial cross section of the specimen at notch.)

As previously pointed out,¹ each of these quantities characterizes some particular aspect of impact behavior. For example, the force at the peak, F_m , represents the highest load that the test piece can sustain in *this* test, while W_m is assumed as the energy to failure and W_b and W_p are tentatively taken as measures of the energy associated with yielding and/or crack propagation and of the energy associated with plastic drawing and/or tearing, respectively. Thus, we assume that when fracture is brittle, $W_p = 0$ (abrupt drop of the force to zero), while completely ductile fracture corresponds to $W_b = 0$. However, of these quantities the force at the peak, F_m , and the energy absorbed up to the peak, W_m , would appear to be particularly important. In fact, it seems reasonable to think of the peak as a threshold beyond which the material fails, either by yielding or by brittle fracture.

On the other hand, the quantities W, W_r , and W_p , which also involve the final portion of the force-deflection curve, may suffer from some inaccuracy in the experimental curves at high deflections due to the hammer nose sliding on the specimen.

Rubber Content

By a qualitative examination of electron photomicrographs of sections of different ABS samples from the series with varying rubber content (Fig. 2), the particle morphology shows no apparent differences at different rubber contents. A quantitative analysis of the same photomicrographs confirms that only the number of dispersed rubbery particles increases as the rubber content is increased, while their average size remains practically constant, as expected in view of the method adopted for the preparation of this series of samples.

The type of force-deflection curves produced with notched specimens varies from (a) to (b) to (c) (referring to Fig. 1) as the rubber content goes from zero to

Rubber F_m , workbed W_m , kg/cm ² W_m , dm, cm W_m , kg cm/cm ² W_m W_m W_m <									
content kg/cm ² d_m , cm kg-cm/cm ² k	R	ubber	Fm,		W _m ,	W _b ,	W_p ,	Wr,	<i>W</i> ,
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	S	ontent	kg/cm ²	d_m , cm	$kg \cdot cm/cm^2$	$kg \cdot cm/cm^2$	$kg \cdot cm/cm^2$	kg · cm/cm ²	$kg \cdot cm/cm^2$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	8	{ notched ¹ unnotched ^b	7.6 ± 3.6ª	0.03 ± 0.02	0.09 ± 0.05	0.07 ± 0.05	0.0	0.07 ± 0.05	0.2 ± 0.1
76 lumotched 102.6 \pm 6.7 0.21 \pm 0.02 11.5 \pm 0.6 3.1 \pm 1.3 14.6 10% lumotched 39.8 \pm 3.0 0.09 \pm 0.01 2.0 \pm 0.3 0.4 \pm 0.1 0.0 3.1 \pm 1.3 14.6 10% lumotched 39.8 \pm 3.0 0.09 \pm 0.01 2.0 \pm 0.3 0.4 \pm 0.1 0.0 0.4 \pm 0.1 2.4 10% lumotched 39.4 \pm 6.6 0.24 \pm 0.04 13.0 \pm 2.9 5.7 \pm 1.8 0.0 0.4 \pm 0.1 2.4 14% lumotched 94.9 \pm 6.6 0.24 \pm 0.04 13.0 \pm 2.9 5.7 \pm 1.8 0.0 0.4 \pm 0.1 2.4 14% lumotched 97.8 \pm 4.1 0.29 \pm 0.05 17.6 \pm 4.5 6.0 \pm 1.8 0.0 6.4 \pm 1.1 2.4 18% lumotched 93.4 \pm 1.9 0.29 \pm 0.05 17.6 \pm 4.5 6.0 \pm 1.8 0.0 6.4 \pm 1.8 2.4 25% lumotched 93.4 \pm 1.9 0.29 \pm 0.05 11.5 \pm 1.1 3.7 \pm 1.3 2.4 0.0 0.1 \pm 0.5 2.4 0.6 1.4 \pm 0.6 0.0 2.4	Loi	f notched	27.0 ± 3.7	0.04 ± 0.02	0.6 ± 0.4	0.3 ± 0.3	0.0	0.3 ± 0.3	0.9 ± 0.4
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	9%0	l unnotched	102.6 ± 6.7	0.21 ± 0.02	11.5 ± 0.6	3.1 ± 1.3	0.0	3.1 ± 1.3	14.6 ± 1.7
10% lumotched 94.9 \pm 6.6 0.24 \pm 0.04 13.0 \pm 2.9 5.7 \pm 1.8 0.0 5.7 \pm 1.8 18.7 = 14% lumotched 97.8 \pm 4.1 0.29 \pm 0.05 17.6 \pm 4.5 6.0 \pm 1.8 0.0 6.4 \pm 0.1 3.0 = 18% lumotched 97.8 \pm 4.1 0.29 \pm 0.05 17.6 \pm 4.5 6.0 \pm 1.8 0.0 0.4 \pm 0.1 3.0 = 18% lumotched 59.8 \pm 5.2 0.20 \pm 0.02 6.6 \pm 1.4 1.1 \pm 0.5 0.0 1.1 \pm 0.5 7.7 = 18% lumotched 59.4 \pm 1.8 0.23 \pm 0.03 11.5 \pm 1.1 3.7 \pm 1.3 2.8 \pm 0.6 6.9 \pm 1.0 18.0 25% lumotched 59.7 \pm 2.0 0.32 \pm 0.03 11.5 \pm 1.1 3.7 \pm 1.3 2.8 \pm 0.6 6.9 \pm 1.0 18.0 32% lumotched 59.7 \pm 2.0 0.32 \pm 0.01 34.6 \pm 0.7 0.0 11.1 \pm 0.5 7.7 = 32% lumotched 59.7 \pm 1.9 3.7 \pm 1.3 3.7 \pm 1.3 2.8 \pm 0.6 6.9 \pm 1.0 18.0 32% lumotched 53.0 \pm 1.4	1000	f notched	39.8 ± 3.0	0.09 ± 0.01	2.0 ± 0.3	0.4 ± 0.1	0.0	0.4 ± 0.1	2.4 ± 0.4
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	¥01	l unnotched	94.9 ± 6.6	0.24 ± 0.04	13.0 ± 2.9	5.7 ± 1.8	0.0	5.7 ± 1.8	18.7 ± 2.6
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	1 400	f notched	44.1 ± 3.8	0.11 ± 0.01	2.5 ± 0.3	0.4 ± 0.1	0.0	0.4 ± 0.1	3.0 ± 0.4
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	14%	unnotched	97.8 ± 4.1	0.29 ± 0.05	17.6 ± 4.5	6.0 ± 1.8	0.0	6.0 ± 1.8	23.6 ± 3.7
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	1 007	f notched	59.8 ± 5.2	0.20 ± 0.02	6.6 ± 1.4	1.1 ± 0.5	0.0	1.1 ± 0.5	7.7 ± 1.9
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	10%	l unnotched	93.4 ± 1.8	0.45 ± 0.06	28.3 ± 4.8	4.1 ± 0.6	0.0	4.1 ± 0.6	32.4 ± 5.4
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0 E ov	Inotched	59.7 ± 2.0	0.32 ± 0.03	11.5 ± 1.1	3.7 ± 1.3	2.8 ± 0.6	6.9 ± 1.0	18.0 ± 2.1
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	94.07	lunnotched	80.4 ± 1.9	0.59 ± 0.01	34.6 ± 0.7	0.0	v	v	v
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	000	Inotched	53.0 ± 1.4	0.40 ± 0.04	13.1 ± 2.6	0.0	11.5 ± 3.0	11.5 ± 3.0	24.6 ± 4.3
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	97.76	l unnotched	62.1 ± 2.8	0.54 ± 0.01	23.7 ± 1.7	0.0	IJ	υ	Ų
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	36%	{ notched { unnotched ^b	46.1 ± 1.2	0.38 ± 0.04	11.5 ± 1.9	0.0	18.6 ± 2.2	18.6 ± 2.2	30.1 ± 1.9
40% humotched 50.0 ± 0.5 0.62 ± 0.05 22.4 ± 1.9 0.0 c c c	200	Inotched	43.2 ± 1.3	0.47 ± 0.02	13.2 ± 0.9	0.0	22.7 ± 0.9	22.7 ± 0.9	35.9 ± 1.3
	40.40	l unnotched	50.0 ± 0.5	0.62 ± 0.05	22.4 ± 1.9	0.0	v	υ	υ

Force-Deflection Curve Parameters in Imnact Tests on ABS Resins with Different Ruhher Content TABLE I

^a The error limits are one standard deviation from the mean.

^b Not determined. ^c Not calculated because specimens did not break during test.

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TABLE II	Force-Deflection Curve Parameters in Impact Tests on ABS Resins at Different Temperatures
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l emperature, °C	<i>rm,</i> kg/cm ²	d_m , cm	W _m , kg-cm/cm ²	W _b , kg-cm/cm ²	W _p , kg-cm/cm ²	W _r , kg-cm/cm ²	W, kg•cm/cm²
-160	35.5 ± 4.2ª	0.07 ± 0.01	1.1 ± 0.3	0.5 ± 0.07	0.0	0.5 ± 0.07	1.6 ± 0.4
-139	35.6 ± 3.8	0.06 ± 0.02	1.1 ± 0.4	0.5 ± 0.1	0.0	0.5 ± 0.1	1.6 ± 0.4
-130	31.3 ± 0.6	0.08 ± 0.01	1.4 ± 0.1	0.5 ± 0.1	0.0	0.5 ± 0.1	1.9 ± 0.1
-101	30.1 ± 8.4	0.07 ± 0.04	1.3 ± 1.2	0.6 ± 0.4	0.0	0.6 ± 0.4	1.8 ± 1.2
-78	34.1 ± 10.6	0.14 ± 0.09	3.2 ± 2.8	0.5 ± 0.2	0.0	0.5 ± 0.2	3.7 ± 3.0
69-	32.9 ± 12.7	0.11 ± 0.06	2.3 ± 1.5	0.5 ± 0.2	0.0	0.5 ± 0.2	2.7 ± 1.7
-60	34.1 ± 4.2	0.11 ± 0.01	2.0 ± 0.5	0.6 ± 0.1	0.0	0.6 ± 0.1	2.5 ± 0.5
-51	47.4 ± 13.3	0.17 ± 0.06	4.9 ± 2.9	0.7 ± 0.3	0.0	0.7 ± 0.3	5.7 ± 3.2
-32	63.9 ± 3.1	0.24 ± 0.01	9.2 ± 0.6	1.6 ± 0.4	0.0	1.6 ± 0.4	10.8 ± 0.7
-18	63.1 ± 3.6	0.24 ± 0.01	9.4 ± 0.4	2.6 ± 0.6	0.0	2.6 ± 0.6	12.2 ± 0.8
မို	61.3 ± 2.7	0.24 ± 0.02	9.1 ± 0.9	2.6 ± 0.6	0.4 ± 0.2	3.1 ± 0.8	12.1 ± 1.8
+17	65.6 ± 3.1	0.31 ± 0.03	12.9 ± 2.0	3.3 ± 3.3	3.0 ± 1.1	6.4 ± 2.9	19.3 ± 2.3
+25	59.7 ± 2.0	0.32 ± 0.03	11.5 ± 1.1	3.7 ± 1.3	2.8 ± 0.6	6.9 ± 1.0	18.0 ± 2.1
+48	61.6 ± 1.0	0.31 ± 0.03	11.6 ± 1.3	5.0 ± 1.3	3.8 ± 0.5	8.8 ± 2.0	20.9 ± 1.7
+64.5	49.2 ± 1.4	0.28 ± 0.01	8.8 ± 0.6	2.9 ± 0.4	3.8 ± 1.0	6.8 ± 0.6	14.8 ± 0.8
+68	48.0 ± 2.3	0.33 ± 0.01	9.6 ± 0.4	2.4 ± 1.4	4.7 ± 1.2	8.9 ± 1.8	18.5 ± 2.1
+81.5	43.0 ± 2.4	0.25 ± 0.03	6.6 ± 1.3	0.0	5.7 ± 1.9	5.7 ± 1.9	12.3 ± 3.1
66+	38.1 ± 0.6	0.22 ± 0.01	4.8 ± 0.0	0.0	5.2 ± 0.4	5.2 ± 0.4	10.0 ± 0.4

^a The error limits are one standard deviation from the mean.



(a)



(b) Fig. 2. (Caption on following page.)



(c)

Fig. 2. Examples of phase-contrast electron photomicrographs of ABS samples with different rubber content studied in this work: (a), (b), (c) correspond to 5, 25, and 40 wt % rubber, respectively. (Photomicrographs supplied by courtesy of ANIC S.p.A.)

40 wt %. That is, the fracture mode is brittle $(W_p = 0)$ up to about 20 wt % rubber and becomes completely ductile $(W_b = 0)$ at about 30 wt % rubber.

The results obtained after processing the experimental data are listed in Table I. Mean values of each parameter resulting from five or more determinations are shown, together with the corresponding standard deviations. Although evaluated on a limited number of observations, they give an idea of the scattering of the results and hence of the reliability of the mean values obtained. Smoothed curves fitted to the mean experimental points are plotted in Figure 3 against rubber content. We will examine only the most significant features of these curves.

Total energy W, which substantially corresponds to the conventional Izod "impact strength," increases with rubber content, in agreement with the findings of other authors.⁵⁻¹⁰ Several mechanisms have been proposed to explain the toughening action of rubber particles embedded into a glassy polymer.¹¹⁻¹⁷ According to today's most accepted view,^{16,18,19} the rubber particles act as stress concentrators and also have a stress-sustaining role such as to cause the surrounding matrix to craze and/or to yield, processes which can involve large absorptions of energy. If other things are equal, the energy absorbed by the unit volume of composite material will increase as the number of dispersed rubber particles increases.

As for the other energy terms, W_p and W_r show the same behavior as total energy W, while the more significant term W_m , i.e., the energy to initiate frac-



Fig. 3. Force F_m at the peak and energy parameters vs. rubber content in impact tests on notched samples.

ture,²⁰ first increases and then reaches a "plateau" beyond a rubber content of about 25 wt %.

The force at the peak, F_m , becomes maximum at 20–25 wt % rubber content. The increase of F_m before the maximum can be understood if we bear in mind the effect of the notch. It is known that a notch concentrates the stresses at its tip and hence reduces the strength of a glassy polymer. In rubber-modified glassy resins, crazing caused by the presence of toughening rubber particles in the glassy matrix under stress will, therefore, start at the tip of the notch. As a consequence of this localized plastic deformation, the radius of curvature at the root of the notch increases, and this reduces the maximum stress at its tip according²¹ to the equation

$$\sigma_{\max} = 2\sigma_0 (c/\rho)^{1/2}$$
 valid for $c \gg \rho$



Fig. 4. Force F_m at the peak vs. rubber content in impact tests on (b) notched and (a) unnotched samples.



Fig. 5. Energy W_m absorbed up to the peak vs. rubber content in impact tests on (b) notched and (a) unnotched samples.

where σ_{\max} is the maximum stress at the tip of the crack or notch, σ_0 is the applied stress, c is the crack or notch depth, and ρ is the radius of curvature at the tip of the crack or notch. Thus, a higher value of external applied force must be reached for fracture to occur, and this effect, originating from the presence of rubbery particles, clearly increases as the amount of rubber increases. Hence, F_m is observed to go up until it reaches a maximum when another effect begins to dominate. This latter effect, causing strength to decrease at higher rubber contents, can be ascribed to interaction between the progressively densening rubber particles until they adjoin each other. As the number of particles increases, the average distance between them decreases and the fields of concentrated stresses around them come to overlap, thus raising the stress concentration in the surrounding matrix.²² If we assume that the toughening efficiency of a



Fig. 6. Deflection d_m up to the peak vs. rubber content in impact tests on (b) notched and (a) unnotched samples.



Fig. 7. Force F_m at the peak and energy parameters vs. temperature in impact tests on notched samples.

single particle remains the same, the material will fail at lower values of external applied force.

To support this view, we made comparative experiments on notched and unnotched specimens of the same samples. Of course, the comparison can be qualitative only since the quantities in question are not intrinsic properties of the material but depend also on the specimen's geometry and dimensions. The results obtained are shown in Figures 4, 5, and 6 for F_m , W_m , and d_m , respectively. It should be noted that unnotched specimens do not break when the rubber content is higher than about 20 wt %. In this case, the force at the peak, F_m , represents a yielding point rather than the force to initiate fracture, and W_m correspondingly represents the energy to yield.

It can be seen in Figure 4 that force F_m is approximately constant or slightly decreasing at low rubber contents in the case of unnotched specimens, while it increases by adding rubber when the specimens are notched. Beyond a certain rubber content, the interaction between the fields of concentrated stresses induced by the particles makes F_m decrease in both cases. As for the terms W_m and d_m (Figs. 5 and 6), the different behavior of notched and unnotched specimens has not been analyzed, although it may have some interest.

Finally, we may just mention that the three-point bending experiments carried out on notched and unnotched specimens at low speed gave very similar results²³ to those illustrated above.

Temperature

Results of impact experiments at different temperatures are listed in Table II and plotted in Figure 7 after smoothing out the irregularities of the experimental data.

All energy terms are low and nearly constant at very low temperatures up to about -80° C, which is expected since both the inclusions and matrix are glassy in this temperature region. Above -80° C, energies W_m and W increase because of the glass-rubber transition of polybutadiene: the dispersed particles, becoming rubbery, can promote their toughening action. Total energy W has been

Degree of grafting	F_m , kg/cm ²	d_m , cm	$W_m,$ kg · cm/cm ²
0	21.3 ± 1.8^{a}	0.09 ± 0.01	0.9 ± 0.2
0.15	49.1 ± 1.0	0.44 ± 0.02	13.7 ± 0.7
0.32	54.2 ± 1.8	0.56 ± 0.05	20.6 ± 1.5
0.495	50.7 ± 1.7	0.47 ± 0.01	16.0 ± 0.7
0.60	51.3 ± 1.2	0.45 ± 0.04	15.9 ± 0.9
0.69	56.7 ± 0.9	0.55 ± 0.03	21.5 ± 1.2
0.80	53.8 ± 1.6	0.52 ± 0.04	18.3 ± 2.4
0.92	53.5 ± 3.0	0.44 ± 0.02	15.8 ± 0.7
1.05	54.5 ± 2.4	0.55 ± 0.04	20.8 ± 1.4

TABLE III Force–Deflection Curve Parameters in Impact Tests on ABS Resins with Different Degrees of Grafting

^a The error limits are one standard deviation from the mean.

found to follow the same trend by other authors, too.^{6,7,24} Energy W_m reaches a broad maximum at about 0°C. When the temperature is raised still further, the mode of fracture gradually changes from brittle to ductile: W_p begins to rise and, consequently, W_r increases more steeply up to about 40°C, where it reaches a maximum. Two mechanisms may be operative at the same time in this temperature range: the naturally occurring yielding of the glassy matrix and the crazing promoted by the rubbery particles. After reaching a maximum, all the energy terms decrease, which may be attributed to a lesser orientation hardening of the crazed and yielded material at the tip of the notch or advancing crack.²⁵

The behavior of the force at the peak, F_m , can be explained once again with reference to the expected behavior of unnotched specimens. It is known that the flexural strength of glassy polymers ("brittle strength") decreases with increasing temperature up to the brittle-ductile transition, beyond which the strength ("yield strength") falls even more steeply.²⁶ Below -80° C, ABS resins are thus expected to show a brittle strength which decreases with increasing temperature. In impact tests on notched specimens, F_m will thus follow the same trend, though at a rather lower level because of the stress concentration brought about by the notch. Above -80° C, polybutadiene becomes rubbery and the rubbery particles can and do promote crazing in the matrix under stress, which reduces the severity of the notch. As discussed above under the heading "rubber content," a higher value of external applied force must then be reached for fracture to occur, so that F_m is observed to increase. Above 0°C, the softening effect of increasing temperature dominates so that F_m starts falling, following the trend normally observed for the flexural strength of polymers.

Degree of Grafting

While the weight fraction of polybutadiene in this series of ABS samples was kept constant, photomicrographs obtained by electron microscopy of sections of the specimens show remarkable morphologic variations as the degree of grafting varies (Fig. 8). Two main features are evident². First, at one extreme (i.e., scarcely grafted samples), the incompatibility of polybutadiene with the 440

matrix polymer induces the particles to coalesce, while at the other extreme (i.e., highly grafted samples), a sort of barrier seems to prevent them from coalescing, which may indicate the existence of an outer shell formed by the glassy copolymer grafted on the rubber particle. Second, as the degree of grafting increases, there







Fig. 8. Examples of phase-contrast electron photomicrographs of ABS samples with different degree of grafting: (a), (b), and (c) correspond to degrees of grafting of 0.15, 0.32, 0.69, respectively. (Photomicrographs supplied by courtsey of ANIC S.p.A.)

is an increasing amount of glassy polymer subinclusions distributed in the rubber particles.

The type of impact force-deflection curves obtained on this series of ABS samples changes immediately from (a) to (c) (refer to Fig. 1) as the degree of grafting passes from 0 to 0.15. At higher degrees of grafting, impact behavior remains ductile, and the deflections reached during the impact experiment are so high as to make the evaluation of the energy terms W_r and W unreliable. In some cases, complete fracture did not even occur, and the hammer nose slid on



Fig. 9. Force F_m at the peak and energy W_m absorbed up to the peak vs degree of grafting in impact tests on notched samples.

the bent test piece. For these reasons, only the results of F_m and W_m are examined (Table III and Fig. 9). As can be seen, both these parameters increase as the degree of grafting increases but soon level off. This behavior can be interpreted as an effect of the increasing degree of interfacial adhesion between the two phases^{2,7,24} which enhances the toughening efficiency of rubber.

Other factors may play a role, too. For example, the increasing amount of glassy subinclusions in the rubber particles should contribute to improving impact resistance as these subinclusions increase the overall volume fraction of the dispersed phase.^{27,28} On the other hand, the presence of glassy subinclusions as such, by reducing the thermal stresses in the matrix surrounding the dispersed particles,²⁹ should have an opposite effect.

COMMENTS

We have reported the results of an extensive and detailed characterization of the impact behavior of ABS resins, obtained by measuring the force-displacement curve generated during impact experiments and analyzing a number of parameters of these curves. Treatment of the data by fracture mechanics analysis to obtain intrinsic properties of the material was not attempted. At this stage, we intended first to enlarge our knowledge of the phenomenology of impact behavior, by varying some constitutive or ambient factors, such as rubber content, degree of grafting, and temperature. The results can tentatively be interpreted in the light of possible micromechanical mechanisms.

From a practical point of view, the results of the present investigation confirm that the conventional characterization of the impact resistance of macromolecular materials by the value of total energy W absorbed in an Izod-type test is inadequate and misleading. We propose¹ to characterize the impact resistance of a material (in *this* test) by the two parameters F_m , the highest load that the test piece can sustain, and W_m , the energy to failure. In fact, it seems reasonable to think of the peak in the impact force-deflection curve as a threshold beyond which the material fails. A good impact resistance will then be achieved when both F_m , which we would rename *impact strength*, and W_m , which we would rename *impact toughness*, are high.

The validity of this proposal is well illustrated by a result emerging from our experiments on ABS samples with varying rubber content. According to the conventional characterization of impact resistance by the Izod test, the higher the rubber content, the higher the resistance to impact (i.e., the higher the total energy W absorbed in this test). Yet, according to our criteria, there is, more realistically, a definite optimal value of the rubber content (in our particular case, 20 wt %) where this material is of the best quality (F_m and W_m both high). A further addition of rubber makes strength F_m decrease while energy to initiate fracture W_m remains constant, even if total energy W, i.e., the conventional measure of impact strength, keeps increasing. Such an increase in W is associated with an increase in the fraction of energy W_r absorbed beyond the peak, where the test piece's ability to bear the impulsive load has already failed.

With respect to temperature, the results obtained for F_m and W_m indicate that the particular ABS resin examined performs best in the temperature range between 0° and 30°C.

Finally, grafting has often been looked upon as an important prerequisite to

provide a better toughening efficiency of the rubbery phase dispersed into a glassy polymer. However, to what extent and in what way the rubber particles had to be grafted in order to achieve maximum toughening efficiency still seems to be a point to be clarified. The present investigation shows that the degree of grafting does not need to be very high.

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