

# The Effect of Grafting on Rubber-Phase Oxidative Etch Resistance in High-Impact Polystyrene

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## Synopsis

A relatively simple, reproducible method for the determination of grafting in high-impact polystyrene (HIPS) shows that high- and low-graft HIPS exhibit differences in morphology following treatment with an oxidative etching solution. Because this method is quite sensitive to small differences, it yields a more definitive evaluation of grafting in the finished polymer than any other previously used analytical procedure. These differences have been quantified, and the data used to compare relative grafting in polystyrenes reinforced with the same or different rubber types. The method shows an increase in grafting when either the peroxide initiator feed level or 1,2-vinyl content of the polybutadiene is increased.

## INTRODUCTION

In the free-radical synthesis of rubber-modified polystyrene, grafting<sup>1-3</sup> is the chemical reaction that connects polystyrene chains to polybutadiene rubber. On prepolymer samples of high-impact polystyrene (HIPS), in which the rubber phase has not experienced excessive crosslinking, the grafting efficiency can be obtained by the weight of polystyrene remaining in the rubber phase after dissolution of the matrix and occluded polystyrene. This technique is only useful in comparing samples at an equivalent state of conversion and has been used to demonstrate the increased level of grafting that is produced by use of peroxide initiator or high 1,2-vinyl content polybutadiene.<sup>4</sup>

In the finished polymer the presence of crosslinks in the rubber phase prevents the extraction of the occluded polystyrene. Therefore when solvent extraction is used in the well-known Ruffing gel test,<sup>5</sup> contributions of both occluded and grafted polystyrene to the percent gel cannot be separated. Ultrasonic degradation of the rubber particles has been used<sup>6</sup> to free the occluded polystyrene, but the drawbacks of incomplete breakdown of the rubber particles and degradation of the polystyrene itself have limited the popularity of this method.

The aim of the present work is to demonstrate a morphological technique for measuring differences in grafting in the finished HIPS polymer. We have used the technique of acid-etching<sup>7</sup> a freshly prepared HIPS surface to provide surface relief between the rubber and polystyrene phases. Under scanning electron microscope (SEM) examination, samples containing various levels of grafting exhibit distinct differences in the response of the rubber particles to the etching treatment. This etched-morphology difference has been quantified in terms of a *PR* value, which is defined as the percentage of rubber particles that retain occlusions following etching.

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TABLE I  
HIPS Samples Examined by the Etching Technique

Sample	Rubber type	1,2-Vinyl unsaturation, % <sup>a</sup>	Initiator <sup>b</sup>	PR value, % <sup>c</sup>	Swelling index <sup>d</sup>
I-a	Taktene 1202	<2	None	43	12.4
I-b	Taktene 1202	<2	150 ppm TBPB	70	12.8
I-c	Taktene 1202	<2	300 ppm TBPB	88	13.3
I-d	Taktene 1202	<2	300 ppm BPO	54	13.1
I-e	Taktene 1202	<2	300 ppm TBPO	58	11.7
II-a	Diene 55	ca. 15	None	61	11.3
II-c	Diene 55	ca. 15	300 ppm TBPB	81	11.5
III-a	Experimental PBD	ca. 25	None	67	9.3
III-c	Experimental PBD	ca. 25	300 ppm TBPB	78	9.6

<sup>a</sup> Manufacturer's data.

<sup>b</sup> TBPB = *t*-butyl perbenzoate; BPO = benzoyl peroxide; TBPO = *t*-butyl peroxide.

<sup>c</sup> PR = the percentage of rubber particles that have retained their occlusions in the etched sample (1-min etch time).

<sup>d</sup> The use of swelling index measurements to characterize crosslinking is discussed in Ref. 4. As the crosslinking increases, the swelling index decreases.

## EXPERIMENTAL

### Materials and Polymerization Method

Each polymerization feed stock contained one of the following polybutadiene rubbers: Taktene 1202 (Polysar Ltd.), Diene 55 (Firestone Tire and Rubber Co.), and an experimental rubber (courtesy of Firestone). In a representative feed, polybutadiene (10%), USP 21 mineral oil (Amoco Chemicals Corp.), and the usual stabilizers were dissolved in styrene (Amoco Chemicals Corp.), and the solution was loaded into a stainless-steel autoclave equipped with agitation capability. In some reactions, a peroxide initiator—either *t*-butyl perbenzoate (TBPB), *t*-butyl peroxide (TBPO), or benzoyl peroxide (BPO)—was added just prior to the run. In the mass thermal polymerization, each reaction mixture was subjected to the same heat cycle (ending at 210°C). Agitation rate and duration were varied from run to run to control rubber particle size.

### Etching Procedure and Morphology Examination

The HIPS samples were compression molded at 185°C into 60-mil-thick plaques, portions of which were sectioned on a Porter-Blum MT2-B ultramicrotome to produce a smooth undistorted face. During sectioning, the sample was cooled to -110°C (below the  $T_g$  of polybutadiene) on an LTC-2 cold-stage attachment to the ultramicrotome to avoid distortion of the rubber phase. After sectioning, the sample was immersed for 1 min in a bath containing<sup>7</sup> 400 ml fuming H<sub>2</sub>SO<sub>4</sub>, 130 ml H<sub>3</sub>PO<sub>4</sub>, 125 ml H<sub>2</sub>O, and 20 g CrO<sub>3</sub> at 70°C. After washing and drying, the samples were coated with a thin layer of gold and examined under the SEM. For comparison, two of the samples were stained with OsO<sub>4</sub> and then thin sectioned for TEM examination.<sup>8</sup>

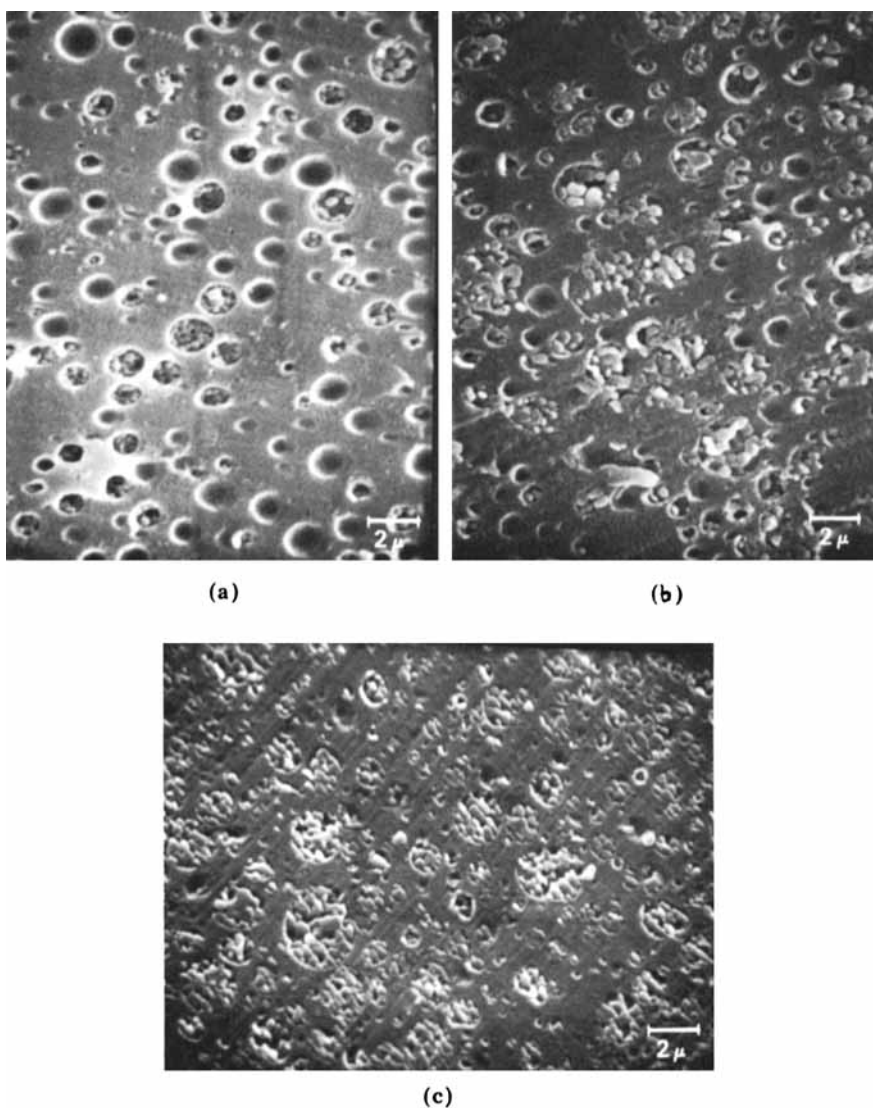


Fig. 1. SEM micrographs of etched samples prepared using Taktene 1202 polybutadiene: (a) sample I-a containing no initiator, (b) sample I-b made with 150 ppm TBPB, (c) sample I-c made with 300 ppm TBPB.

### ***PR Determination***

The percentage of rubber particles that retained polymer occlusions during etching was estimated by a simple counting technique. Translucent graph paper or mylar sheet was placed over a  $5000\times$  photomicrograph, and the particles with and without occlusions were indicated by different marks. In most cases individual rubber particles either retained large numbers of occlusions or none at all. Particles less than 1  $\mu\text{m}$  in diameter ( $0.2\ \mu\text{m}$  at this magnification) were not counted, because they were considered too small to contain occlusions. Generally, between 100 and 150 particles per micrograph were counted, and a minimum of two micrographs of different regions were counted for each sample. Reproducibility was usually better than 3%; but sometimes it reached 10% if the

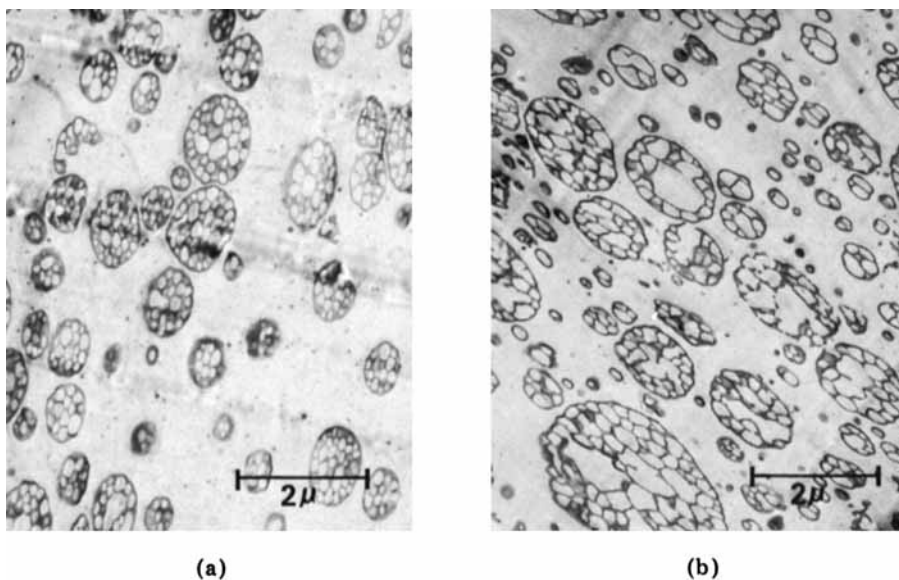


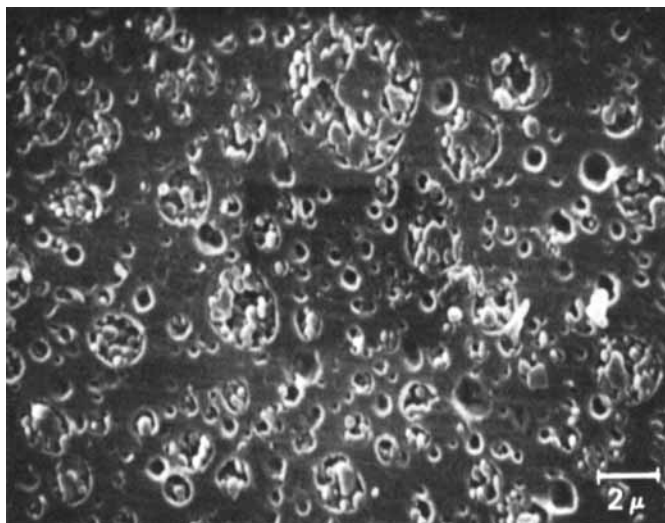
Fig. 2. TEM micrographs of  $\text{OsO}_4$  stained samples prepared using Taktene 1202 polybutadiene: (a) sample I-a containing no initiator and, (b) sample I-c made with 300 ppm of TBPB.

sample was especially heterogeneous or the absence of occlusions was difficult to discern. In order to gauge the effect of any etching time uncertainty on the resultant morphology, sample I-a (Table I) was etched for periods of 0.5, 1.0, 2.0, and 4.0 min and then examined under the SEM. The PR values measured for these four conditions were 41, 43, 42, and 33%, respectively. Since the uncertainty in the standard etching time of 1 min is estimated to be no more than 5 sec, any effect of etching time variability on the morphology would be negligible.

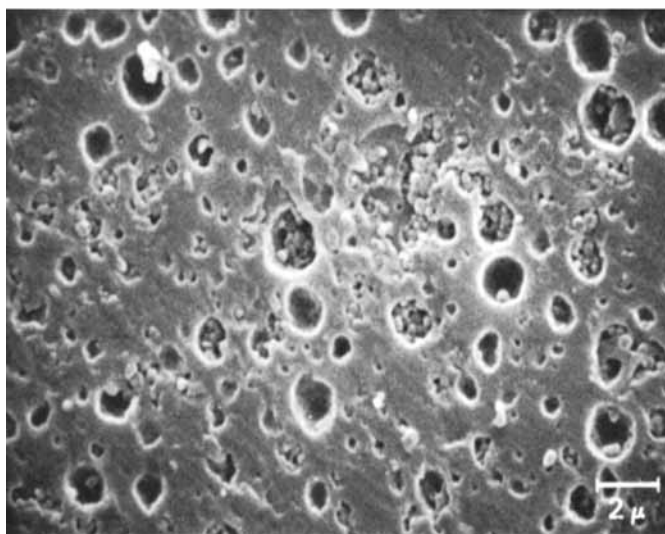
## RESULTS AND DISCUSSION

Table I lists the various samples we examined. The swelling index values indicate that the addition of an initiator caused a negligible increase in crosslinking for a given rubber. Such crosslinking generally occurs by the coupling of live polystyrene chains attached to separate rubber molecules. However, the rate of termination by this step must be slow, since the concentration of live grafts is low at any instant. SEM photomicrographs of the etched surfaces of samples I-a-c are shown in Figure 1. Dramatic differences are evident between those made with and without initiator. In particular, the etched morphology of the initiator-containing samples, I-b and I-c, show that most of the rubber particles have retained their polystyrene occlusions in contrast to what one observes for the noninitiator containing resin (I-a). This same difference in the etched morphology was consistently seen in other pairs of samples made using Taktene 1202, with and without TBPB.

The original rubber-phase morphologies of samples I-a and I-c are illustrated by the TEM micrographs shown in Figure 2. These micrographs show the samples to be quite similar with virtually all the rubber particles in both samples containing polystyrene occlusions. Sample I-a has some very small (ca.  $0.1 \mu\text{m}$ ) particles without occlusions, but these are too small to have contributed to the



(a)



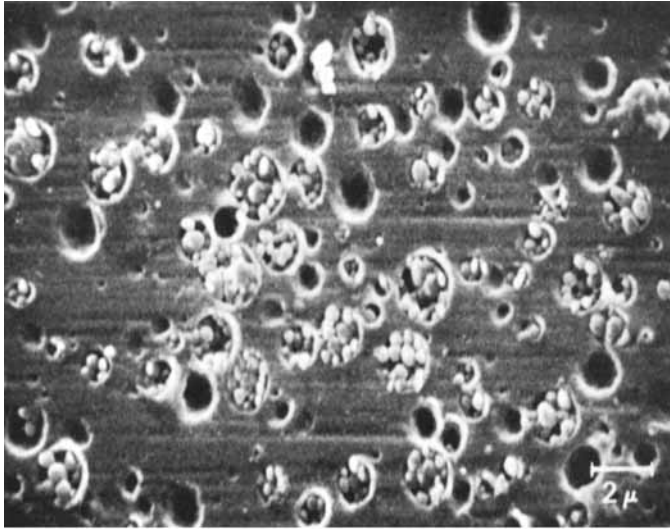
(b)

Fig. 3. SEM micrographs of etched samples prepared using Taktene 1202 polybutadiene: (a) sample I-d made with 300 ppm BPO and (b) sample I-e made with 300 ppm TBPO.

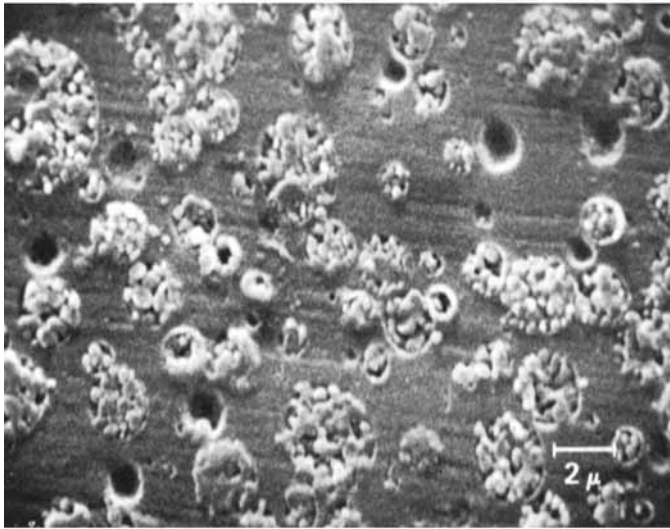
etched-morphology differences between the samples. There are no features in the micrographs shown in Figure 2, which would account for the large differences in etched morphology that are seen in Figure 1.

Certain other samples made with Taktene 1202 were also studied in order to determine the effect of other initiators, BPO (I-d) and TBPO (I-e), on the grafting and etched morphology. SEM photomicrographs of etched surfaces of these samples are shown in Figure 3.

Since the microstructure of the rubber is also known to affect grafting,<sup>4</sup> HIPS samples made with rubber having a higher 1,2-vinyl content were also studied.



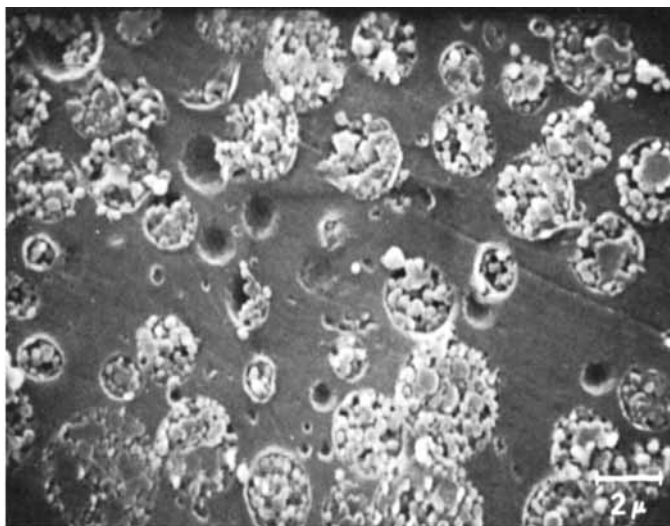
(a)



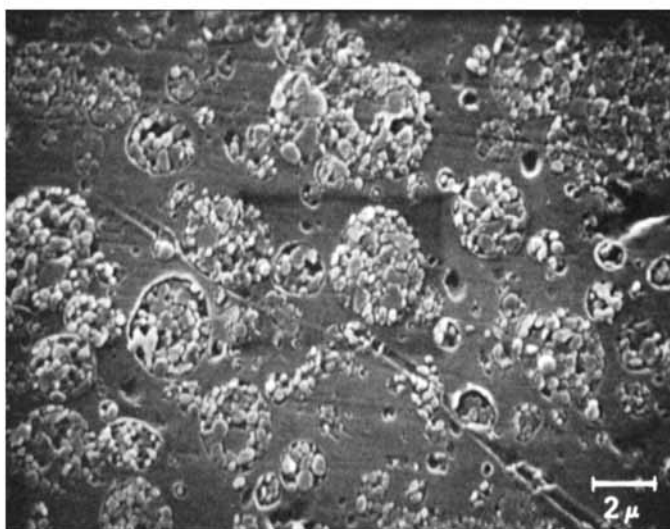
(b)

Fig. 4. SEM micrographs of etched samples prepared using Diene 55 polybutadiene: (a) sample II-a made without initiator and (b) sample II-c made with 300 ppm TBPB.

In Figure 4, micrographs of samples made with Diene 55 (ca. 15% 1,2-vinyl unsaturation), both with (II-c) and without (II-a), 300 ppm of TBPB are shown. Figure 5 illustrates the morphology of samples made using an experimental rubber with a still higher (ca. 25%) 1,2-vinyl unsaturation, both with (III-c) and without (III-a), 300 ppm of TBPB. The *PR* values measured for the various samples shown in Figures 1–5 are given in Table I. The samples known to have undergone increased grafting exhibited a systematic and consistent change in their etched morphology. These changes, quantified by the *PR* value, can be used to interpret relative grafting differences in the finished polymer that have resulted from variations in the initiator used or in the rubber microstructure.



(a)



(b)

Fig. 5. SEM micrographs of etched samples prepared using an experimental polybutadiene: (a) sample III-a made without initiator and (b) sample III-c made with 300 ppm TBPB.

The effect of rubber microstructure on grafting can be seen by comparing *PR* values. When no initiator is present, an increase in the 1,2-vinyl content of the rubber is accompanied by an increase in the *PR* value. This correlation may be partially due to higher crosslink densities in the resins modified with higher 1,2-vinyl content rubber. A preliminary investigation on the effect of crosslinking\* has indicated that excessive crosslinking of the HIPS induced by postpolymerization heat treatment can also increase the *PR* value. Nevertheless,

\* The effect of crosslinking on the etched morphology of HIPS will be dealt with more extensively in a subsequent paper.

the presence of TBPB during the preparation of the samples containing these three rubber types does indicate a further increase in grafting. For the Taktene 1202 samples, the level of grafting is seen to increase monotonically with TBPB concentration in the series I-a-c. For a TBPB concentration of 300 ppm, the greatest change in grafting with the addition of initiator is seen for the low 1,2-vinyl (high-*cis*) content rubber where the *PR* value increases by 45% relative to I-a.

In the case of the two samples prepared with BPO (I-d) and TBPO (I-e), a lesser degree of grafting has been achieved relative to I-a (no initiator). These differences in grafting can be explained by the relative rates of thermal decomposition of the peroxides. For a given reaction temperature cycle, PBO is consumed at a faster rate than TBPB, so that more BPO cleavage products are used to initiate styrene polymerization. In the case of TBPO, a less reactive initiator than TBPB, the average *t*-butoxy radical exists in a higher viscosity, phase-inverted medium. In order to explain the relationship between the etched morphology of HIPS and the level of grafting, one must take into account the selectivity of the etching treatment. The etching solution attacks the rubber phase much more readily than it degrades the polystyrene phase. This selective degradation provides surface relief between the two phases, thereby permitting observation of the size and internal morphology of the rubber particles. The polystyrene occlusions will be retained if the rubber membranes anchoring them to the polystyrene matrix have not been completely eaten away. As the level of grafting increases, the rubber should become more etch resistant, since the polystyrene content of the rubber is increasing. The manifestation of this greater etch resistance is the retention of occlusions by a greater fraction of the rubber particles.

## SUMMARY AND CONCLUSIONS

A technique has been presented for assessing the level of grafting in HIPS. This technique utilizes differences in the response of the rubber phase in various HIPS samples to selective etching. These differences arise from changes in the grafting level of the samples and manifest themselves in the etched morphology. Through use of this technique one can monitor the effect of a given preparation variable on the level of grafting produced in the finished polymer.

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