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Effects of the degree of graft on the tensile and dynamic behavior of high impact polystyrene

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Abstract

High Impact Polystyrene (HIPS) polymers varying widely in the degree of graft, size of the rubber particles and volume fraction of the rubber phase have been tested in uniaxial tension. From these tests, it is shown that the yield stress and tensile modulus decrease as the degree of graft increases up to about 120%, and then increase. Increasing the rubber volume fraction and the size of the rubber particles also reduces the yield stress.

A dynamic test is conducted and it is verified that the glass transition temperature of the rubber phase increases with increasing the degree of graft. In addition to this, the maximum tan δ increases with increasing the degree of graft up to about 120%, and then decreases.

It is also shown that the yield stress and tensile modulus of HIPS have a relationship with the dynamic behavior of the rubber phase, i.e. the yield stress and tensile modulus decrease almost linearly as the maximum tan δ increases. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Yield; Dynamic; Mechanical

1. Introduction

Acrylonitrile Butadiene Styrene (ABS) and High Impact Polystyrene (HIPS) are good examples of ways in which the tensile properties of bulk polymers can be modified through a change in the microstructure of rubbery particles. Generally, the rubbery particles are grafted by a brittle polymer which is the same as a matrix. These grafted chains enhance the interfacial bonding between the rubbery particles and the brittle matrix, and also make the rubbery particles disperse through into the matrix polymer to match the thermodynamic parameters.

Many authors have observed that some of the most important factors in controlling the mechanical properties of ABS and HIPS are rubber particle size [1,2] and the volume fraction of the rubbery phase [3,4]. One of the other important factors is the degree of graft, which was found to have a remarkable effect on the microstructure of ABS polymers [5–7]: the increasing of the graft frequency results in an improvement in the dispersion of the rubber particles into the matrix. Aoki and Doi [6,7] studied the effects of the degree of graft on the rheological properties of ABS polymers and concluded that there is an optimum degree of graft which yields the minimum storage shear modulus. They explained that the particles having a graft level lower than the optimum one attract other particles by the van der Waals attraction between the particles, and thus the agglomeration of the rubber particles occur. On the other hand, the particles having a graft level higher than the optimum one expel the matrix by the attraction force between the grafted chains, this also induces the agglomeration of the rubber particles.

Studies on the tensile deformation of ABS polymers having various degrees of graft exhibited that the materials having higher degree of graft show more profound stress drops on yielding compared to the materials of lower ones [8]. This phenomenon was explained by good dispersion of the rubber particles in the matrix, which enhances interfacial bonding.

The objective of this paper is to investigate the effects of the degree of graft on the tensile properties of HIPS which is different from ABS in the internal structure of the rubber particles and in the deformation mechanism, and to find a

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Table 1
Characteristics of model HIPS used

HIPS	Average particle diameter (μm)	Rubber volume fraction	Degree of graft (%)	Rubber weight fraction (%)
L-0.36-63	2.85	0.36	63	6
L-0.36-94	2.80	0.36	94	6
L-0.36-121	2.91	0.37	121	6
L-0.36-185	2.84	0.36	185	6
L-0.46-66	2.76	0.46	66	8
L-0.46-101	2.72	0.46	101	8
L-0.46-121	2.80	0.47	121	8
L-0.46-180	2.72	0.45	180	8
S-0.28-71	1.65	0.28	71	6
S-0.28-94	1.60	0.27	94	6
S-0.28-102	1.70	0.29	102	6
S-0.28-125	1.60	0.28	125	6
S-0.37-63	1.72	0.37	63	8
S-0.37-91	1.72	0.37	91	8
S-0.37-115	1.66	0.36	115	8
S-0.37-163	1.70	0.37	163	8

correlation between these tensile properties and dynamic mechanical properties.

2. Experimental

2.1. Materials

Materials were prepared by bulk polymerization. We dissolved the polybutadiene rubber in styrene monomers at 60°C in a reactor with an anchor-type stirrer rotating at a speed of 300 rpm. Then we heated up the solution to 90°C and added the initiator (lauryl peroxide) to the solution. To control the size of rubber particles, we varied the stirring speed from 400 to 800 rpm. We stopped the stirring when the torque for rotating the stirrer was higher than some limit, and poured the pre-polymer into test tubes. The pre-polymers in the test tubes were polymerized completely in an oven for 1–3 days. We varied the oven temperature from 90 to 140°C to control the degree of graft of the materials under the condition that the size of rubber particles was constant. The characteristics of the materials are listed in Table 1. The average particle diameter is the number average value of the diameters of the particles which were measured from the photographs taken by a transmission electron microscope (TEM) with the aid of an image analyzer (Image Pro Plus). Since the area fraction of the rubber particles in TEM photographs can be used as a volume fraction of the rubber particles with the error not greater than 5% [3], we adopted the area fraction of the rubber particles measured by the image analyzer as the volume fraction of the rubber particles directly. There were some fluctuations in average particle diameters and rubber volume fractions even for the same series, but we thought of them as experimental errors. We took average rubber volume fractions for each series, and coded each sample in the format of rubber particle size—rubber volume fraction—degree of graft as in Table 1.

The degree of graft is calculated as follows [1]:

$$\text{degree of graft (\%)} = 100 \times (\text{gel\%} - \text{PBD\%})/\text{PBD\%},$$

where gel% is the weight fraction of the methtyl-ethyl-ketone non-soluble part in the sample and PBD% is the weight fraction of polybutadiene in the sample. The degree of graft includes both the surface graft and occlusion.

All materials have number average molecular weights higher than 50,000, which is greater than $2M_e$ (M_e, the molecular weight between the entanglement, $\approx 19{,}000$ for polystyrene).

2.2. Tensile test

All materials were compression molded in a 1 mm thick plate at 230°C for 2 min, and were grooved by a rotating knife to make dumb-bell type specimens whose dimensions of the parallel part were 20 mm in length with a cross-section of $10 \times 1\ \text{mm}^2$.

Tensile tests were conducted on a Universal Testing Machine (AG2000E, Shimadzu) at a constant cross-head speed of 1.0 mm/min (strain rate: $0.0008\ \text{s}^{-1}$) at 23°C and 50% RH.

2.3. Dynamic mechanical test

Specimens for the dynamic mechanical test were cut into 40 mm long, 15 mm wide pieces. The storage and loss moduli and tan δ were measured on the Dynamic Mechanical Thermal Analyzer (DMTA, Rheometric Scientific) in the bending mode at a frequency of 0.1 Hz with the temperature ranging from −100°C up to 120°C.

2.4. Morphology

The microstructure of the graft materials was analyzed from ultramicrotomed sections, which were prepared from whitened areas adjacent to the fracture surface of the specimens by using a TEM.

3. Results and discussion

3.1. Morphology and tensile behavior

The microstructures of L-0.36-63, L-0.36-94, L-0.36-121 and L-0.36-185 are shown in Fig. 1. This figure shows that there are many occlusions (PS sub-inclusion) in the particles of rubber. In samples L-0.36-63 and L-0.36-94, the occlusions are relatively small and well developed, whereas in sample L-0.36-185, the occlusions are large and the rubber–occlusion interfaces become obscure. This indicates that the grafted chain changes the internal structure of rubber particles, i.e. with increasing the degree of graft, the occlusion

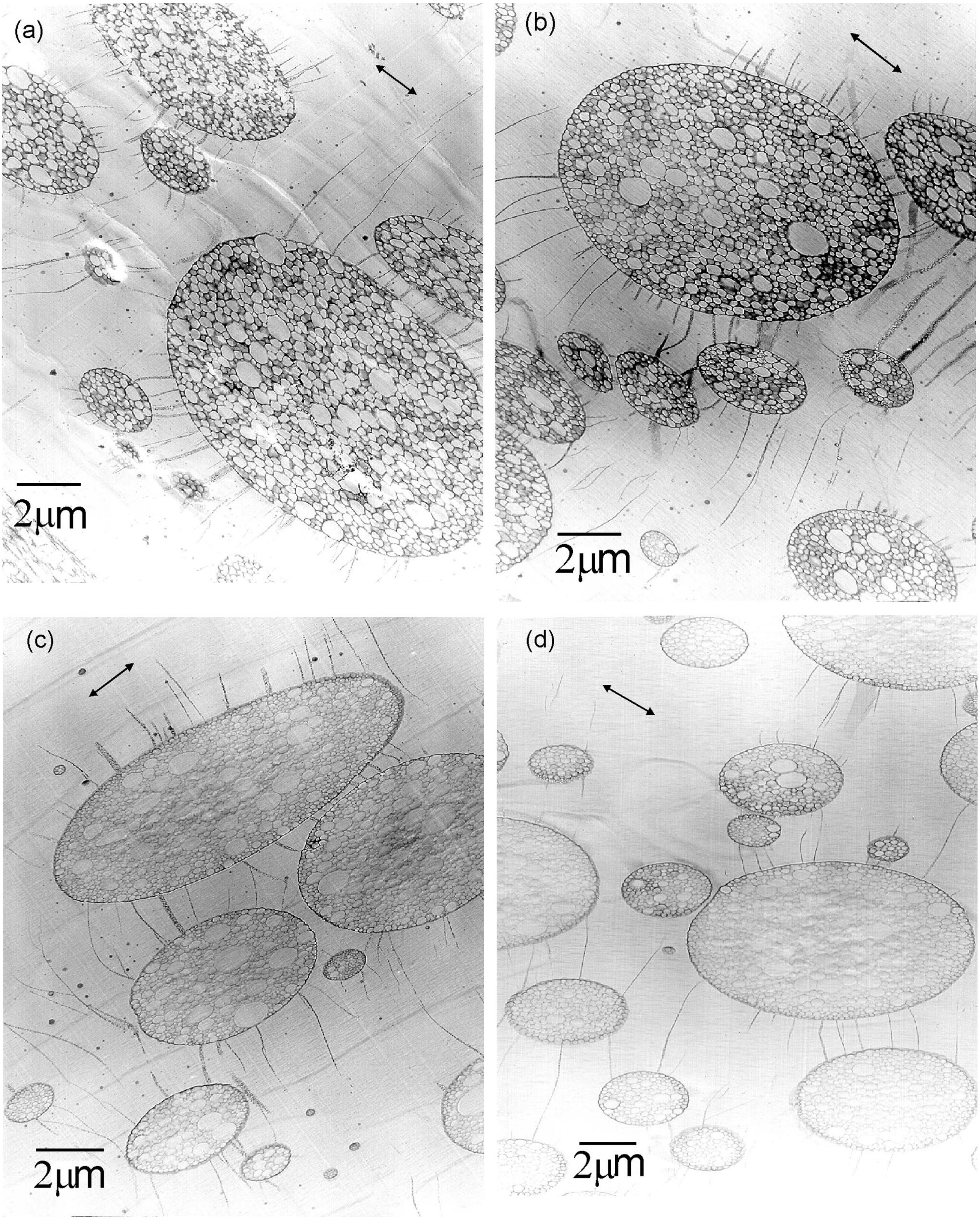

Fig. 1. TEM photographs of whitened areas adjacent to the fracture surface of the specimens of the L-0.36 series. Arrows indicate the tensile axis: (a) L-0.36-63; (b) L-0.36-94; (c) L-0.36-121; and (d) L-0.36-185.

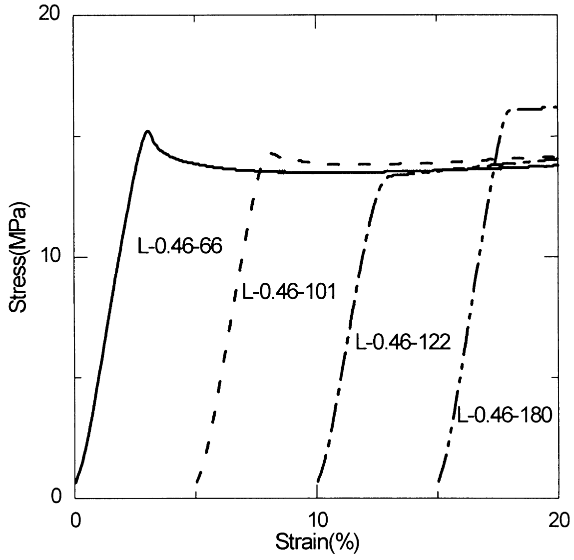

Fig. 2. Stress–strain curves of the L-0.46 series.

becomes larger and is not enclosed well by the rubber layers. At the interfaces between the rubber and the matrix, there are numerous crazes which are formed during the tensile test, and all the crazes initiated at the rubber–matrix interfaces propagated in the direction perpendicular to the tensile axis. From the direct observation of Fig. 1, it can be seen that there are more crazes in samples L-0.36-63, L-0.36-94 and L-0.36-121 than in the sample L-0.36-185.

Typical stress–strain curves for the series of L-0.46 are given in Fig. 2. To distinguish the curves, the starting strains are shifted horizontally to 0, 5, 10 and 15% in the order of increasing degree of graft, respectively. A distinct yield point is observed in the samples L-0.46-66 and L-0.46-101, whereas in the samples of higher degree of graft, L-0.46-122, L-0.46-180, the yield points are not distinct. This figure also shows that the yield stress is gradually decreased as the degree of graft increases up to 120% and then increases, although the two samples do not have distinct yield points. To discuss the yield stress behavior, we define the yield stress as follows: for the materials showing a distinct yield point, the yield stress is the stress at the maximum stress point around the yielding region, and for the materials not showing a distinct yield point, we adopted the 0.5% offset yield [9]. The yield stress dependence on the degree of graft for various rubber volume fractions and rubber particle sizes are plotted in Fig. 3. As seen from this figure, there are minimum values in the yield stress regardless of rubber volume fraction and size of the rubber particles: the yield stress decreases as the degree of graft increases up to about 120% for L-0.36, L-0.46 and S-0.37 and then increases, whereas that of S-0.28 has a minimum at the degree of graft of 90%. For all cases, the yield stress depends on the rubber volume fraction and the rubber particle size: the samples of higher rubber volume fraction and larger rubber particles have lower yield stresses.

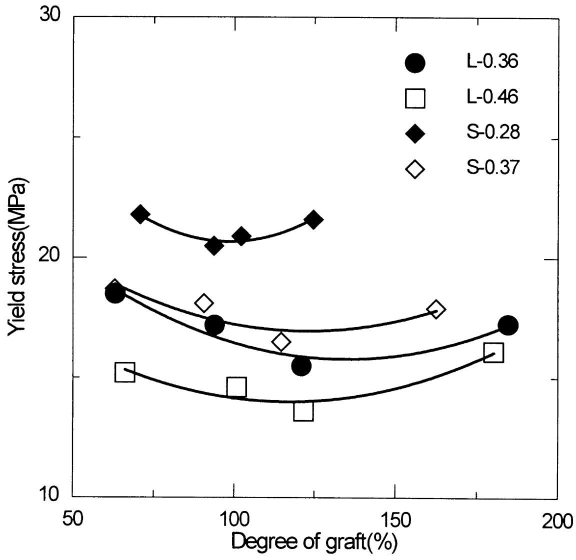

Fig. 3. Yield stress as a function of the degree of graft for various rubber particle sizes and rubber volume fractions.

Several reasons to explain this reduction in yield stress with increasing the degree of graft can be discussed as follows. First, the surface graft increases the effective volume of the rubber particle. Aoki [6] calculated the grafted layer thickness by using a core–shell structure. He showed that the ratio of the grafted layer thickness to the diameter of the rubber is changed from 3 to 12% with increasing the degree of graft from 41 to 111%. This increase in thickness increases the effective rubber particle size and the effective volume fraction of the rubbers. According to the Ishai–Cohen model [4], the tensile yield stress, $\sigma_{yt}(\phi)$ of a composite containing a volume fraction, ϕ, of voids or low modulus inclusions can be expressed as follows:

$$\sigma_{yt}(\phi) = \sigma_{yt}(0)(1 - 1.21\phi^{2/3})$$

where $\sigma_{yt}(0)$ is the yield stress of the matrix.

Applying this model to a HIPS polymer, we can see that the increased volume fraction of a rubbery particle by a grafted layer decreases the yield stress of the HIPS polymer. Second, the surface graft enhances the bond strength between the rubber particle and the matrix. It can be imagined that the grafted chain, at the region of the degree of graft less than a critical value associated with the molecular weight between the entanglement, is expected to disentangle easily when external stress is applied, and therefore yielding will occur at a very low stress. In this region, the yield stress will increase as the degree of graft increases. At the region beyond the critical value, the grafted chain will act as an effective agent for transferring the stress to the rubber particle. Since craze may be preferentially initiated at the occlusion–rubber interface in materials containing highly occluded rubber particles [10], the rubber particles in this region, having a higher degree of

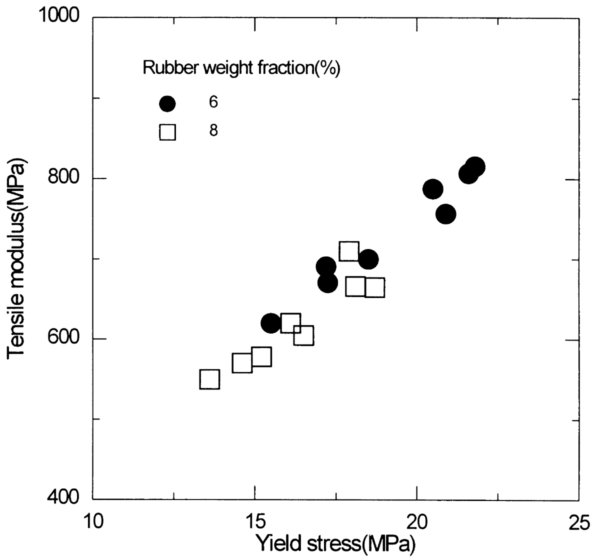

Fig. 4. The tensile modulus as a function of yield stress for the HIPS having different rubber weight fractions.

graft, can be deformed by a relatively lower stress, so that craze may be initiated at the occlusion–rubber interface at a lower stress and subsequently propagate through the matrix. Because of this, the yield stress drops with increasing degree of graft in this region, which corresponds to the region less than 120% in this study for HIPS. Third, according to several studies on the rheological properties of grafted polymers, there is an optimum degree of graft in dispersing the rubber particles into the matrix [6,7]. If the degree of graft exceeds the optimum level (about 40% for an ABS polymer having particles of 170 nm in diameter), a repulsion between the rubber and the matrix may occur, and thus the rubber particles agglomerate. However, this theory is not appropriate in explaining the HIPS behavior, because the rubber particles in this study did not make any agglomerations even at the highest degree of graft.

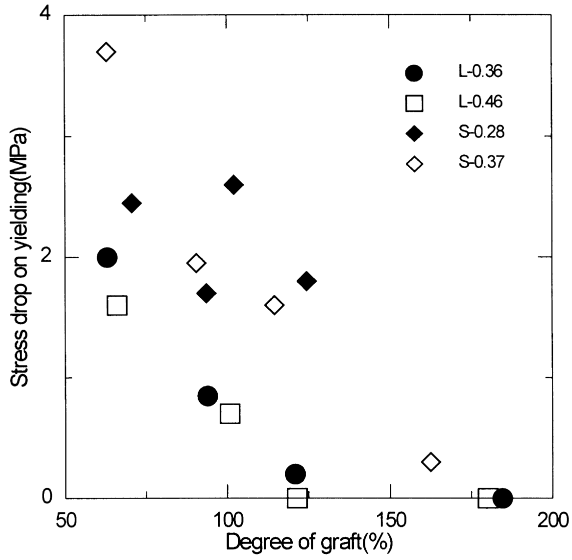

Fig. 5. Stress drop on yielding as a function of the degree of graft for various rubber particle sizes and rubber volume fractions.

It is thought that the increase in yield stress at the region with the degree of graft higher than about 120% is due to the change in the morphology of the occlusion. As shown in Fig. 1, the microstructure of sample L-0.36-185 is different from the other samples. For the other samples of relatively low graft, the occlusion in the rubber particles is enclosed well by the rubber layer, whereas for the sample of L-0.36-185, the occlusion is very large and is not enclosed well by the rubber layers. Several studies on the microstructure of HIPS suggested that the rubber particles having occlusions well enclosed by rubber layers act as better craze nucleators and also play a role in minimizing the large void [2,11,12]. Following their explanation, when an occluded particle (the rubber particles having occlusions) responds to an externally applied strain, the rubber elongates, whereas the PS occlusions remain essentially undeformed because of the much higher value of its Young's modulus. Locally, the rubber will break up into fibrils but no large voids are formed because of the occlusions separating the various domains of fibrillation. Hence, it can be considered that the rubber particles containing large occlusions which are not enclosed by rubber layers such as the particles of sample L-0.36-185, do not act as good craze initiators, and therefore the materials composed of these particles yield at higher stresses. In addition to that, particles having these characteristics create large voids leading to the failure of the matrix at low strains. It can be thought that the surface graft and the small occlusions well enclosed by the rubber shell lower the yield stress, whereas the large occlusions increase the yield stress, whereas the large occlusion increases the yield stress resulting from the reduction of the occlusion–rubber interfaces.

Fig. 4 shows that there is a good correlation between the tensile modulus and yield stress. This figure indicates that the tensile properties can be modified widely by changes in the rubber volume fraction, the degree of graft and particle size, even though the rubber weight fraction is the same. The tensile modulus also increases in a manner similar to the yield stress with increasing the degree of graft.

Another peculiar phenomenon in this tensile experiment is the stress drop on yielding (yield drop) which is defined as the difference between the stress at the yield point and the minimum stress after yielding. The yield drop decreases linearly with increasing degree of graft and finally reaches zero except for S-0.28 as shown in Fig. 5. The samples having large particles seem to have lower yield drops than those having small particles. For the polymers, which form necks in the tensile test, the stress drops beyond the yield point mainly due to the reduction in the cross-sectional area of the sample. Hence, these polymers do not show any stress drops in true stress–strain curves. On the contrary, the deformation of HIPS seems to be mainly due to craze, and therefore the specimen hardly has any changes in the cross-sectional area (<5%) during tensile deformation. Hence, it

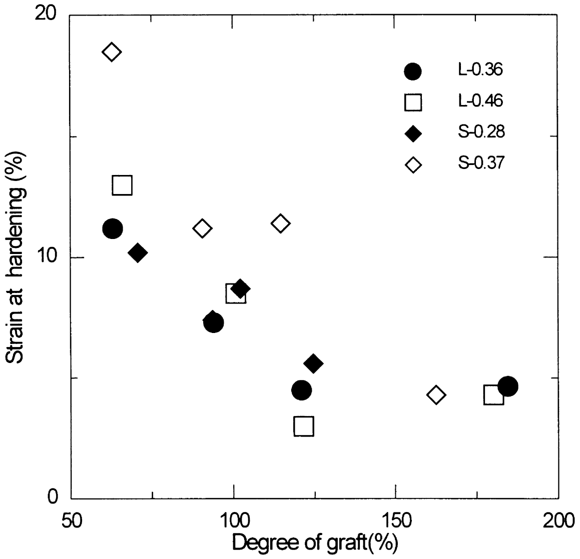

Fig. 6. Strain at hardening as a function of the degree of graft for various rubber particle sizes and rubber volume fractions.

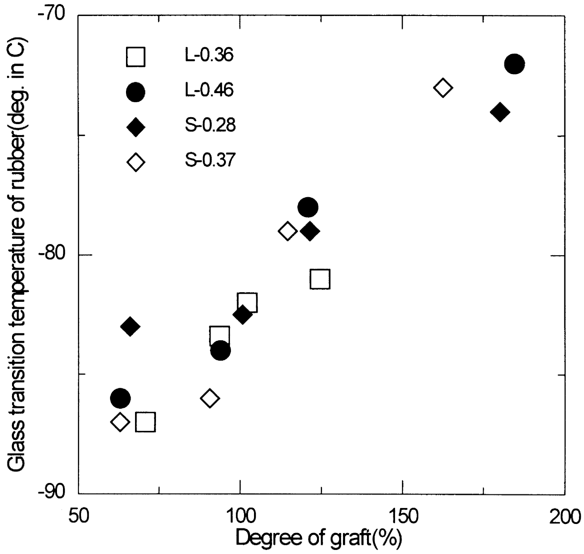

Fig. 8. Glass transition temperature of the rubber phase as a function of degree of graft for various rubber particle sizes and rubber volume fractions.

is considered that the stress drop on yielding in HIPS is related to the craze density and the strain propagation rate throughout the specimen. Truss [13] revealed that the rate of crazing is initially higher than the constant rate recorded through volume strain measurement after the post-yield drop in the load. The imposed strain to the specimen creates crazes at the localized areas, which are seen as stress whitened and these areas are expanded. The localization of stress whitening gives rise to a significant drop in stress after yielding [8]. For the sample with low graft, the strain makes many large crazes, whereas a few crazes are examined in the samples of higher degrees of graft. Thus it can be said that the reduction in yield drop with increasing degree of graft comes from the reduction in the number of crazes and the crazing rate in the region of stress drop after yielding. In addition to this, the strain at which the strain hardening begins in stress–strain curves may be a strain at which the propagation of the whitened region ends. The strain at hardening decreases with increasing degree of graft as shown in Fig. 6. Therefore, it can be said that the propagation rate of localized strain is higher in higher grafted materials than in lower grafted ones. By these reasons, the stress drop on yielding declines as the degree of graft increases.

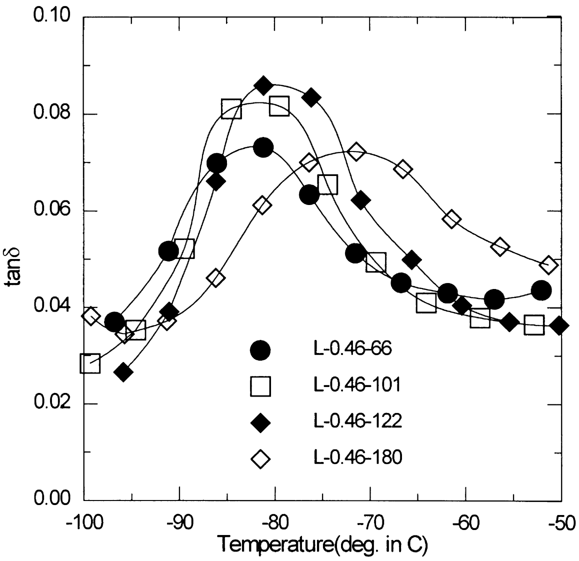

Fig. 7. The tan δ curves of the L-0.36 series measured at the frequency of 0.1 Hz.

3.2. Dynamic behavior

The two components of the HIPS systems show distinct glass transitions: one, in the region around −80°C, belongs to the rubber phase (polybutadiene), and the other, in the region of about 120°C, belongs to the PS phase. In the following, only the glass transition of the rubbery phase is discussed. The tan δ curves of L-0.46 measured at 0.1 Hz ranging from −100 to −50°C are illustrated in Fig. 7. As shown in this figure, the temperature at which the tan δ has the maximum value (T_g of polybutadiene) shifts to a higher temperature as the degree of graft grows, and the value of maximum tan δ increases and then decreases with an increase in the degree of graft. The glass transition temperatures of all the samples are plotted against the degree of graft in Fig. 8. This shows that the T_g of polybutadiene shifts to a higher temperature almost linearly with increasing degree of graft regardless of the rubber volume fraction and rubber size, as expected. The maximum tan δ shows a peak at the degree of graft around 100–120%, and the materials having larger rubber volume fractions have a higher maximum tan δ (Fig. 9). It also indicates that the materials having larger rubber particles have higher maximum tan δ as the

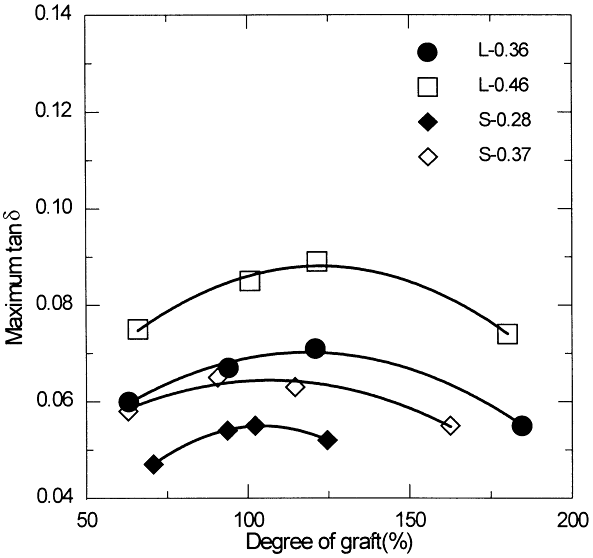

Fig. 9. Maximum tan δ belonging to the rubber phase as a function of degree of graft for various rubber particle sizes and rubber volume fractions.

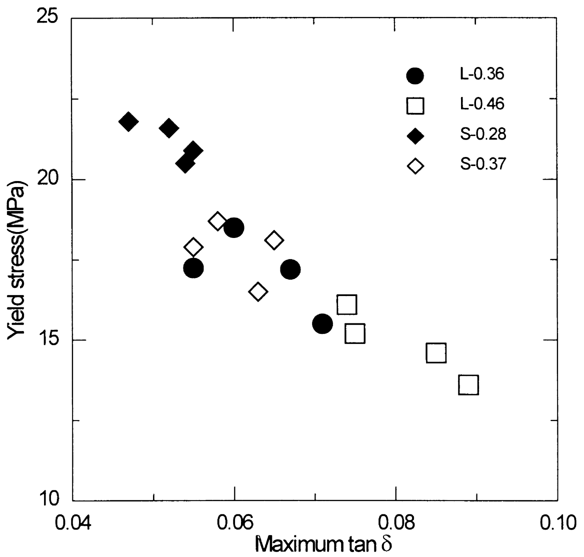

Fig. 10. Correlation between yield stress and maximum tan δ of the rubber phase.

two series, L-0.36 and S-0.37, which have similar rubber volume fractions, are compared. Since it is known that the maximum tan δ increases with increasing rubber volume fraction [3,14], the increase in maximum tan δ with the degree of graft can be explained by the increase in the effective volume of the rubber particles. Another explanation, which can be considered, is that more energy is transferred to the rubber chains for the materials having highly grafted rubber, through the chains grafted to the rubber surface. Thus, the material having highly grafted rubber dissipates the applied energy more effectively than that of a lower grafted rubber, which eventually increases the maximum tan δ. The decrease in the maximum tan δ value at the highest degree of graft seems to result from the restriction of rubber motion by highly grafted chains and large occlusions. It is also shown that large particles have higher maximum tan δ values than small ones.

To interpret the tensile properties through the dynamic response, we choose the test frequency 0.1 Hz, which is equivalent to the strain rate of the tensile test, 0.0008 s^{-1} [15]. The yield stress is plotted against the maximum tan δ in Fig. 10. It appears that there is a correlation between the yield stress and maximum tan δ: the yield stress decreases linearly with increasing the maximum tan δ. Because the response to the applied strain is the same within the linear region even though the deformation modes are different from tensile to dynamic tests, the tensile behavior has a correlation with the dynamic behavior. From this relation, it can be said that the yield stress in HIPS is primarily affected by the energy dissipation by the rubber phase, which is controlled by the rubber volume fraction, rubber particle size and degree of graft.

4. Conclusions

We have investigated the effects of the degree of graft on the tensile properties of HIPS. The yield stress and tensile modulus decrease with increasing the degree of graft up to about 120%, and then increase. The earlier part of this behavior arises from the increase in effective volume fraction of the rubber phase and/or from the increase in the stress transferred to the rubber particles. The latter part comes from the large occlusions, which are not enclosed by rubber layers.

The dynamic test revealed that the degree of graft depresses the mobility of the rubber chain, and thus increases the glass transition temperature of the rubber linearly, and showed that the maximum tan δ value varies with increasing degree of graft in a way contrary to the tensile properties.

The yield stress decreases linearly with increasing maximum tan δ.

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