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On the Size of the Secondary Mechanical Loss Peak in Rubber-Modified Polymers

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The relationships between the structure and dynamic mechanical properties of rubber-modified plastics have been studied theoretically using linear viscoelasticity theory combined with Hashin's equations for elastic composites. The results show that the size of the secondary loss peak depends upon both the concentration of rubber in the material and the proportion of hard sub-inclusions within the rubber particles.

1. Introduction

Dynamic mechanical tests upon rubber-modified plastics such as ABS (acrylonitrile-butadiene-styrene polymer) and high-impact polystyrene (HIPS) show that there is a prominent secondary loss peak at low temperatures. Typical peak temperatures at a frequency of 1 Hz are − 80° C for polymers containing polybutadiene and − 40° C for those containing SBR (styrene-butadiene rubber). The primary loss peak at about 100° C. is due to the glass transition in the glassy matrix, i.e. SAN (styrene-acrylonitrile copolymer) or polystyrene, and there is ample evidence that the secondary peak is due to the glass transition in the dispersed rubber phase. The secondary peak is observed only when rubber is present, and for any given set of manufacturing conditions its size increases with the amount of rubber added. The peak temperature is usually a little higher than the glass temperature of the rubber, as indicated earlier.

If the concentration of rubber in the composite is kept constant, and the conditions of manufacture are varied, the size of the secondary loss peak (defined as the area under the curve of loss tangent against temperature) can vary within wide limits. The smallest peaks are observed in mechanical blends of rubber with polystyrene (or equivalent glassy polymer), and the largest in "mass" polymers, which are made by dissolving an uncrosslinked rubber in a suitable monomer (e.g. styrene) and polymerising the monomer. Smaller, but nevertheless significant, variations are observed within a given manufacturing process. For example, the peak can be reduced to half its normal size in a "mass" polymer by altering the conditions of stirring during the prepolymerisation stage of the process; other process variables can have a similar effect. An understanding of these variations in peak size is clearly of interest to the manufacturer of rubber-modified polymers, as an aid to controlling the properties of the product.

Interest in the secondary loss peak has centred less upon the loss process itself, and the accompanying drop in stiffness with rising temperature over the transition region, than upon the large-strain mechanical properties such as impact strength, yield stress, and elongation at break, which appear to be related in some way to the size of the peak. Karas and Warburton obtained a linear relationship between notched Izod impact strength and loss peak size for a series of HIPS polymers [1], and Turley [2] showed that "mass" polymerised HIPS polymers are tougher and have larger loss peaks than mechanical blends of the same overall composition. Keskkula, Boyer, and Turley [3] have recently shown, however, that impact strength can be correlated satisfactorily with peak size only for polymers that have all been prepared under similar conditions, and that peak size can be a very poor guide to toughness in comparing, for example, "mass" polymers with emulsion polymers. Some clarification of the problem is obviously needed, and the first step is to consider how the dynamic mechanical properties of rubber-modified polymers are related to their structure. This aspect of the problem is the subject of the present paper.

Kato [4-6] and other workers [7,8] have shown that the rubber particles in most commercial HIPS and ABS polymers are composite, consist-

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ing of up to 80 or even 90% by volume of glassy sub-inclusions (polystyrene or SAN) embedded in a matrix of rubber. The effects of this structure upon the shear modulus of the composite rubber particles and upon the stiffness of the rubber-modified polymer at room temperature were discussed in an earlier paper [9], in which the time-dependence of properties was ignored, and the rubbery and glassy polymers were treated as elastic materials of widely different moduli. The present work is an extension of the study to cover viscoelastic effects within the glass transition region of the rubber.

2. Method

The analysis was based upon a simple model. The rubber-modified polymer was considered as consisting of a continuous matrix of glassy plastic in which were embedded large numbers of composite spherical rubber particles, the rubber particles themselves consisting of a continuous matrix of rubber in which were embedded large numbers of spherical sub-particles of glassy plastic (of the same composition as the matrix). Both the rubber and the glassy plastic were treated as having the same properties as they would have in the bulk. In other words, the molecular chains of the rubber and glassy polymer were assumed to have undergone complete phase separation during manufacture, and no account was taken of any transitional zones or shifts in relaxation behaviour that may have arisen as a result of grafting. This assumption is based upon the low entropy of mixing of macromolecules, and applies to all except the shortest of the grafted chains. Possible refinements and modifications of the model are discussed in section 4.

For convenience, the analysis was carried out for a range of HIPS polymers containing SBR, but the results are of course perfectly general. There are two parts to the problem: firstly, to calculate dynamic mechanical properties for composite rubber particles containing various concentrations of polystyrene sub-inclusions, using experimental results on SBR and polystyrene as input data; secondly, to calculate dynamic mechanical properties for HIPS polymers containing known concentrations of rubber particles of known composition, using the results from the first calculation as input data. The results for HIPS are presented as a comparison of two materials with the same rubber content, one containing simple rubber particles, and the other containing composite rubber particles with a high loading of polystyrene sub-inclusions.

Experimental data on the time-dependent Young's modulus of SBR were obtained from a master curve published by Tobolsky [10]. The following quantities were taken as elastic constants: shear modulus of polystyrene = 1.41 × 10^{10} dynes/cm^2; bulk modulus of polystyrene = 3.00 × 10^{10} dynes/cm^2; bulk modulus of SBR = 2.00 × 10^{10} dynes/cm^2.

2.1. Hashin's Equations

As in the previous paper, both parts of the calculation were based upon Hashin's equations for composites consisting of spherical inclusions embedded in a continuous matrix [11]. Hashin's equations apply to elastic composites exhibiting perfect interfacial adhesion. The results are in the form of upper and lower bounds upon shear modulus, since Hashin has concluded that there is little hope at present of calculating rigorously the moduli of a composite containing many interacting inclusions.

The assumptions in Hashin's treatment are satisfied quite well in rubber-modified polymers. In most commercial polymers there is sufficient grafting to ensure good interfacial adhesion between rubber and glassy polymer. In isotropic samples both the rubber particles and the sub-inclusions are usually spherical and small compared with the body of matrix in which they are embedded. The extension of the relevant elasticity theory to viscoelastic composites will be discussed in section 2.2.

There are numerous approximate equations that could have been used to obtain single-valued solutions, avoiding the complication of discussing bounds. However, Hashin's equations have the advantage that they define rigorously the range of magnitudes of the effects under discussion, and in particular the range of peak sizes that can be obtained from any given combination of polystyrene matrix, SBR, and polystyrene sub-inclusions. Consequently, the conclusions reached are more firmly based than they would otherwise be. The limitations of the present analysis arise from the choice of the morphological and physical model, and not from the mathematics.

2.2. Viscoelasticity Theory

The accepted procedure in problems involving viscoelasticity is to obtain an equivalent solution for the purely elastic case, and to replace the elastic moduli in the elastic solution by transforms describing the corresponding time-dependent moduli [12]. This procedure was followed in the present analysis. Hashin's equations represent the equivalent elastic solutions, into which Carson transforms of the relevant time-dependent moduli were substituted.

First, an analytical function describing the stress relaxation data for SBR was obtained according to the method of Schapery [13], by collocating the following equation for the time-dependent Young's modulus $E(t)$ to the data at 20 points:

$$E(t) = E(\infty) + \sum_{i=1}^{20} E_i \exp(pt)\,(-\,t/\tau_i) \qquad (1)$$

where t = current time, τ = relaxation time.

This is equivalent to a 21-element generalised Maxwell model. The equilibrium moduli of the SBR in the rubber-like and glass-like states are then given by $E(t) = E(\infty)$ and $E(t) = E(\infty) + \sum_{i=1}^{20} E_i$ respectively, and the Carson transform $p.\bar{E}(p)$ for the Young's modulus of SBR is given by:

$$p.\bar{E}(p) = p \int_0^\infty \exp(-pt).\, E(t)\,\mathrm{d}t = E(\infty) + \sum_{i=1}^{20} \frac{p\tau_i E_i}{p\tau_i + 1} \qquad (2)$$

The transform variable p, which is defined by equation 2, replaces real time t as the independent variable, so that the moduli are expressed as p-dependent quantities rather than as time-dependent quantities.

Hashin's equations involve shear modulus G and Poisson's ratio ν. Carson transforms for the time-dependent shear modulus and Poisson's ratio of SBR were obtained from the equivalent solutions of elasticity theory. The transformed equations are:

$$p.\bar{\nu}(p) = 0.5 - (p.\bar{E}(p)/6K) \qquad (3)$$

$$p.\bar{G}(p) = 3Kp.\bar{E}(p)/(9K - p.\bar{E}(p)) \qquad (4)$$

The Carson transforms given by equations 2, 3 and 4 were substituted into Hashin's equations to obtain expressions for the shear moduli of the composite rubber particles. In order to evaluate these expressions numerically, they were inverted to the real-time plane by means of the substitution $p = j\omega$, where $j = \sqrt{-1}$, and ω is the frequency of oscillation in radians per second. A digital computer was then used to calculate numerical values for the real and imaginary components of shear modulus of the composite rubber particles, as functions of oscillation frequency and composition. Stress relaxation modulus $G(t)$ was calculated from these results.

Analytical equations representing the numerical results for $G(t)$ were obtained using equation 5:

$$G(t) = G(\infty) + \sum_{i=1}^{20} G_i \exp(-\,t/\tau_i) \qquad (5)$$

The Carson transform of equation 5 is:

$$p.\bar{G}(p) = p \int_0^\infty \exp(-pt).\, G(t)\,\mathrm{d}t = G(\infty) + \sum_{i=1}^{20} \frac{p\tau_i G_i}{p\tau_i + 1} \qquad (6)$$

The Carson transforms given by equation 6 were used in the second stage of the calculation, to obtain numerical values for the bounds on the dynamic moduli of HIPS. As in the first stage, bulk moduli were assumed to be independent of time.

The same equation of Hashin gives upper bounds at both stages of the calculation, as indicated in relationship 55 of Hashin's 1962 paper [11]; conversely, the same lower bound equation applies at both stages of the calculation. The validity of this relationship is demonstrated in the computed results. In the case of rubber particles in a polystyrene matrix, the results for a dispersion of simple rubber spheres identify the bounds, since the input data are the same for both equations.

3. Results

3.1. Composite Rubber Particles

Figs. 1 and 2 show the results for the upper bound equation, representing the maximum effect of the sub-inclusions upon the dynamic properties of the composite rubber particles. The sub-inclusions raise the shear modulus $G'(\omega)$, especially at low frequencies, and reduce the loss tangent tan δ (defined as G''/G'). The double peak in tan δ at high loadings of sub-inclusions arises from the form of Hashin's equations.

Figs. 3 and 4 show the corresponding results for the lower bound equation, representing the minimum effect of the sub-inclusions upon the dynamic mechanical properties of the composite. The upper and lower bounds show a wide divergence, but this is to be expected in view of the differences in moduli between rubbers and glassy polymers.

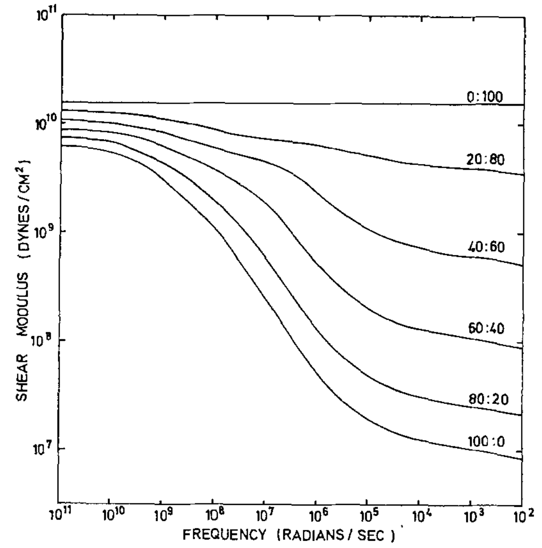

Figure 1 Upper bounds on storage modulus $G'(\omega)$ for composite rubber particles of different compositions. The labels on the curves specify the volumetric ratio of SBR:Polystyrene in the particles. The curve labelled 100:0 corresponds to Tobolsky's master curve [10].

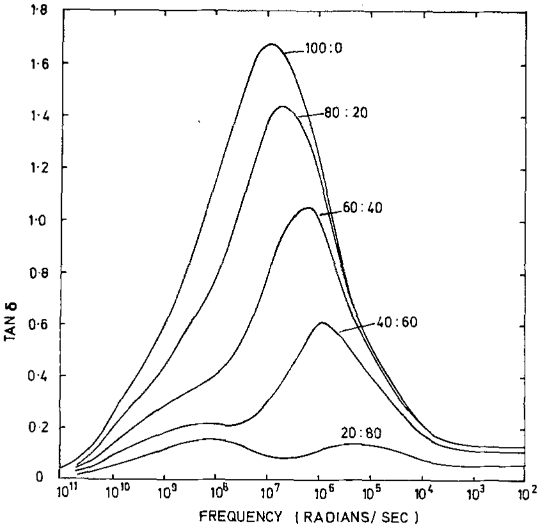

Figure 2 Bounds on tan δ corresponding to the upper bounds of $G'(\omega)$ shown in fig. 1.

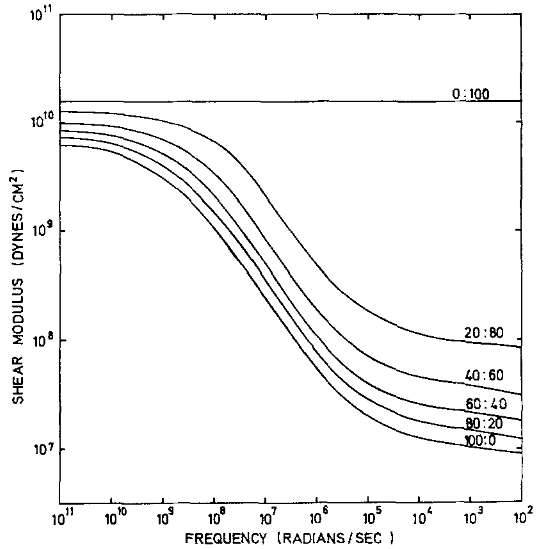

Figure 3 Lower bounds on storage modulus $G'(\omega)$ for composite rubber particles of different compositions.

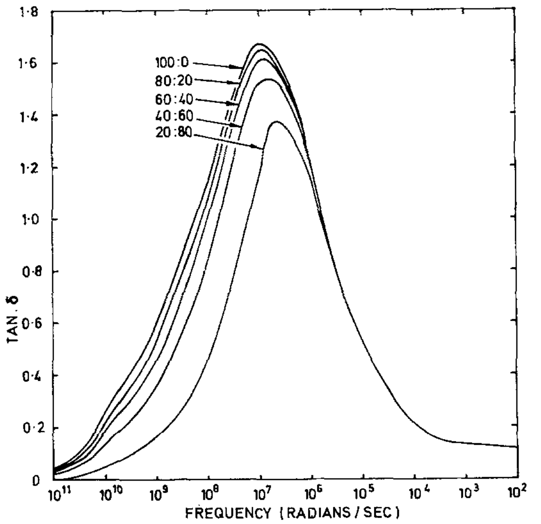

Figure 4 Bounds on tan δ corresponding to the lower bounds on $G'(\omega)$ shown in fig. 3.

3.2. Rubber-Modified Polymer

The results for the rubber-modified polymer are presented in the form of a comparison between two HIPS polymers, both containing 5% by volume of SBR. One polymer consists of 5% simple rubber particles embedded in a polystyrene matrix which occupies the remaining 95% of the volume. The other polymer contains 25% by volume of composite rubber particles, consisting of 5 parts SBR and 20 parts polystyrene sub-inclusions, embedded in a polystyrene matrix which occupies 75% of the total volume.

Upper bound results for $G(t)$ of the composite rubber particles were used to calculate upper bounds for $G'(\omega)$ of the HIPS. Similarly, lower bound results for $G(t)$ of the particles were used to calculate lower bounds for $G'(\omega)$ of the HIPS.

The results of this second stage in the calculation are presented in figs. 5 and 6. For the material containing 5% of simple rubber particles, the upper and lower bounds on both $G'(\omega)$ and tan δ are quite close together, the shear moduli are only a little below that of polystyrene, and there is a relatively small loss peak. For the material containing 25% of composite rubber particles, on the other hand, the upper and lower bounds upon both $G'(\omega)$ and tan δ are widely spaced, both bounds on $G'(\omega)$ are well below the shear modulus of polystyrene, and the area enclosed by the loss peaks is much greater.

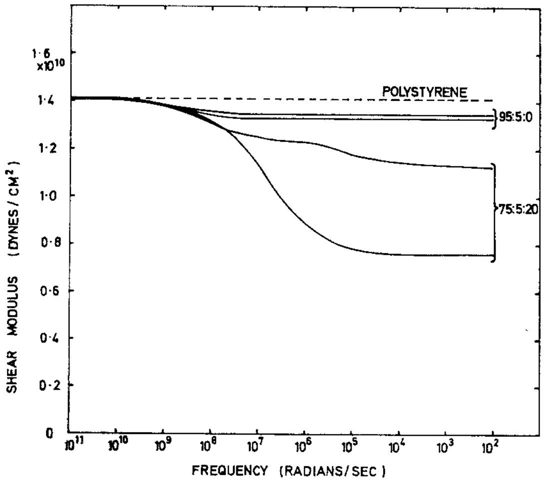

Figure 5 Upper and lower bounds on storage modulus $G'(\omega)$ for two HIPS polymers, both containing 5% by volume of SBR. The labels on the curves specify the volumetric ratio of matrix polystyrene:SBR:polystyrene sub-inclusions in the HIPS.

In short, the fact that an appreciable proportion of the polystyrene is in the form of sub-inclusions within the rubber particles rather than as part of the matrix means that the HIPS has a lower shear modulus, and a larger secondary mechanical loss peak, than it would otherwise have.

The exact magnitudes of these effects are not estimated by the present treatment, but the trends and the approximate magnitudes are quite clearly indicated.

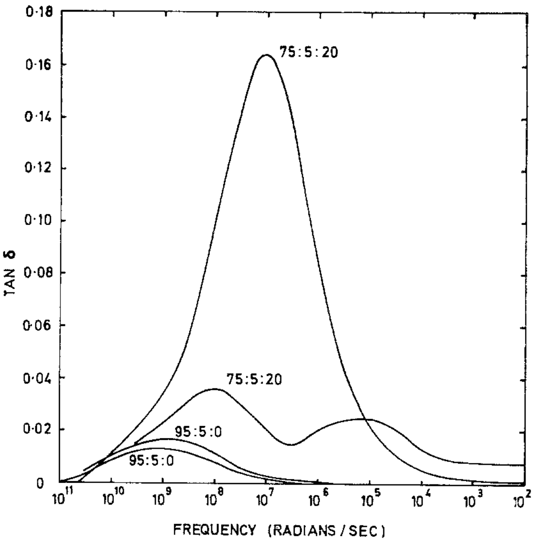

Figure 6 Bounds on tan δ, corresponding to the bounds on $G'(\omega)$ shown in fig. 5.

4. Discussion

This study clearly shows that the dynamic mechanical properties of rubber-modified polymers depend not only upon the amount of rubber present, but also upon the morphology of the composite. The observed variations in peak size with manufacturing conditions can thus be attributed in some, if not in all cases, to variations in the proportion of sub-inclusions embedded in the rubber particles.

The main effect of the sub-inclusions is to increase the total volume of the (composite) rubber particles; for example, the HIPS polymers discussed in section 3.2 both contained 5% SBR, but the volume of the rubber particles was 5% of the whole material in one case and 25% in the other. The increase in the volume fraction of the composite rubber particles in the HIPS outweighs the effects of the sub-inclusions in increasing the modulus and decreasing the loss tangent of the rubber. The overall effect upon the HIPS is a decrease in modulus and an increase in loss tangent in the glass transition region of the rubber.

The relationship between loss peak size and toughness is a more complex problem. Both sets of properties must obviously depend upon the volume fraction of the rubber particles present, and it is probable that the relationships that have been observed [1, 2] derive from this dependence. Under tensile stress, the rubber particles act as stress concentrators, generating large numbers of crazes in the surrounding matrix [14, 15]. The crazes absorb large amounts of energy and allow the material to deform rather than fracture, as it would in the absence of the rubber.

However, although the volume fraction of rubber particles is an important factor in the multiple crazing mechanism of rubber-toughening, there are other factors that may be of equal or greater importance. The levels of the stress concentrations within the matrix are also determined by the shear modulus of the composite rubber particles [9]. A large amount of a rubber with a high modulus may be less effective as a toughening agent than a smaller amount with a lower modulus; this consideration would explain the poor correlation between peak size and toughness observed by Keskkula, Boyer, and Turley [3].

Under impact loading, or where crack propagation is involved, the relaxation behaviour of the composite rubber particles becomes important. Bucknall and Street have shown that the time taken by the rubber to relax from the glassy state to a lower modulus determines whether a rubber-modified polymer is tough or not at any given temperature [16, 17]. Figs. 1 and 3 show that a rubber particle containing a large proportion of sub-inclusions takes longer than a simple rubber particle to relax to a given low modulus (e.g. 10^9 dynes/cm^2), which implies that the transition from brittle to tough fracture behaviour will occur at a higher temperature in the material containing composite rubber particles.

Two papers published recently contain experimental evidence that supports the conclusions of the present theoretical study. Keskkula and Turley [18] dissolved a sample of HIPS in a mixture of MEK and acetone and centrifuged to separate the composite rubber particles from the matrix polymer. Electron micrographs established that the gel obtained in this way consisted largely of composite rubber particles similar in appearance to those in the original polymer. The gel contained $\frac{1}{3}$ polybutadiene and $\frac{2}{3}$ polystyrene by weight; its dynamic shear modulus between -50 and $+50°$ C. at torsion pendulum frequencies was about 5×10^8 dynes/cm^2, compared with 10^{10} for polystyrene and 10^7 for polybutadiene. This result is closer to the upper than to the lower bound. The disadvantage of this type of measurement is that there is a layer of grafted polystyrene on the outside of the rubber particles which is not removed by the centrifuging procedure, and which in the gel could form a continuous network making a disproportionate contribution to stiffness. The thickness of this external layer is independent of the diameter of the rubber particles, so that its importance increases with decreasing particle size. Gels separated from emulsion polymers, which contain very small rubber particles, have unexpectedly high shear moduli, probably for this reason [19].

The second of the recent papers, by Kraus, Rollman, and Gruver [20], describes the dynamic mechanical properties of SBR – polystyrene composites made by latex blending. The blends contained 400 Å polystyrene particles embedded in a matrix of SBR. No evidence was offered on the morphology of the blends, but care was taken to avoid softening the polystyrene during preparation. The storage modulus of the rubber was increased very substantially upon adding the polystyrene, but the maximum in the loss modulus was unchanged; the maximum value of loss tangent was therefore lowered, as predicted by Hashin's equations and by the Takayanagi model employed by Kraus, Rollmann, and Gruver. In this experiment, contact between neighbouring polystyrene particles may have contributed to stiffness, especially at the higher loadings.

Experiments of the type outlined above provide valuable evidence concerning the dynamic mechanical properties of the composite rubber particles, although there are difficulties of interpretation, as already indicated, and it is also difficult to determine whether the isolated gels and prepared blends studied precisely reproduce the behaviour of the rubber particles within the rubber-modified polymer.

Chemical reactions occurring during polymerisation can have an important effect upon the dynamic mechanical properties of the product. In particular, excessive crosslinking of the rubber increases its modulus and raises T_g. These effects can be accommodated in the present treatment simply by changing the input data for the rubber component. A similar approach could be used to allow for the effects of grafting, although these are probably much less important; most of the grafted chains are of high molecular weight, and therefore likely to form a separate phase rather than alter the properties of the rubber phase. Previous discussions of the dynamic mechanical properties of rubber-modified polymers have tended to concentrate upon chemical effects, and a central aim of the present work is to demonstrate the importance of physical and morphological effects, so that the chemical shifts in loss peak and other characteristics can be discussed upon a sounder basis.

Further progress in this field depends upon experimental work. The concentration of sub-inclusions within the rubber particles has been determined in only a very few cases. There is a need for many more such determinations, and for a more general realisation of the importance of particle composition and structure in relation to mechanical properties, at both high and low strains.

5. Conclusions

This study has shown that the dynamic mechanical properties of rubber-modified plastics are determined largely by the volume fraction of the composite rubber particles present, which is in turn determined by the amount of rubber in the material and by the amount of glassy sub-inclusions embedded in the rubber.

However, the volume fraction of composite rubber particles is not the only important factor affecting mechanical properties. A composite rubber particle is not equivalent to a simple rubber particle of the same size and shape; composite rubber particles are stiffer, and therefore have a smaller effect upon the stiffness of the rubber-modified polymer at a given volume loading.

Experimental studies, especially those of Keskkula, Boyer, and Turley [3], suggest that the large-strain mechanical properties, including impact strength and yield behaviour, are particularly sensitive to the differences in properties between particles containing different amounts of sub-inclusions, with the result that there is a poor correlation between toughness and loss peak size. The stiffening effect of the hard sub-inclusions reduces the efficiency of the rubber particles as stress concentrators, and hence reduces the capacity of the rubber-modified plastic to deform and absorb energy through multiple craze formation. This effect requires further investigation.

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