A Theoretical Development of the Relationship Between Grafting and Particle Size on Impact in Two Phase Plastics

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Synopsis

A new theory is developed which relates the graft level, graft molecular weight, and particle size to the probability of hitting a rubber particle as a crack propagates in a two-phase impact-modified plastic. It is shown theoretically that the particle size average of interest in evaluating the impact properties of two-phase plastics is the surface-average particle size D_s. The theory predicts a maximum probable impact at a specific particle size that depends on the graft level required to achieve compatibility between the two phases.

Introduction

Various theories have been proposed to explain the impact properties of two-phase polymers. A number of these theories have been concerned with particle size and/or grafting. Merz, Claver, and Baer[1] indicated that impact should increase with a decrease in particle size until a not-so-clearly defined "domain size" of the continuous glassy phase is reached. Dinges and Schuster[2] developed a model and supported this model with some data which indicated that impact should increase with a decrease in particle size. Kambour[3] indicated that the impact strength in high-impact polystyrene increases with decreasing particle size down to a limit of about 1 mm. Other studies[2,4] and patents[5,6] suggest that impact increases with an increase in particle size in ABS two-phase materials.

It was the purpose of this study to extend the two-phase impact model of Dinges and Schuster to better understand the effects of grafting and particle size on impact. The model resulting from the present study indicates that impact should best correlate with the surface-average particle size D_s. This new model also indicates that each two-phase material should have two regions where impact is affected differently by the surface-average particle size. In one of these regions it will be shown that impact should decrease with an increase in the surface-average particle size, and in the other region it will be shown that impact should increase with an increase in the surface-average particle size.

Model Analysis of Rubber-Reinforced Polymers

Following the approach of Dinges and Schuster, it will be assumed that a rubber-modified polymer consists of a rectangular specimen which has a propagating crack that will eventually reach a length a. If such a specimen as illustrated in Figure 1 is considered to be split into K slices, then the total cross-sectional area A_i of the ith particle size population in the Kth slice will be

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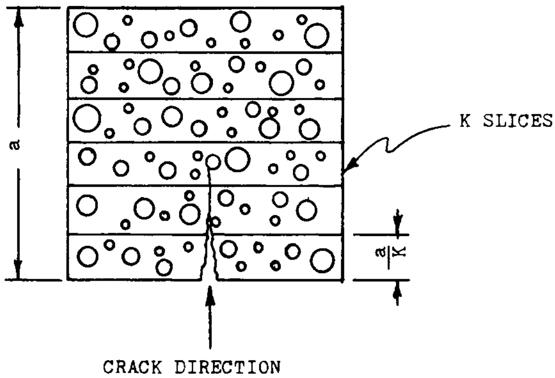

Fig. 1. Model for the probability of hitting a rubber particle.

$$A_i = (\pi/4)n_iD_i^2\,(1/K) \tag{1}$$

where n_i = total number of particles in sample of the ith diameter, and D_i = diameter of the ith particle size population.

The cross-sectional area A_{xs} exposed to the crack tip will then be

$$A_{xs} = V_T/a \tag{2}$$

where V_T = total volume of specimen, and a = crack length. Thus, the probability of the crack tip hitting the ith particle size population in the Kth slice, P_i, is given as

$$P_i = \frac{(\pi/4)n_iD_i^2(1/K)}{V_T/a} \tag{3}$$

The total volume of the specimen is given as

$$V_T = \frac{(\pi/6)\Sigma n_iD_i^3}{f_{RV}} \tag{4}$$

where f_{RV} = volume fraction of rubber in the sample. Substituting gives

$$P_i = \frac{1}{K}\left(\frac{(3/2)an_iD_i^2f_{RV}}{\Sigma n_iD_i{}^3}\right) \tag{5}$$

Let P_{iK} = probability of not hitting any of the particles in the ith population in all of the K slices. Then,

$$P_{iK} = (1 - P_i)^K \tag{6a}$$

$$= \left[1 - \left(\frac{1}{K}\right)\left(\frac{(3/2)an_iD_i{}^2f_{RV}}{\Sigma n_iD_i{}^3}\right)\right]^K \tag{6b}$$

Now, as K approaches infinity (∞),

$$P_{iK} \rightarrow e^{-[(3/2)an_iD_i{}^2f_{RV}/\Sigma n_iD_i{}^3]} \tag{7}$$

Now let $1 - P_T$ = probability of missing all particles in all of the particle size populations. Then

$$1 - P_T = P_{1K}P_{2K}P_{3K}P_{4K}\cdots P_{nK} \tag{8a}$$

$$= e^{-[(3/2)af_{RV}(\Sigma n_iD_i{}^2)/\Sigma n_iD_i{}^3]} \tag{8b}$$

But

$$D_s = \frac{\Sigma n_iD_i{}^3}{\Sigma n_iD_i{}^2} \tag{9}$$

where D_s = surface average particle size. Hence,

$$P_T = 1 - \exp\left(\frac{-3af_{RV}}{2D_s}\right) \tag{10}$$

where P_T = probability of hitting at least one particle in at least one of the particle size populations in at least one of the K slices.

The model developed by Dinges and Schuster was only able to empirically account for both a characteristic particle size average and particle size distribution. However, in this study both of these factors have been shown to be taken into account theoretically, as indicated in eq. (10), with the evaluation of the surface-average particle size D_s.

Before grafting, the effective diameter of the low-modulus rubber substrate is D_i, as shown in Figure 2. However, if grafting is assumed to occur uniformly from the surface of the original substrate inward, then the grafted polymer (i.e., styrene–acrylonitrile copolymer) will penetrate a thickness T, as indicated in Figure 2. The modulus of the graft layer will be higher than that of the original substrate due to the attachment of high-modulus styrene–acrylonitrile copolymer. If the modulus of the graft layer is assumed to increase to the point that it is essentially equal to that of the free rigid or matrix phase, then the effective diameter of low-modulus substrate after grafting, D_{EFF}, would be

$$D_{EFF} = D_i - 2T \tag{11}$$

The new effective volume fraction of low-modulus rubber in the specimen can be calculated as

$$f_{RVEFF} = f_{RV}\frac{\Sigma n_i D_{EFF}{}^3}{\Sigma n_i D_i{}^3} \tag{12}$$

Also the new effective surface-average particle size D_{SEFF} can be calculated as

$$D_{SEFF} = \frac{\Sigma n_i D_{EFF}{}^3}{\Sigma n_i D_{EFF}{}^2} \tag{13}$$

After grafting, the probability of desirable impact, P_T, can be calculated by substituting into eq. (10) to give

$$P_T = 1 - \exp\left(\frac{-(3/2)af_{RVEFF}}{D_{SEFF}}\right) \tag{14}$$

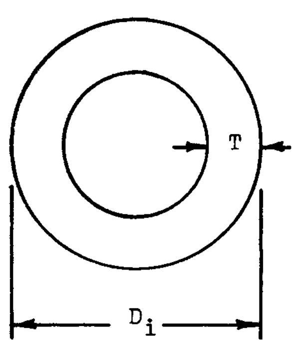

Fig. 2. Model for a grafted rubber particle.

It can easily be shown, however, that eq. (14) can be rewritten in terms of the correction factor for graft thickness, C_{GT}, as

$$P_T = 1 - \exp\left(\frac{-(3/2)af_{RV}C_{GT}}{D_s}\right) \tag{15}$$

where f_{RV} = volume fraction of rubber before grafting, D_s = surface average particle size before grafting, and

$$C_{GT} = \frac{\Sigma n_i(D_i - 2T)^2}{\Sigma n_i D_i{}^2} \tag{16}$$

Based on the assumptions introduced in this development, an estimate of the probability of desirable impact, P_T, can be calculated using eqs. 15 and 16.

Comparison of the Dinges and Schuster Model with the Model from this Study

A summary of the probability of impact as calculated from two models is given in Table I. The probability of desirable impact, P_T, as calculated using the model from this study relates the following variables to impact: (1) volume fraction of ungrafted substrate in the final two phase plastic, f_{RV}; (2) a representative length of a propagating crack, a; (3) the average particle size, D_s; (4) the particle size distribution as indicated by both D_s and the ratio C_{GT}/D_s; and (5) the level of grafting as indicated by the correction factor for graft thickness, C_{GT}. The first two of these variables are evaluated and accounted for relative to impact in effectively the same way in both models. It can be shown, also, that both models give exactly the same calculated probability of impact for all particle sizes for the simple case of no grafting ($T = 0$), a monodisperse substrate ($D_s = 2r_g = 2r_h$), and comparable crack lengths ($L = a$). This simple case at different rubber levels is illustrated in Figure 3.

The fact that the probability of desirable impact increases as the rubber level increases is in good agreement with the experimental results in the literature[4,5,7,8] for rubber-modified plastics. In all of the nongrafted cases indicated in Figure 3, the maximum impact at each rubber level always approaches a maximum probability of impact as the surface-average particle size approaches zero.

However, for the model developed in this study a maximum impact can occur at a specific surface-average particle size other than $D_s = 0$. In particular, a maximum probability of desirable impact for the model from this study will be achieved for a monodisperse substrate at each graft thickness, T, when the surface-average particle size is equal to $(D_s)_{\max} = 6T$. The effect of rubber level on this maximum is illustrated in Figure 4. The effect of the grafting level on the maximum is illustrated in Figure 5. Note in Figure 5 that an increase in the graft thickness results in an increase in the surface-average particle size at which the maximum probability of desirable impact is achieved. The effect of rubber level increases the probability of impact achieved at the maximum as indicated previously, but (according to the model) the rubber level does not apparently shift the surface-average particle size at which this maximum probability of desirable impact is achieved.

TABLE I
Comparison of Theoretical Models Used to Predict Impact in Two-Phase Materials from Probability Considerations

A. Dinges and Schuster Model

$$P_T = 1 - \exp\left(-\frac{(3/4)Lf_{GV}}{r_g(r_g/r_h)^{5/2}}\right)$$

where
L = characteristic length of propagating crack
f_{GV} = volume fraction of grafted substrate
r_g = geometric mean value (median value, 50% value) of the dispersion of particle radii
r_h = most prevalent particle ratios (radius at maximum) of dispersion of particle radii

B. Sudduth Model

$$P_T = 1 - \exp\left(-\frac{(3/2)af_{RV}C_{GT}}{D_s}\right)$$

where
a = characteristic length of propagating crack

$D_s = \dfrac{\Sigma n_i D_i^3}{\Sigma n_i D_i^2}$ = surface average particle size before grafting

$C_{GT} = \dfrac{\Sigma n_i (D_i - 2T)^2}{\Sigma n_i D_i^2}$ = correction factor for graft thickness

f_{RV} = volume fraction of ungrafted substrate or rubber in the sample
T = graft thickness

The Significance of the Surface-Average Particle Size

In order to appreciate the significance of the surface-average particle size, it may be useful to review briefly the different types of particle size averages. In general, most of these averages can be written as

$$D_x = \frac{\Sigma n_i D_i^x}{\Sigma n_i D_i^{x-1}} \tag{17}$$

where $x = 1,2,3,4.\ldots$ These D_x averages have been characterized by Herdan[9] who showed that

$$D_1 \leq D_2 \leq D_3 \leq \cdots \lesssim D_n \tag{18}$$

The two average particle sizes r_g and r_h introduced empirically by Dinges and Schuster would both be expected to be similar in magnitude to the number-average particle size $D_N(D_1)$. Hence, the surface-average particle size $D_s(D_3)$ is always greater than or equal to the number-average particle size $D_n(D_1)$. For a broad particle size distribution, the empirically introduced particle size ratio in the Dinges and Schuster model would not be expected to agree with the surface-average particle size D_s for the model from this study. Thus, even for the nongrafted case, the two models may predict a significantly different probability of desirable impact for a broad particle size distribution.

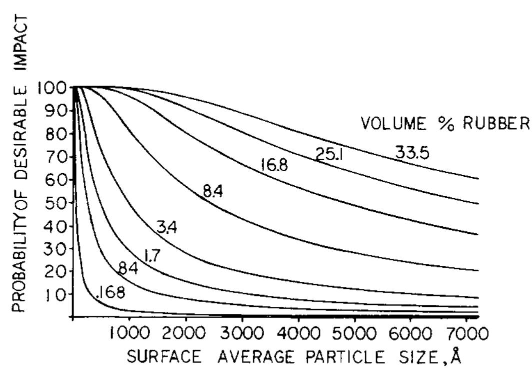

Fig. 3. Probability of desirable impact vs surface-average particle size, Å. Effective crack length = 20,000 Å; particles not grafted, or $T = 0.0$.

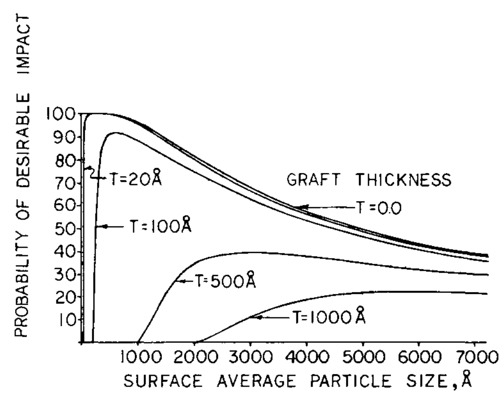

Fig. 4. Probability of desirable impact vs surface-average particle size, Å. Effective crack length = 20,000 Å; graft thickness T = 100 Å. Sudduth model.

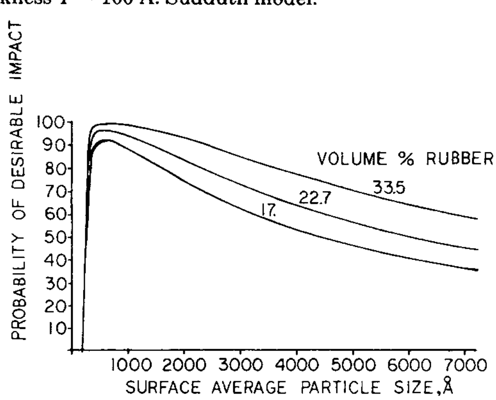

Fig. 5. Probability of desirable impact vs surface-average particle size, Å. Effective crack length = 20,000 Å; volume % rubber = 17%. Sudduth model.

The Influence of Graft Level on the Maximum Probability of Desirable Impact

The level of grafting is usually evaluated using one of two related parameters:

$$G = \frac{W_G}{W_R} \tag{19}$$

or

$$\%\,\text{graft} = \left(\frac{W_G}{W_G + W_R}\right) \times 100 \tag{20A}$$

$$= \left(\frac{G}{1 + G}\right) \times 100 \tag{20B}$$

where G = graft to rubber ratio, W_G = weight of the grafted polymer (i.e., polySAN), and W_R = weight of the rubber charged.

It can be shown using the model from this study that the graft-to-rubber ratio G can be calculated in general as

$$G = \frac{M_{NG}\Sigma n_i[D_i^3 - (D_i - 2T)^3]}{\rho_R V_M N \Sigma n_i D_i^3} \tag{21}$$

where M_{NG} = number-average molecular weight of the graft polymer (i.e., PolySAN), g/g-mole; N = Avagadro number, molecules/g-mole; V_M = average volume available per graft polymer and (i.e., PolySAN) molecule in the rubber substrate; and ρ_R = density of the rubber, g/Å^3.

For the model in this study, a monodisperse substrate can be shown to give a maximum probability of desirable impact when the surface-average particle size D_s is equal to $6T$. The calculated graft parameters at this maximum are

$$(G)_{\max} = \left(\frac{19}{27}\right)\frac{M_{NG}}{\rho_R V_M N} \tag{22}$$

or

$$(\%\,\text{graft})_{\max} = \left(\frac{19M_{NG}}{19M_{NG} + 27\rho_R V_M N}\right) \times 100 \tag{23}$$

Thus, the above grafting parameters, eqs. (22) and (23), describe the level of grafting obtained for the particle size $D_s = 6T$, which achieves a maximum probability of desirable impact for a given graft thickness T. It is important to recognize, however, that the maximum possible probability of desirable impact for each particle size does not necessarily occur when $D_s = 6T$. The maximum possible probability of desirable impact for each particle size occurs when $T = 0$. It is still true, however, that for each graft thickness, even zero, there is theoretically only one particle size at which a maximum impact is achieved. Also note that the graft level at the maximum probability of desirable impact as indicated by eqs. (22) and (23) is independent of graft thickness T. For this reason, the graft level at this impact maximum is theoretically identical for all graft thicknesses.

Discussion

A number of generalized conclusions for rubber-modified plastics can be obtained from the model from this study as indicated in Figure 5:

(1) The better the compatibility between the substrate and the rigid or matrix before grafting, the smaller the necessary graft thickness and the smaller the substrate particle size should be to get the maximum possible impact. For perfect compatibility, no grafting and the smallest possible particle size possible should give the optimum impact.

(2) If only a minimum graft thickness is required to achieve good compatibility between the substrate and rigid, then the particle size substrate which achieves

maximum impact will be determined by the minimum graft thickness that can be obtained in the graft reaction. For particle sizes less than this, optimum overgrafting would result and impact would be expected to increase with increase in particle size. For particle sizes greater than this optimum, a decrease in impact with an increase in particle size would be expected.

(3) If poor compatibility exists between the substrate and the rigid before grafting, then the graft thickness necessary to achieve good compatibility will determine the particle size at which the optimum impact is achieved. Overgrafting will result in particles less than the optimum to have poor impact. Particle sizes greater than the optimum would be expected to result in a decrease in impact with an increase in particle size; primarily as a result of the decrease in the cross-sectional area per total volume of particles.

Each of the above conclusions attempts to relate the model developed in this study to expected experimental limitations relative to the graft thickness T. However, as indicated earlier in eq. (21), the level of grafting in the substrate is dependent not only on the graft thickness T but also on the molecular weight of the grafted polymer, M_{NG}, as well as the available volume/grafted molecule, V_m, in the graft layer. Thus, it is possible to change to an apparent poor compatibility case, and vice versa, simply by changing the molecular weight of the graft and/or the available volume per grafted molecule by modifying the graft reaction.

From an evaluation of the predicted results for the model from this study as well as from compatibility considerations, impact would be expected to increase with particle size up to some critical particle size which achieves the most desirable balance between compatibility and grafting. Such a balance would be expected to be most effectively achieved if the number-average molecular weight of the graft polymer and the available volume/graft molecule can be maintained reasonably constant.

As indicated earlier, some results in the literature indicate that impact increases with an increase in particle size.[2,4–6] Other studies[2,3] suggest that impact can also increase with a decrease in particle size. Each of these cases is understandable using the model described in this study. However, experimental data clearly defining the critical particle size indicated in this study below which impact increases with an increase in particle size and above which impact decreases with an increase in particle size is not presently apparent in the literature.

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