# Grafted Stock Synthesis of ABS at the Ultimate High Ratio of Polybutadiene to Poly(styrene-*co*-acrylonitrile)

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**ABSTRACT:** This study describes the emulsion grafting of styrene and acrylonitrile onto 60–70% polybutadiene (PB), in the presence or absence of *tert*-dodecanetiol as a chain transfer reagent with a radical initiator, and the properties of the obtained grafted stock. There was no significant difference in terms of effect of the initiation mode on the grafting efficiency resulting from the high grafting reactivity of PB. However, the grafted stock with 70% PB prepared in the presence of *tert*-dodecanetiol and the adequate selection of an initiation system gave a homogeneous dispersion of the PB particles into poly(styrene-*co*-acrylonitrile) (SAN) matrix. The initiation system involves *tert*-butyl peroxylaurate, *tert*-butyl peroxyacetate, and *tert*-butyl peroxyisopropylcarbonate coupled with ferrous sulfate. The efficient coverage of the SAN grafted layer around 70% PB particles was observed by TEM to eventually give excellent impact resistance, high surface gloss, and good thermal resistance. The absence of *tert*-dodecanetiol resulted in a toughness reduction of ABS. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 3462–3470, 2001

**Key words:** grafting; ABS; emulsion; *tert*-dodecanetiol

## INTRODUCTION

The use of dispersed particles of rubber to enhance the toughness of a normally brittle glassy plastic is well established. ABS, which consists of a polybutadiene (PB) embedded within a matrix of a styrene/acrylonitrile copolymer (SAN), is the most successful rubber-toughened thermoplastic that has several attractive properties.[1] These properties include excellent impact resistance and also applications in the automotive industry because its surface finishes are very smooth and can be easily decorated. Nowadays, a wide range of ABS-toughened plastics are produced and research into these materials remains as one of the more attractive areas of study in industrial and academic polymer laboratories, for example, polycarbonate/ABS,[2] inorganic/ABS,[3] polyamido/ABS,[4] poly(butylene terephthate)/ABS,[5] and polyoxazoline/ABS.[6] As a result of this extensive research and applications, the global amount of ABS production has reached about 6,000,000 tons per year.[7]

The synthesis of grafted stock of ABS—that is, the grafting of a styrene–acrylonitrile mixture onto PB using a radical-formatting initiator—has been intensive and is now a commercially established process.[8] After its preparation, the graft stock is mechanically mixed with separately prepared SAN in the required proportion to give the desired ratio of PB to SAN.

Manufacturers of ABS, however, must fulfill the criteria by producing ABS with good properties as well as increasing the productivity to survive keen global competition. Producing a grafted stock at a low SAN/PB ratio provides not only high productivity but also flexibility in producing a product line with different rubber levels with a minimum of reaction formation. Decreasing the monomers/PB ratio, however, results in a decreasing level of grafting onto PB. It is generally agreed that grafting of SAN to the PB particles is crucial to obtain maximum benefit from the rubber.[7] If the PB domains are not completely covered by a graft SAN layer, PB can coalescence, resulting in reductions in toughness, surface gloss, and thermal stability.[1]

On the other hand, the present authors recently demonstrated that the poly(dimethlylsiloxane) (PDMS) is inert against radical grafting; however, PDMS was able to be efficiency grafted by a selected grafting initiator.[9] As a result of further investigations about the grafting reactions, this study elaborates on the synthesis of ABS at the ultimate high PB/SAN ratio, that is, PB/SAN = 70/30.

## EXPERIMENTAL

### Preparation of the Grafted Stock of ABS

The graft polymer latices were prepared using the conditions described previously,[9] except for using PB latex instead of PDMS latex.

### Graft Ratio of the Polymer and Intrinsic Viscosity of Nongraft Copolymer

The graft ratio and grafting efficiency of the polymer were determined by solvent extraction with acetone (a solvent for SAN but not for PB).[10] Acetone solutions of the dried polymer (5% by volume) were prepared in 2-oz bottles, which were capped and shaken for 6 h at room temperature. The solutions were centrifuged at 30,000 rpm in a Hitachi Model CR-26H preparation ultracentrifuge (Hitachi, Japan) for 30 min at 0°C, then the supernatant layers were poured into a tared aluminum pan and dried, first at 60°C and then 24 h at 90°C *in vacuo*. The samples were cooled in a desiccator for 6 h and weighed. The fraction of soluble SAN was determined from the percentage solid corrected final monomer conversion. The

graft ratio and grafting efficiency were calculated by the following equations:

$$\text{Graft ratio (\%)} = \frac{\text{weight of grafted SAN}}{\text{weight of PB}} \times 100$$

Grafting efficiency (%)

$$= \frac{\text{weight of grafted SAN}}{\text{total weight of polymerized SAN}} \times 100$$

The fraction of soluble SAN : nongraft copolymer, having an intrinsic viscosity of 0.5 g/L, was measured at 30°C in 2-butanone. Replicate determinations were carried out for each latex recipe, and the grafting efficiency and the intrinsic viscosity were averaged.

### Preparation of Test Sample for Practical Properties

The blends of the grafted stock and SAN were obtained by molding with a single screw extruder at 200°C and were employed for injection molding at 220°C.

### Melt Flow Rate

The melt flow rate was measured according to JIS K7210.

### Rockwell Hardness

Rockwell hardness was measured according to ASTM D785.

### Thermal Resistance

The thermal exposure of 26.6% PB content ABS was carried out in an injection cylinder at 260°C for 30 min. After exposure, a test piece was molded via injection, then the tone of color (E) and yellow index (YI) were measured with a color tester (type MSC-1C; Suga Co., Japan). The ΔE and ΔYI were calculated as the gap of E or YI before thermal exposure and after thermal exposure.

### Other Properties

The other properties of the grafted stock and ABS were measured using the conditions previously described.[9]

## RESULTS AND DISCUSSION

There are two main synthetic methods of ABS.[1,2(c)] The methods involve bulk and emulsion
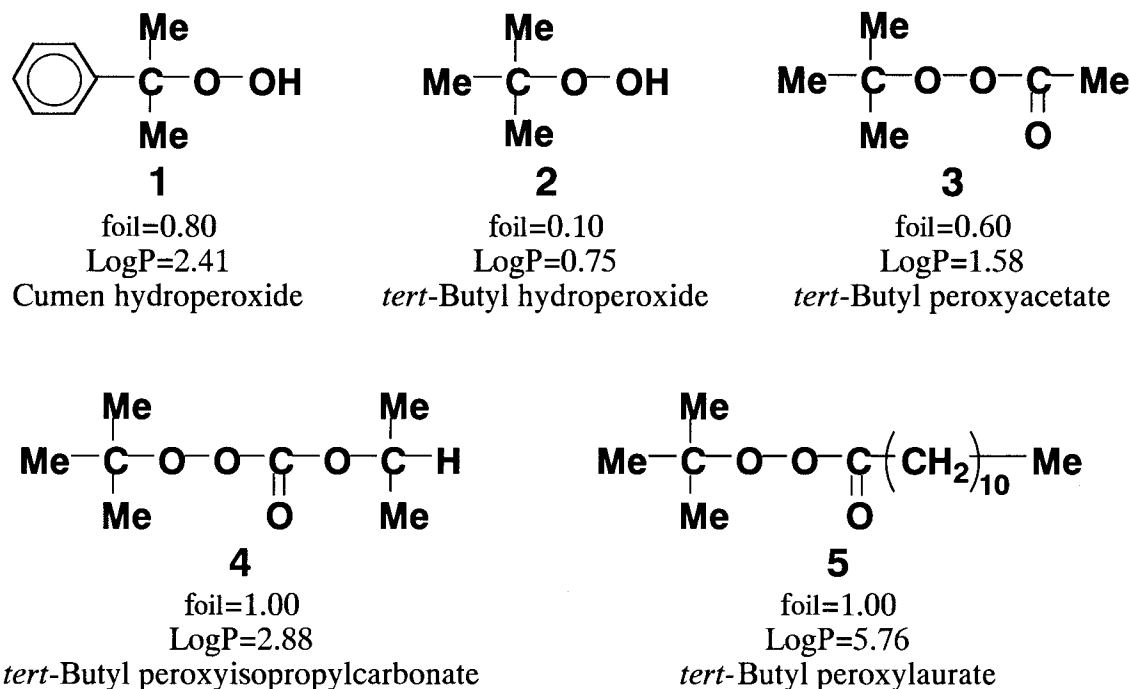
**Scheme 1.** Initiator molecular structure, name, $f_{oil}$, and log $P$.[9]

processes. Bulk ABS is made by the copolymerization of styrene and acrylonitrile monomers in the presence of a dissolved PB to which some grafting occurs. As the SAN copolymer is formed, phase separation proceeds followed by phase inversion, trapping some SAN within the PB phase.

The resulting PB particles have SAN occlusions and their particle distributions are relatively broad (0.5–1 $\mu$m). The amount of PB that can be incorporated into bulk ABS is limited by the viscosity and by the reaction stability (i.e., gelation of PB) to about 18% by weight.[2(c)] On the other

**Table I   Effect of Initiation Mode on Grafting at Monomers: PB = 40 : 60 Ratio[a] and Properties of 26.6% PB Content ABS Made by Melt Blending of the Grafted Stock and a SAN**

| Number | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Initiator[b] | 1 | 2 | 3 | 4 | 5 |
| Monomer conversion (%)[c] | 98.61 | 98.04 | 98.24 | 98.51 | 99.14 |
| Graft ratio (%) | 35 | 39 | 38 | 38 | 38 |
| Grafting efficiency (%) | 30 | 33 | 33 | 33 | 33 |
| $[\eta]_{MEK}^{40°C}$ of nongrafted SAN | 0.212 | 0.236 | 0.210 | 0.210 | 0.210 |
| Form of coagulum | Powder | Powder | Powder | Powder | Powder |
| Falling dart impact strength (J/m) | 3620 | 3920 | 4180 | 3940 | 4000 |
| Izod impact strength (J/m) | 461 | 490 | 461 | 470 | 470 |
| Melt flow rate (g/min) | 9.8 | 9.5 | 9.6 | 9.9 | 10 |
| Heat deflection temperature (°C) | 89 | 85 | 88 | 88 | 86 |
| Rockwell hardness | 87 | 85 | 86 | 86 | 88 |
| Surface gloss (%) | 83 | 82 | 82 | 85 | 83 |

[a] [PB]/([styrene]/[acrylonitrile]) = 150/(71.5/28.5) (g); [initiator] = $4.06 \times 10^{-3}$ mol, [*tert*-dodecanetiol] = $8.04 \times 10^{-3}$ mol.
[b] See Scheme 1.
[c] Measured by gas chromatography.

**Table II  Effect of Initiation Mode and *tert*-Dedecanetiol on Grafting at Monomers: PB = 30 : 70 Ratio[a] and Properties of 26.6% PB Content ABS Made by Melt Blending of the Grafted Stock and SAN[b]**

| Number | 1-1[c] | 1-2 | 1-3 | 2-1 | 2-2 | 3-1 | 3-2 | 4-1 | 4-2 | 5-1 | 5-2 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| PB (%) | 60 | 70 | 70 | 70 | 70 | 70 | 70 | 70 | 70 | 70 | 70 |
| Initiator[d] | **1** | **1** | **1** | **2** | **2** | **3** | **3** | **4** | **4** | **5** | **5** |
| *tert*-Dodecanetiol (×10⁻³ mol) | 8.04 | None | 6.03 | None | 6.03 | None | 6.03 | None | 6.03 | None | 6.03 |
| Monomer conversion (%)[e] | 98.61 | 96.87 | 97.10 | 96.21 | 96.10 | 96.51 | 96.70 | 98.12 | 98.20 | 98.81 | 98.71 |
| Graft ratio (%) | 35 | 36 | 26 | 37 | 28 | 36 | 29 | 36 | 26 | 35 | 28 |
| Grafting efficiency (%) | 30 | 73 | 61 | 74 | 65 | 72 | 68 | 72 | 61 | 71 | 65 |
| Form of coagulum | Powder | Rubber | Rubber | Rubber | Rubber | Powder | Powder | Powder | Powder | Powder | Powder |
| Falling dart impact strength (J/m) | 3620 | 3470 | 3530 | 2600 | 3100 | 3310 | 3750 | 3470 | 3528 | 2303 | 3820 |
| Izod impact strength (J/m) | 461 | 265 | 441 | 274 | 431 | 304 | 441 | 314 | 431 | 245 | 451 |
| Melt flow rate (g/min) | 9.8 | 6.5 | 7.7 | 5.7 | 6.3 | 7.0 | 10.1 | 7.1 | 7.7 | 8.0 | 8.1 |
| Heat deflection temperature (°C) | 89 | 91 | 91 | 91 | 91 | 91 | 92 | 91 | 92 | 92 | 92 |
| Rockwell hardness | 87 | 92 | 92 | 89 | 88 | 93 | 92 | 94 | 94 | 95 | 92 |
| Surface gloss (%) | 83 | 79 | 70 | 78 | 52 | 83 | 89 | 87 | 84 | 83 | 84 |

[a] [PB]/([styrene]/[acrylonitrile]) = 175/(53.6/21.4)/(g); [Initiator] = 4.06 × 10⁻³ mol.
[b] Blend recipe: ABS/SAN = 44.3/55.7 (wt %).
[c] No. 1 in Table I.
[d] See Scheme 1.
[e] Measured by gas chromatography.
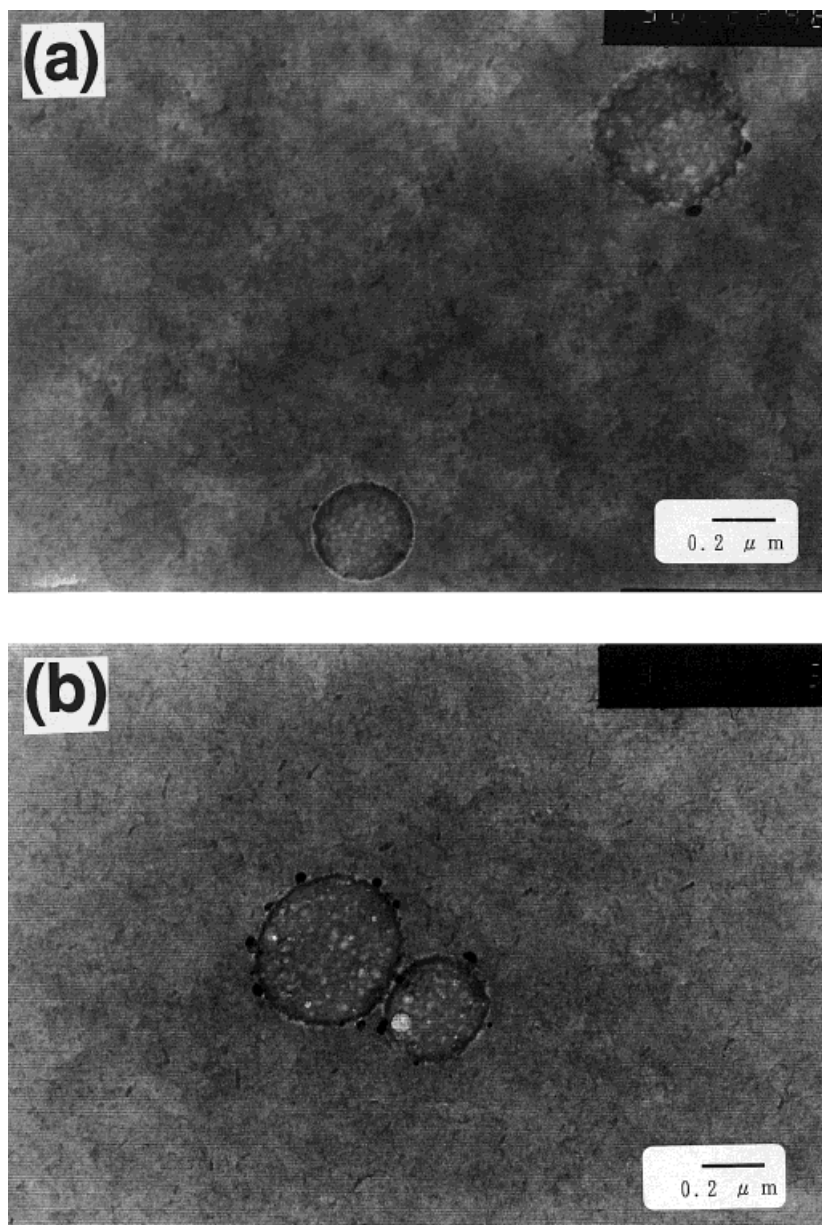
**Figure 1.**    TEM of the grafted stock isolated with acetone: (a) with 60% PB (no. 1-1 in Table II); (b) with 70% PB (no. 5-2 in Table II).

hand, emulsion polymerization methods employ various possibilities to prepare ABS with a high PB content and PB controlled particle diameters and crosslinking density within a SAN matrix.[1] The monomers are added to a latex of PB and are polymerized by the addition of a radical initiator. A glassy polymer is formed, which diffuses outward, forming a shell around the rubber particle because it cannot remain dissolved in the rubber. The particles continue to grow as the monomer diffuses in and are converted to an additional

glassy polymer. The grafted stock of ABS is recovered from the latex via coagulation through the addition of electrodes. The coagulum is isolated by centrifugation and washed thoroughly with water to remove all salt residues, followed by drying and granulation, although spray drying can also be used. Finally, the grafted stock thus obtained was mixed with a SAN via thermal plasticizing, extruding, and granulating.

The graft SAN chains would not only disperse and stabilize the PB particles in a SAN matrix
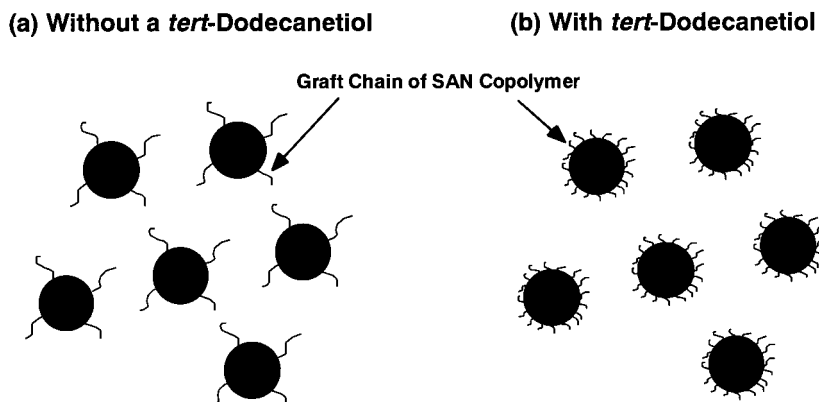
**Figure 2.** The schematic presentation of the grafted stock obtained: (a) without *tert*-dodenanetiol; (b) with *tert*-dodenanetiol.

but also be a stable producer of ABS. The stable producer is defined as follows. The graft layer of SAN with a high $T_g$ around the PB particles with a low $T_g$ prevents the coalescence of particles during the drying process. It is very difficult to convert the rubbery coagulum with a poor graft layer from a coagulation tank to the dryer process because the rubbery coagulum adheres to the coagulation tank. Criteria for the grafted stock syntheses of ABS with a high PB content, therefore, are not only to maintain a sufficient graft ratio but also efficient surface grafting around the PB particles using a limited amount of the feed monomers. The amount of PB that can be incorporated into the emulsion ABS is considered to be limited to about 55 wt %.[11] Thus, we investigated the grafted stock synthesis at an ultimate high ratio of PB to SAN, that is, the emulsion grafting onto 60 and 70% PB.

**Grafting at Monomer Ratio of PB = 40 : 60**

The influence of radical initiators, as shown in **Scheme 1**, on the emulsion grafting onto 60% PB in the presence of *tert*-dodecanetiol as a chain transfer reagent was studied. Table I shows the results of the grafting reactions and properties of 26.6% PB content ABS made by melt-blending of the grafted stock and a SAN. In all cases, the copolymerization proceeded with a quantitative yield and no drastic difference in terms of grafting efficiency, coagulability, and ABS properties was observed. Daniells et al.[10] also reported no difference in the grafting efficiency during the synthesis of grafted stock initiated by cumen hydroperoxide **1** and *tert*-butyl hydroperoxide **2**. These results are contrary to grafting onto PDMS, as

previously reported.[9] This is because the hydrogen abstraction rate of the PB's allyl position hydrogen is 400 times higher than that at the site of the pendant silylmethyl groups of the PDMS chain.[12] Any oxygen radical, therefore, could produce an efficient polymeric free radical as the site of grafting under this condition. Thus, we investigated the grafting with further smaller amounts of feed monomers in the following section.

**Grafting at Monomer Ratio of PB = 30 : 70**

*Effect of Initiation Mode*

Table II shows the results of the grafting onto 70% PB in the presence or absence of *tert*-dodecanetiol with a grafting initiator and their properties. In all cases, the effect of the initiation mode on the grafting efficiency was also not observed. The grafting efficiency increased with increasing PB/monomer ratio because the lower the monomer concentration in the PB particles, the greater the probability of hydrogen abstraction as opposed to propagation.[8(e)] In contrast, the grafting efficiency decreased with the addition of *tert*-dodecanetiol because the hydrogen abstraction depressed as well as decreased the molecular weight of SAN.[8(c),13] Drastic differences, however, in terms of the form of the grafted stocks via coagulation, and the properties of the ABS were observed. The grafted stock prepared by the cumen hydroperoxide **1** and *tert*-butyl hydroperoxide **2** system gave a rubbery coagulum with a large size (diameter 3–7 cm) and reduced the surface gloss of ABS. These results indicate that PB with low $T_g$ particles are not completely covered by the SAN graft layer with a high $T_g$; therefore,
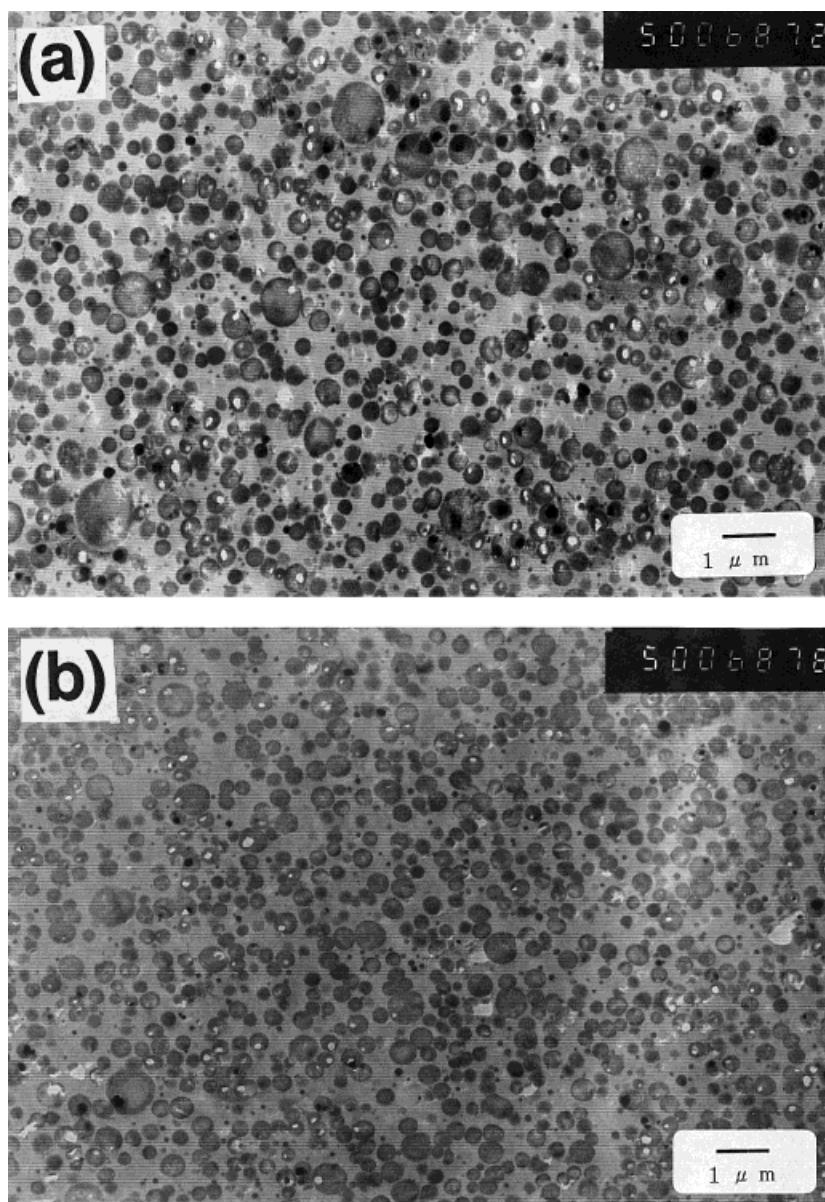
**Figure 3.** TEM of the 26.6% PB content ABS using the grafted stock: (a) with 60% PB (no. 1-1 in Table II); (b) with 70% PB (no. 5-2 in Table II).

PB particles can coalescence, resulting in the formation of a rubbery coagulum. The low surface gloss of ABS is attributed to the rough surface caused by the existence of large PB particles produced by the aggregation of PB particles into the SAN matrix.

In contrast, as initiators, the *tert*-butyl peroxyacetate **3**, *tert*-butyl peroxyisopropylcarbonate **4**, and *tert*-butyl peroxylaurate **5** systems gave a very fine powdery coagulum (diameter 0.5–2 mm) and high surface gloss to the ABS. The good initiators may fulfill the criteria for producing ABS

with excellent properties by generating only the *tert*-butoxy radical, which, because it is hydrophobic, is reluctant to form a carbon radical via $\beta$-scission.[14] They could produce a dense graft layer because of the high reactivity of the hydrogen abstraction reaction. Among them, the *tert*-butyl peroxylaurate **5** system gave the highest monomer conversion and highest impact resistance. To clarify the dense SAN graft layer, the TEM observations of the graft polymer particles containing 70% PB obtained with *tert*-butyl peroxylaurate **5** system were studied. The grafted
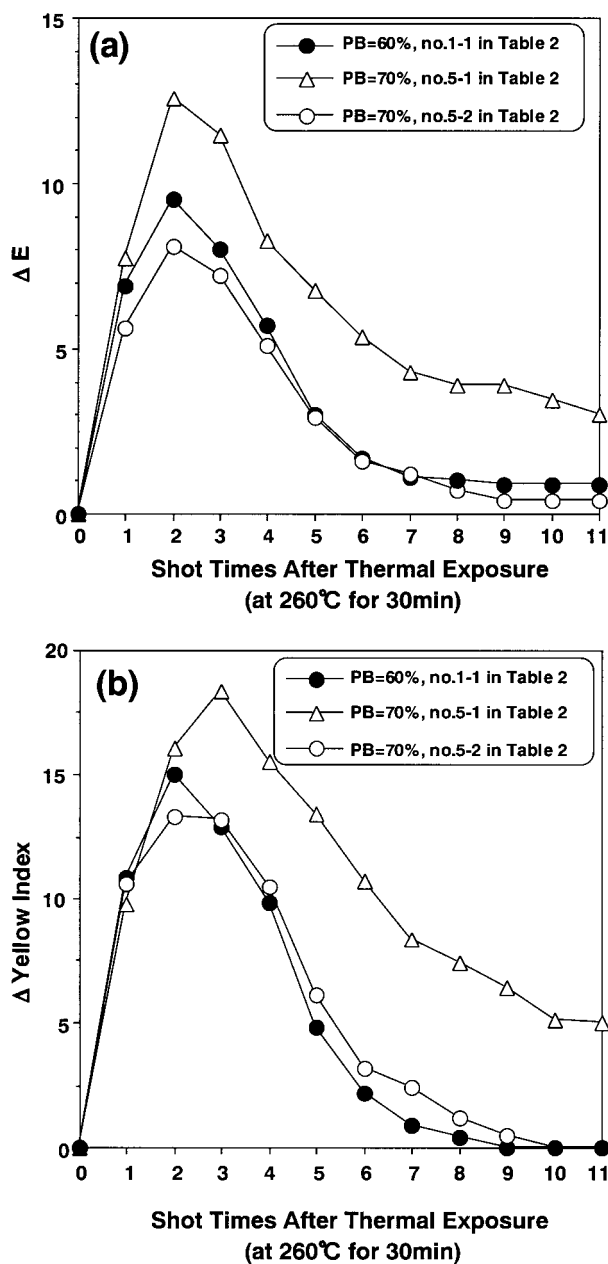
**Figure 4.** Relationship between shot times and $\Delta E$ (a) and shot times and $\Delta YI$ (b).

stock was recovered via coagulation and the free SAN was removed from the crude product with acetone. Finally, the isolated grafted stock was mixed with an epoxy resin. Figures 1(a) (PB = 60%, initiator; cumen hydroperoxide **1**, no. 1-1 in Table II) and 1(b) (PB = 70%, initiator; *tert*-butyl peroxylaurate **5**, no. 5-2 in Table II) show the TEM pictures of the isolated grafted stock. It was clearly observed that the light SAN graft layer surrounded the PB particles in both samples.

*Effect of Chain Transfer Agent*

In all cases, the grafted stock obtained with the addition of *tert*-dodecanetiol resulted in a drastic increase in the toughness of the 26.6% PB content ABS, even though the graft ratio was smaller than that obtained without *tert*-dodecanetiol, a result attributed to the following:

1. The addition of *tert*-dodecanetiol resulted in an increase of melt flow rate in Table II. The results indicate that the presence of *tert*-dodecanetiol decreased the molecular weight of the SAN copolymer.[12] Therefore, the grafting density of the grafted stock (i.e., the number of SAN graft chains per PB particle) prepared by the addition of *tert*-dodecanetiol may increase, as shown in Figure 2(b). The good coverage induced a homogeneous dispersion of PB into the SAN matrix, as shown in the TEM picture in Figure 3, and eventually gave a good toughness to the ABS.
2. The melting viscosity of the grafted stock is much higher than that of the SAN matrix. The decreasing molecular weight of the graft chain resulted in reducing the melting viscosity gap between the grafted stock and the SAN, and produced a homogeneous dispersion of the grafted stock into the SAN.

The toughness of ABS with the grafted stock containing 70% PB (nos. 3-2, 5-2 in Table II) is higher than that containing 60% PB (no. 1-1 in Table II). As shown in Figures 1 and 3, the amount of SAN occlusion into the PB particles with 70% PB is smaller than that with 60% PB. The presence of glassy subinclusions may reduce the flexibility of the rubber; therefore, the grafted stock with 70% PB has both a high degree of void formation and a high force dispersion ability.

**Thermal Resistance**

The PB-toughened resin generally shows a poor thermal resistance and bad weather resistance, which is caused by the oxidation of PB after periods of outdoor and thermal exposure. These poor resistances could be improved by the good coverage of a SAN shell over a PB core. Figure 4 shows the thermal resistance after thermal exposure at 260°C for 30 min. Fewer gaps indicate a good thermal stability. The grafted stock prepared by

the absence of *tert*-dodecanetiol with the *tert*-butyl peroxylaurate **5** system (△: no. 5-1 in Table II) changed drastically, which suggests a poor graft layer of SAN surrounding PB particles, as shown in Figure 2(a). In contrast, the grafted stock with 70% PB prepared by the presence of *tert*-dodecanetiol with the *tert*-butyl peroxylaurate **5** system (○: no. 5-2 in Table II) showed an excellent thermal stability as well as the grafted stock with 60% PB prepared by cumen hydroperoxide **1** system (●: no. 1-1 in Table II). These results suggest that the efficient coating of SAN over the PB core was able to be achieved using a small amount of feed monomers such as in Figure 2(b).

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