Impact Thermoplastics: Combined Role of Rubbery Phase Volume and Particle Size on Toughening Efficiency

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Synopsis

A relationship has been found for OSA (olefin-acrylonitrile-styrene) polymers between normalized Izod impact strength ($\Delta I/N$) or yield stress ($\Delta\sigma y/N$) with mean particle radius. These normalized functions (which analytically include radius and rubbery phase volume) are representative of the toughening effect of a single particle with respect to the styrene-acrylonitrile (SAN) rigid matrix. $\Delta I/N$ and $\Delta\sigma y/N$ increase exponentially as a function of the radius. This approach, for Izod, was also applied to HIPS and toughened nylon reported in the literature and similar results were obtained. In the case of nylon, however, the $\Delta I/N$ values are split in two different curves related to the tough-brittle transition described in that literature. Referring to OSA, three samples (with the largest radii more than 0.22 μm) fail in a brittle manner and do not fit the curve of $\Delta I/N$: they fit, however, that of $\Delta\sigma y/N$. Further work must be done in order to investigate a decisive role either of interfacial adhesion (eventual lack for these three materials) or of tough-brittle transition mentioned before for shear-yielding deforming materials. In fact, OSA has behavior intermediate between that of nylon and HIPS which deforms by crazing.

INTRODUCTION

For rubber-toughened polymers an extensive literature exists concerning the role of such parameters as dispersed rubbery phase volume, size of rubbery particles, and interfacial adhesion. Regarding mechanical properties and especially impact strength, results were described in which the Izod increases with particle size (e.g., in HIPS[1,2] and in ABS[3,4] or presents an optimum particle size,[5-7] and in general is influenced by the rubbery volume fraction.[8,9] Also, a previous work of ours[10] gave indications on HIPS series with different particle size, relatively constant swelling index of the dispersed phase, and molecular weight of the continuous phase: for these the Izod increases as a function of volume fraction (expressed as gel%) with increments having a maximum as a function of particle size.

It was emphasized[8] that the results must be considered carefully due to the possible interrelations between particle size and interfacial tension. What has been described here refers to a class of products in which there is considerable deformation by crazing.

For products deforming essentially by shear yielding the main aspect controlling the impact strength is the presence of a tough-brittle[11,12] transition dependent on interparticle distance (ID). The brittleness takes place over a critical value of this parameter, keeping constant and sufficient the interfacial adhesion (a minimum value of 1000 J/m^2 was suggested.) For matrices

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showing both crazing and shear yielding, as for example SAN (styrene-acrylonitrile copolymer) and PP (polypropylene), the competition between the two mechanisms was also described. Besides the influence of the deformation rates,[13,14] an effect of particle size on the two mechanism balance was also reported.[13,15,16]

Shear yielding is induced preferentially by small particles while crazing is induces by large ones: this was shown for ABS,[13] rubber-toughened PP,[15] and epoxy.[16] A particle size was also described for a pure crazing deforming material such as HIPS. Small particles are ineffective in toughening because they cannot control craze growth[8] and/or craze nucleation[17] or they can nucleate crazes only at low deformation rates.[7] In this work, an attempt is made to better understand the combined effect of volume fraction and particle size in toughened plastics. This is done by normalizing the considered mechanical characteristics (Izod and yield stress), supposing sufficient interphase adhesion (on the basis of chemicophysical characterization), due to presence of suitable graft copolymer at the interface.

EXPERIMENTAL

Materials

A series of OSA products (styrene-acrylonitrile copolymer toughened by an olefinic-based rubbery phase) was investigated (Table I). The process conditions (bulk continuous process) were chosen in order to obtain suitable structure and amount of rubber-SAN-grafted copolymer, suitable SAN molecular weights, and different rubbery particle sizes. Different levels of rubbery

TABLE I
Characterization Results for OSA Polymers

Sample	R_w (μm)	Rubbery Phase Volume	Elastic Modulus (MPa)	Yield Stress (MPa)	Izod 1/2 × 1/2" (J/m)
A	0.081	0.413	1500	35.0	65
B	0.118	0.412	1400	30.0	350
C	0.124	0.450	1200	23.7	590
D	0.147	0.414	1450	29.0	710
E	0.145	0.375	1600	32.5	590
F	0.097	0.203	2400	41.5	85
G	0.083	0.203	2350	43.5	45
H	0.157	0.418	1450	30.0	725
I	0.124	0.407	1500	30.6	345
J	0.177	0.468	1000	21.6	700
K	0.118	0.313	1800	35.0	320
L	0.210	0.353	1400	28.6	780
M	0.142	0.337	1850	34.0	470
N	0.107	0.236	2250	43.5	160
O	0.222	0.352	1600	26.5	240
P	0.248	0.287	1900	26.7	100
Q	0.270	0.441	1000	16.7	220

phase volume ϕ were obtained, in some cases by blending the original materials with SAN.

The SAN matrix molecular weights of all samples were similar (with variations smaller than 7%) to assure a good processability. The products were characterized at various stages of the reaction with separation methods to obtain the amount of the components: SAN, rubber, and SAN-rubber graft copolymer. The mean values and distribution of the molecular weights of the components and the graft copolymer composition distribution were determined by multidetector GPC.[18] The amount, composition, molecular weight, and hypothetical structures of the components (in particular the graft ones) are believed to produce a sharp decrease in interfacial tension (with respect to the pure, ungrafted SAN/rubber system). Slightly higher values of interfacial tension are reasonably expected for the samples with particle radius larger than 0.22 μm (O, P, Q Table I). The interfacial adhesion is supposed to be sufficient for mechanical response at least, in all the other cases.

Rubbery Phase Volume and Particle Size

As volume fraction ϕ we considered the weight percent of the sum of the rubbery phase components: the rubber and the SAN-rubber graft copolymer. Apart from minor corrections made to account for density differences, this parameter well represents ϕ. Support is given in Figure 1, in which the correlation is shown with the elastic modulus in analogy to that reported for HIPS.[19] Using only rubber content as ϕ leads to a worse correlation. As indicative of particle size, the weight average radius R_w was chosen (the

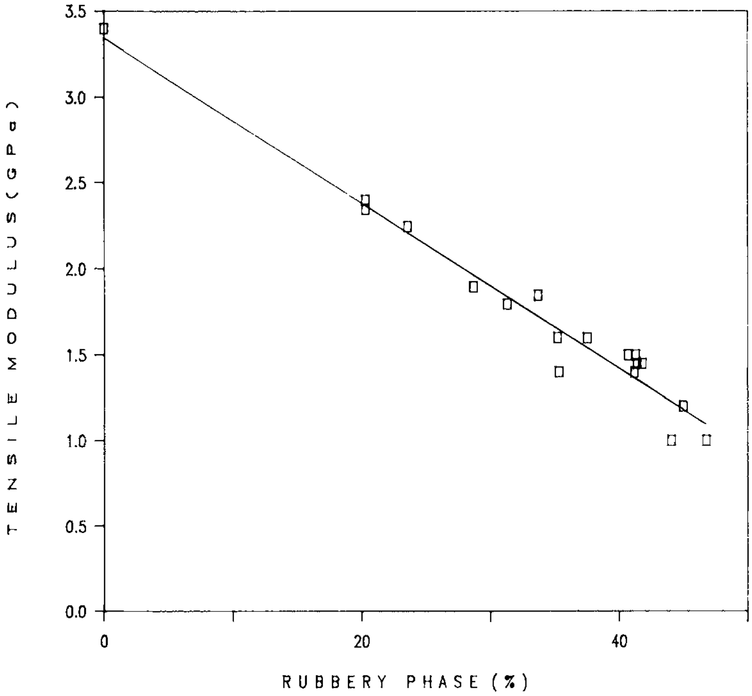

Fig. 1. OSA polymers: variation of tensile elastic modulus vs. rubbery phase volume percent.

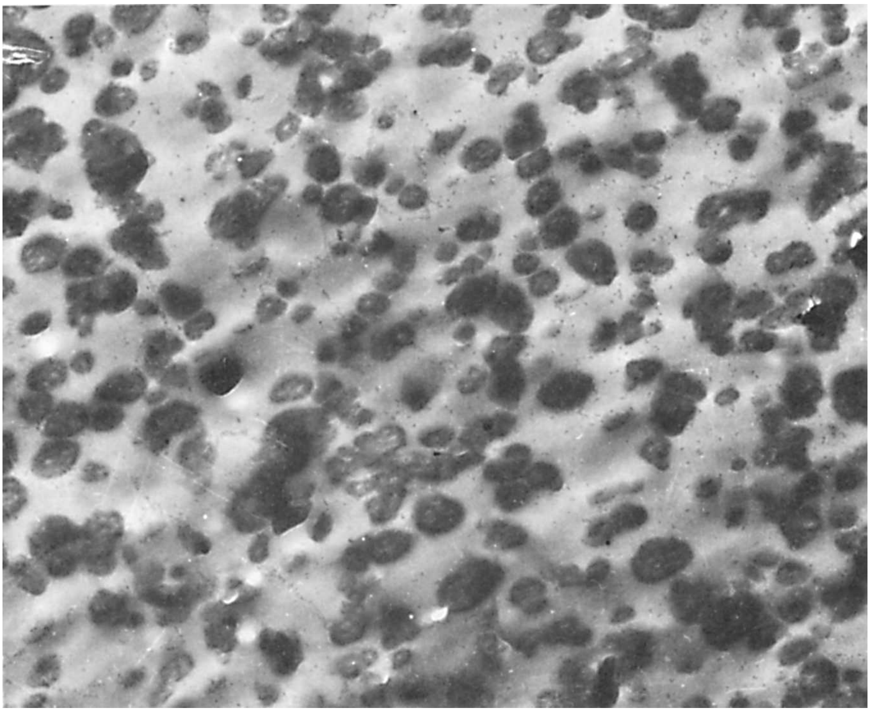

Fig. 2. TEM micrograph (21,000 ×) of an OSA polymer (material K of Table I).

essential features of our results are similar using the number average radius R_n). The radii were calculated by counting and measuring the particles on a statistically representative number of transmission electron mycrographs(TEM). All OSA materials have a modomodal particle size distribution and very similar polydispersities (R_w/R_n about 1.3). The technique used is essentially that described by Kato[20] with some optimization for enhacing the olefinic rubbery phase contrast. In Figure 2 an example of a micrograph relative to sample K is reported.

Mechanical Testing

Izod impact strength (ASTM D256) was measured on 1/2″ thick specimens. Tensile modulus and yield stress were measured (ASTM D638) on dumbbell, 1/8″ thick specimens. The molding conditions were chosen in order to reduce the anisotropy at low levels. In general, this was more easily achieved on Izod specimens due to their larger thickness.

RESULTS AND DISCUSSION

OSA

In Table I the experimental results relative to OSA materials are reported: they include ϕ, R_w, elastic modulus E, yield stress σy, and notched Izod impact strength. It is shown (Fig. 1) that E is in good correlation with ϕ; on

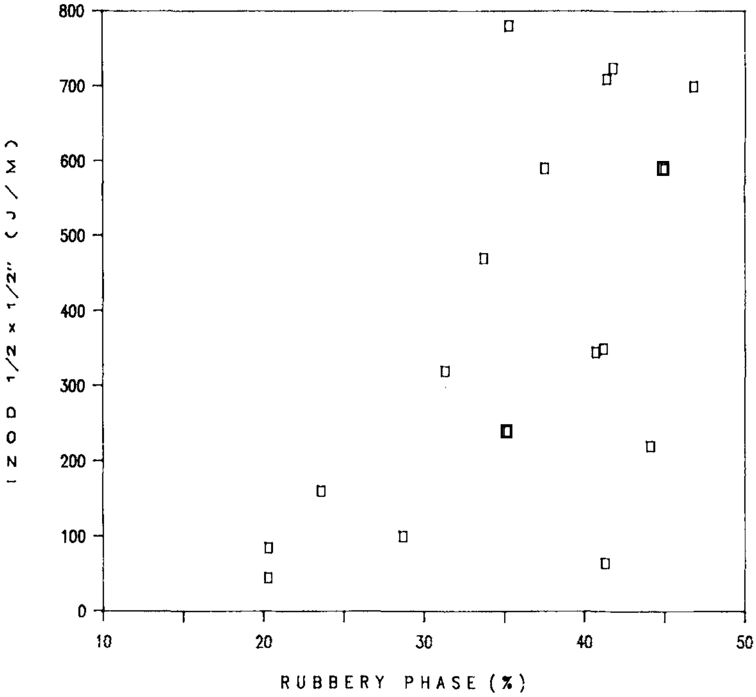

Fig. 3. OSA polymers: plot of Izod impact strength (1/2 × 1/2" specimens) vs. rubbery phase volume percent.

the contrary, Izod impact strength presents only a general increasing trend as ϕ increases, but with a large scattering (Fig. 3). It is evident that other structural parameters must be considered to obtain clearer insight into this mechanical property. Considering morphological parameters such as particle size, interfacial surface per unit volume, interparticle distance (ID), and number of particles per unit volume, better correlations with Izod values have not been found. Therefore, we made the hypothesis that a specific toughening effect per single particle should be correlated in some way with particle radius. For this purpose we introduce the quantity $\Delta I/N$ in which: ΔI is the difference between the Izod value of a toughened sample and that of SAN brittle continuous phase (for this a constant value of 15 J/m was assumed), and

$$N = \frac{\phi}{\frac{4}{3}\pi R^3}$$

represents the particle number per unit volume. So $\Delta I/N$ gives an estimate of the Izod increase produced by a single particle. Figure 4 shows the exponential increase of $\Delta I/N$ as a function of R_w; therefore, the larger the particle size, the larger the normalized toughening effect. One can see that the samples with the largest particles ($R_w > 0.22$ μm, samples O, P, Q, in Table I) do not fit this correlation. An interpretation of the behavior of these samples will be attempted later. At the moment they are not considered. A direct observation

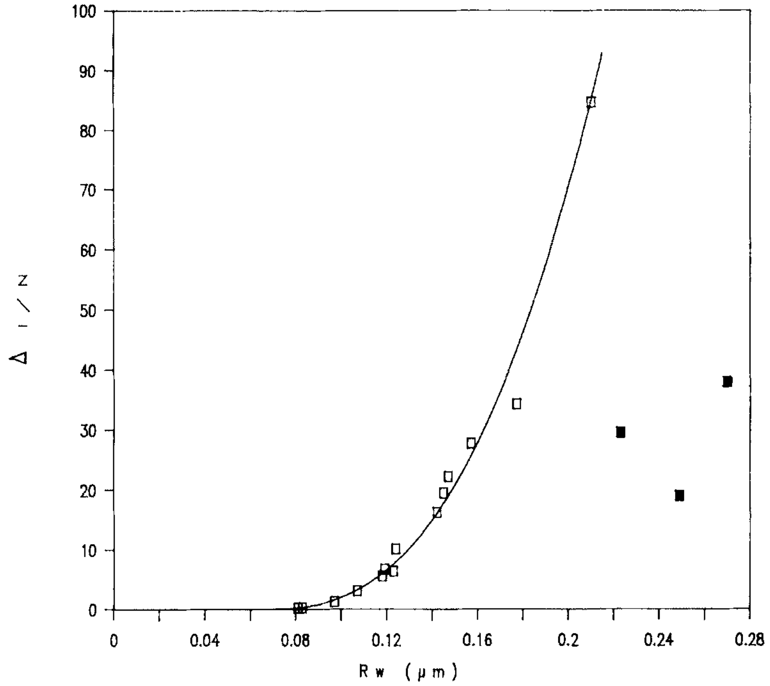

Fig. 4. OSA polymers: normalized Izod increase $\Delta I/N$ vs. weight-average particle radius R_w. Full symbols refer to materials O, P, Q of Table I. The continuous curve is the regression (excluding materials O, P, Q).

of the diagram of Figure 4 suggests the existence of a critical radius value R_c below which the specific toughening effect appears to vanish. The exponential form of the curve could have an analytical expression by a linear regression between $\mathrm{Log}(\Delta I/N)$ and $\mathrm{Log}(R_w)$. The existence of a critical radius is supported by the fact that the correlation coefficient R^2 improves by introducing R_c [i.e., making the regression between $\mathrm{Log}(\Delta I/N)$ and $\mathrm{Log}\,(R_w - R_c)$]. The maximum value of R^2 was obtained with $R_c = 0.065$ μm. The equation results

$$\Delta I/N = 13706 \cdot (R_w - 0.065)^{2.633} \tag{1}$$

where R_w is expressed in μm and ΔI in J/m. The bilogarithmic representation of the experimental points and of the regression is reported in Figure 5. From Eq. (1) it is possible to compute the values of ΔIzod (Izod-15 J/m) as a function of the radius at various ϕ levels. This is shown in Figure 6 where it is possible to observe that ΔI tends to zero when R_w tends to R_c. A theoretical Izod maximum is predicted, by Eq. (1), at R_w about 0.53 μm. It also marks the radius of the sample L as the largest one fitting the regression. Even if this is an approximation from Eq. (1) it is possible to compare the experimental Izod values with the calculated ones. This is reported in Figure 7 and a rather good agreement is observed (of course, excluding materials O, P, Q).

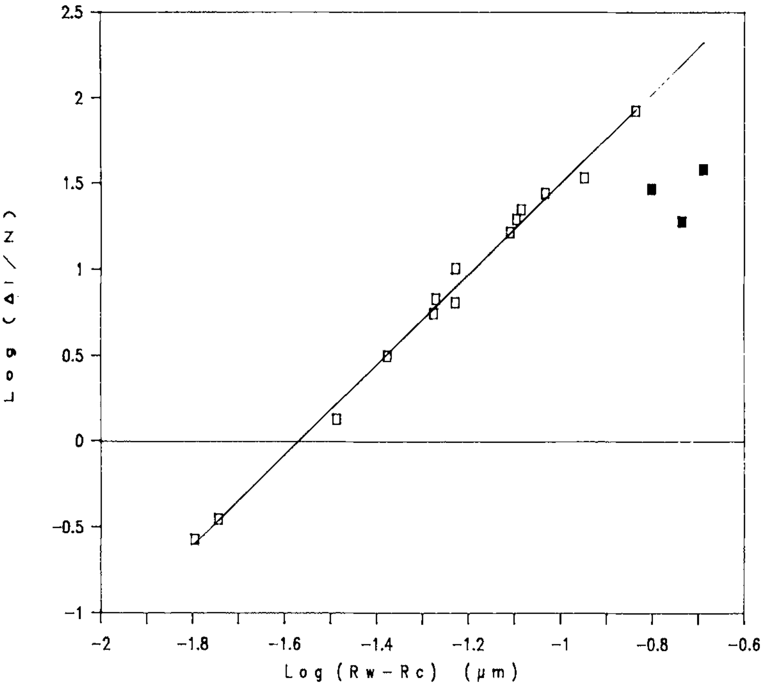

Fig. 5. OSA polymers: bilogarithmic plot of $\Delta I/N$ vs. $R_w - R_c$. The critical radius R_c has been estimated 0.065 μm. The straight line is the regression. Full symbols refer to materials O, P, Q, of Table I.

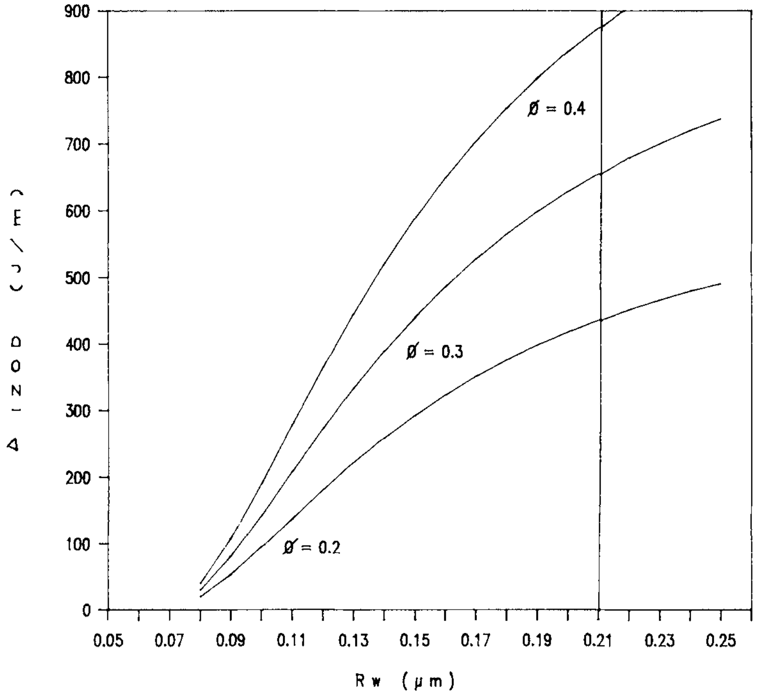

Fig. 6. OSA polymers: calculated Izod increase ΔI vs. R_w at various ϕ levels. The radius of material L of Table I is marked (see text).

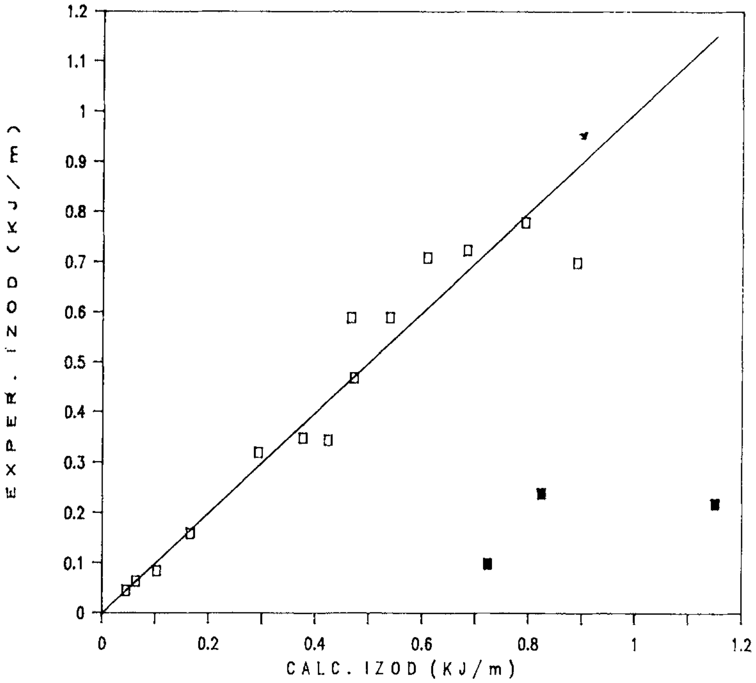

Fig. 7. OSA polymers: plot of experimental Izod values vs. calculated ones. The line represents the ideal case of perfect agreement. Full symbols refer to materials O, P, Q of TAble I.

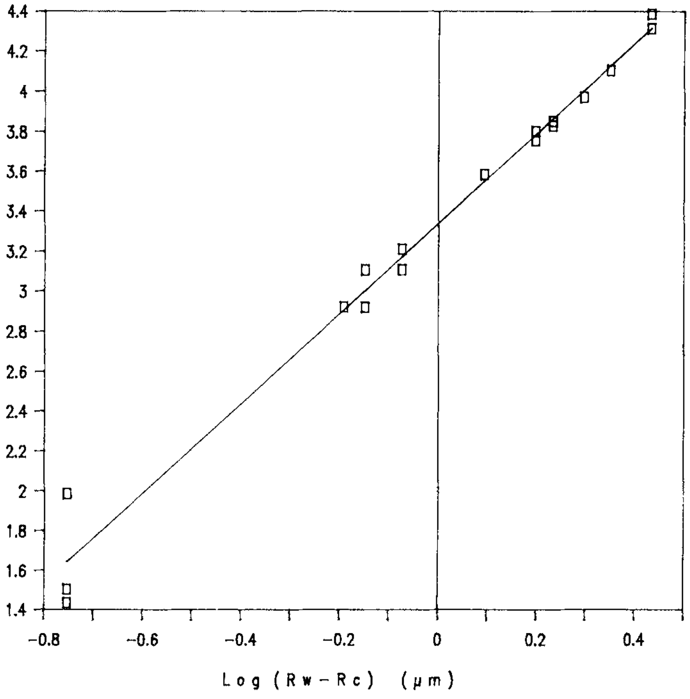

Fig. 8. HIPS polymers: bilogarithmic plot of $\Delta I/N$ vs. $R_w - R_c$. R_c has been estimated 0.29 μm. The straight line is the regression.

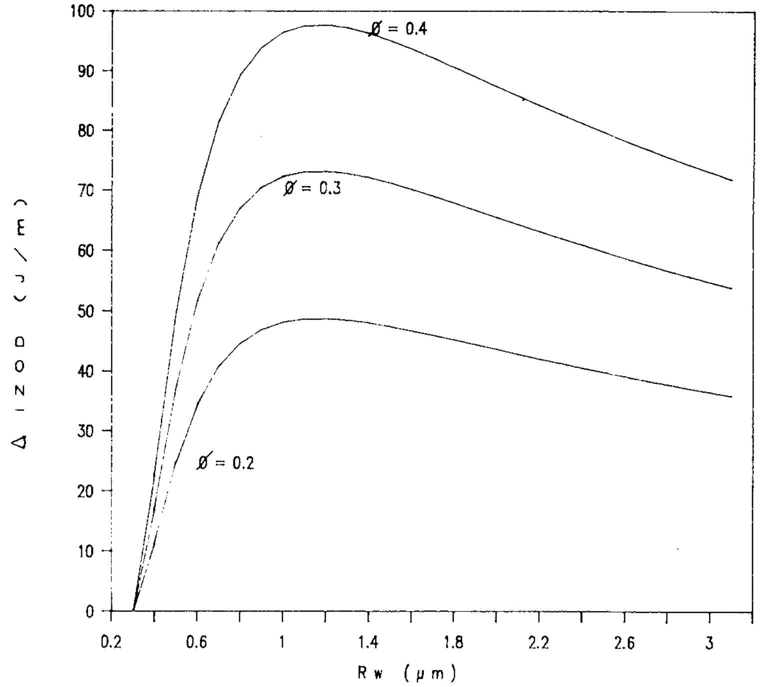

Fig. 9. HIPS polymers: calculated Izod increase ΔI vs. R_w at various ϕ levels.

HIPS

This approach was applied to some HIPS series; one of them was reported in a previous work.[10] It was shown that the impact strength of HIPS as a function of ϕ (gel%), fixing other parameters (as swelling index and PS molecular weight), has approximate trends characterized by different slopes at different particle sizes. At fixed ϕ the maximum efficiency appears to occur in the mean cord range 1.2–1.5 μm (R_w range $0.8 - 1$ μm assuming[21] $R_w = 2/3 \cdot c$ where c is the mean cord). Calculating $\Delta I/N$ (assuming Izod of PS 15 J/m and $R_w = 2/3 \cdot c$) and plotting it versus R_w gives indications comparable to those found for OSA. For HIPS the bilogarithmic graph is reported in Figure 8. In analogy with OSA, Figure 9 reports the calculated curves of Izod versus R_w at various ϕ and Figure 10 the correlation between calculated and experimental values. The equation with the best R^2 is in this case

$$\Delta I/N = 2186 \cdot (R_w - 0.29)^{2.252} \tag{2}$$

For HIPS, the maximum toughness, at fixed ϕ, appears from Eq. (2) at R_w values around 1.15 μm.

It is known[8,22] that SAN matrix deforms by shear yielding more easily than the PS one does. The two materials described show formal similarites in this approach although OSA is characterized by much higher Izod values, lower R_c, and lower particle dimensions at which Izod is optimized. These last considerations give further support to the easier shear yielding deformability

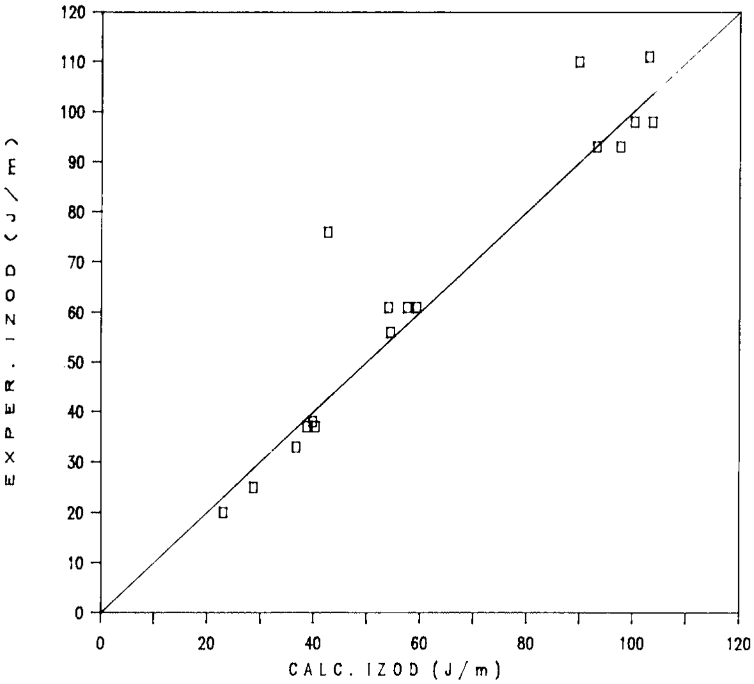

Fig. 10. HIPS polymers: plot of experimental Izod values vs. calculated ones. The line represents the ideal case of perfect agreement.

of SAN with respect to PS. Some evidence is given also by the presence of necked zones in the OSA specimens after Izod and tensile tests.

Rubber-Toughened Nylon

For materials substantially deformed by shear yielding, for instance, rubber-toughened nylon, a particular behavior is described in the literature:[11,12] they undergo a morphological tough-brittle transition explained in terms of a critical interparticle distance T_c. In this case, at constant good adhesion level and different ϕ and R_n, materials behave tough (Izod range 500–1150 J/m) below T_c (0.304 μm) and brittle (Izod range 50–200 J/m) above T_c. The Izod values of each group depend on ϕ and R_n. Recently,[12] for rubber-toughened nylon, the temperature dependence of T_c was also discussed.

$\Delta I/N$ values were calculated from Izod, ϕ, and R_n data reported in Tables 1, 2, 3, of Ref. 11 and plotted against R_n. This is shown in bilogarithmic plot in Figure 11. Two different correlation lines are observed for tough (upper curve) and brittle products (lower curve). In this case for the evaluation of ϕ the density difference was also taken into account even though it plays a minor role. In Table II, the obtained exponential functions of the two nylon groups, together with those relative to OSA and HIPS, are reported. For the tough samples, the regression optimization does not support the existence of a critical radius below which particles lose their toughening capability. Even if this cannot be excluded for certain, at least the critical value appears to be very small, according to indications that ductile matrices have smaller particle

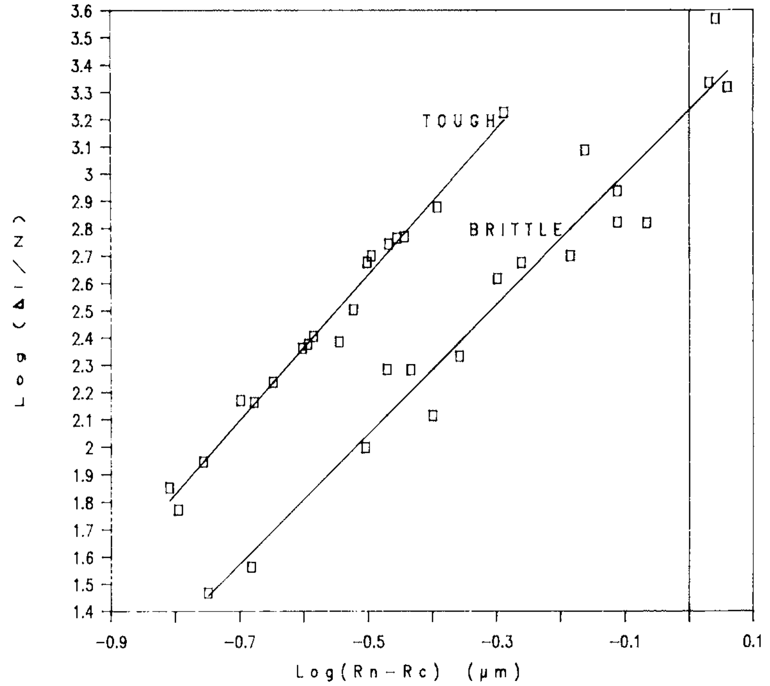

Fig. 11. Toughened nylon 66: Izod, ϕ and R_n values from ref. 2. Bilogarithmic plot of $\Delta I/N$ vs. $R_n - R_c$. The upper curve refers to tough materials (ID $< T_c$, $R_c = 0$ μm), the lower to brittle ones (ID $> T_c$, $R_c = 0.062$ μm). The straight lines are the regressions.

TABLE II

Correlation Equations Between Normalized Izod Increase and Particle Radius for the Various Materials Examined

OSA	$\Delta I/N = 13706 \cdot (\mathrm{Rw} - 0.065)^{2.633}$
HIPS	$\Delta I/N = 2186 \cdot (\mathrm{Rw} - 0.29)^{2.252}$
Nylon tough	$\Delta I/N = 9243 \cdot (\mathrm{Rn})^{2.667}$
Nylon brittle	$\Delta I/N = 1726 \cdot (\mathrm{Rn} - 0.062)^{2.375}$

dimensions for optimizing toughness.[23] For brittle nylons, a critical radius appears analytically probable. However, it was obtained by extrapolation of the $\Delta I/N$ curve at very small radii where ductile behavior is dominant. So the significance of this R_c is less clear. For lack of a critical radius in the tough nylon group, the Izod versus R_n diagrams, at various ϕ, result in decreased exponential functions. Of course, each of them must be sharply interrupted at the radius corresponding to the critical interparticle distance T_c.

Hypothesis of Equations Interpretation

This normalized Izod approach appears to be applicable to rubber-toughened polymers with different deformation mechanisms. The equations in Table II show the relative similarity of the radii exponents, evident differences for the

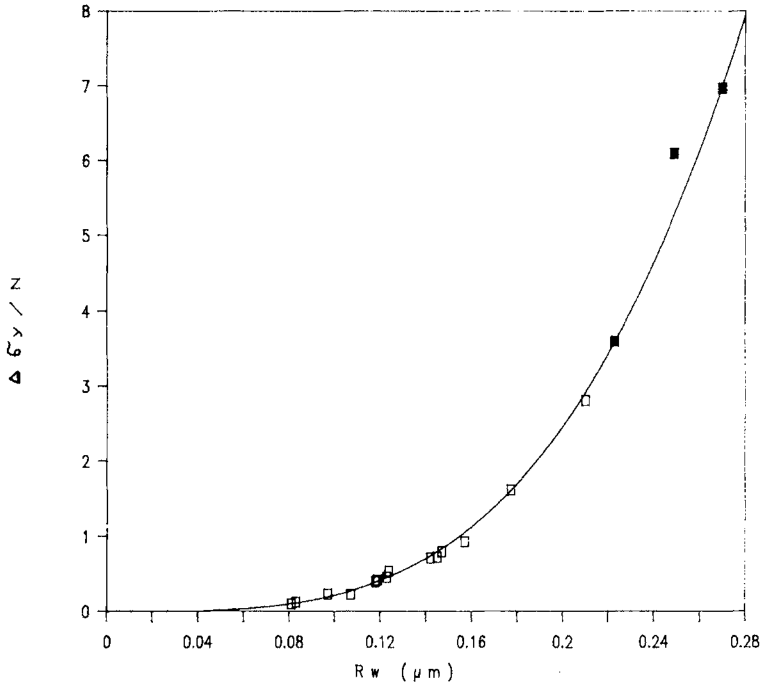

Fig. 12. OSA polymers: normalized tensile yield stress decrease $\Delta\sigma y/N$ vs. R_w. Full symbols refer to materials O, P, Q of Table I. The continuous curve is the regression.

critical radius, the coefficient of multiplication, and the radius that optimizes the Izod. Further work on the real similarity of the exponents and their meaning for the mechanical micromechanism is ongoing in our laboratory. We may emphasize that an exponent 2 of the radius could indicate proportionality with particle section πR^2, effective for stopping craze, or with particle surface $4\pi R^2$, eventually related to the probability of craze (shear bands) nucleation. The critical radius and the radius of maximum toughness appearing in the substantially craze-deformed materials are probably related to craze thickness (which is larger in PS than in SAN).

Yield Stress for OSA

For OSA, introducing $\Delta\sigma y/N$ in a quantity where $\Delta\sigma y$ is the difference between tensile fracture stress of SAN (about 54 MPa) and the tensile yield stress of the toughened SAN results again in an exponentially increasing function, once plotted against the radius (Fig. 12). In this case we did not find evidence of a critical radius below which particle efficiency is lost (the best R^2 is obtained without R_c). It is remarkable that in this correlation the three products with the largest particles (O, P, Q Table I) are included even if they are not in the $\Delta I/N$ correlation (these three materials are also included in the modulus-rubbery phase volume correlation shown in Figure 1).

Large Particle OSA Products

Concerning the impact behavior of these three products, at least two hypotheses can be made related either to interphase adhesion or to morphology.

In the first case, they could lack sufficient adhesion due to higher interfacial tension hypotheorized on the basis of physicochemical characterization of the components, especially the graft copolymer (for all the other materials both characterization data and the presence of very small dispersed particles suggest a sufficient adhesion level).

In the second hypothesis, the interfacial tension of samples O, P, Q, even if higher, could be sufficient for adhesion during impact test: the brittle behavior could be explained in terms of the morphological T_c transition described for shear-yielding deforming materials. In fact, these three materials also have, besides the radius, the largest ID of all the others. Another possible morphological explanation could be an increased role of crazing due to the higher particle dimensions, as already suggested.[13,15,16] This tough-brittle transition was not observed for pure crazing materials like HIPS having particles up to about 3 μm radius. The coexistence of the two deformation mechanisms in OSA does not allow a positive conclusion on the matter. Further investigation will be done on this point and the fact that normalized yield stress correlates large particle materials while normalized Izod does not.

CONCLUSION

The proposed normalization per single particle of the mechanical characteristics correlates exponentially rather well with the article radius.

This correlation was applied to Izod and yield stress of OSA and to Izod of HIPS and toughened nylon. For this last material two different correlations were found for the two classes of products separated by morphological transition, indicated in the literature as typical for shear-yielding deforming materials.

This transition was not observed in HIPS which deforms by crazing.

There are some indications that a similar transition could be present in OSA which deforms in an intermediate way: in fact, the normalized Izod correlation does not hold for all the OSA polymers investigated. On the contrary, all of these polymers correlate in the yield stress normalization. Preliminary considerations of this fact, the similarity of the exponents, and the differences of the other parameters of the exponential equations for the considered materials are made. Nevertheless further work is believed to be necessary for a clearer comprehension.

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