Rubber Particle Agglomeration Phenomena in Acrylonitrile-Butadiene-Styrene (ABS) Polymers. I. Structure–Property Relationships Study on Rubber Particle Agglomeration and Molded Surface Appearance

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SYNOPSIS

The effects of molecular structures of ABS fabricated under a severe molding condition on rubber particle agglomeration and molded specular gloss were studied. An agglomeration index (N_P) obtained by measuring particle size was used to determine the degree of rubber particle agglomeration. It was found that as graft level decreased, agglomeration increased. The rubber particle agglomeration also increased when graft molecular weight was increased. Lowering the particle size also led to a higher degree of agglomeration. Furthermore, increasing the compositional acrylonitrile mismatch between the grafted and matrix styrene-acrylonitrile copolymers increased the rubber particle agglomeration. Molecular structures that increased rubber particle agglomeration decreased the molded gloss. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Rubber particle agglomeration phenomena in rubber-dispersed thermoplastics such as acrylonitrile-butadiene-styrene (ABS), acrylonitrile-styrene-acrylate (ASA), and high-impact polystyrene (HIPS) have been reported.[1-12] Factors such as compositional difference between acrylonitrile level of grafted and matrix styrene-acrylonitrile copolymers (SAN) in ABS systems,[2,6,9] level of grafted SAN on dispersed rubbers,[1,6,9,12] rubber level,[1,3-5,7,9-11] molecular weight of matrix,[8] and rubber particle size[1,4-7,9-11] have been studied.

According to these studies, rubber particle agglomeration phenomena can be caused by various molecular structures: large compositional acrylonitrile mismatch, insufficient or too high graft coverage, high rubber level, high matrix molecular weight, and small rubber particle size. Rubber particle agglomeration phenomena can be experimentally detected by transmission electron microscopy (TEM). It can also be shown indirectly by a viscoelastic function such as G' (storage shear modulus),

which shows a peculiar behavior at low frequency regions (terminal zone), displaying a plateau region called the "second plateau," in addition to the rubbery plateau. The second plateau has a very long relaxation time, around 10^3 seconds.[3-5,10]

This study examines structure–property relationships for rubber particle agglomeration phenomena in ABS parts fabricated under a severe condition, rather than a mild condition such as an extrusion process, as was done in the earlier works. The use of a severe condition allows a closer approximation of the thermodynamic equilibrium state driven by the incompatibility between components in the system. In addition, it provides a structural tool to study the polymer field performance under aggravated conditions. The effects of molecular structures of ABS on the specular gloss of molded parts are also reported in this paper.

EXPERIMENTAL

ABS Preparation and Structural Analysis

The ABS materials were prepared using standard emulsion polymerization techniques. The rubber was

polymerized in a semi-batch mode using standard potassium persulfate initiator and fatty acid based surfactants. The emulsion rubber was a SBR rubber (10% styrene and 90% butadiene) type with a primary particle size D_w of about 0.08 μm diameter. The primary particle size was increased by acetic acid agglomeration to prepare particle sizes of about 0.19 and 0.50 μm before graft polymerization to give three primary particle size cases.

ABS polymers with different graft levels (GL = wt grafted SAN/wt rubber), acrylonitrile (AN) contents of the grafted SAN, molecular weights of the grafted SAN, and rubber particle sizes were prepared and analyzed (Table I). Graft level was evaluated by performing a gel separation on an acetone solvent dispersed ABS polymer using standard ultra centrifugation techniques. The AN composition was evaluated by an elemental analysis of the SAN components. The compositional acrylonitrile mismatch between the grafted and matrix SANs was calculated from the difference between the matrix SAN composition (26.5% AN, kept constant) and the grafted SAN composition (varied and measured by carrying out an ozonolysis treatment of the separated gel, followed by an analysis of the remaining SAN graft). Gel-permeation chromatography (GPC) was used to evaluate weight-average molecular weights M_w of the grafted SAN.

Polymer Fabrication

The final ABS materials for molding were made by Banbury mixer compounding of the rubber crumb concentrate and a dried SAN emulsion diluent (26.5% AN). This process gave an ABS final material containing a 17% rubber level and a matrix composition of 26.5% acrylonitrile.

The ABS pellets were molded under a severe condition (condition C) using a high stock temperature (270°C) and a long cycle time (injection time = 8 sec; holding + cooling time = 90 sec). When parts were injection molded under condition C, they showed rubber particle agglomeration that was sensitive to the ABS structures under study. In contrast, a mild molding condition (condition P) applied a lower stock temperature (230°C) and a shorter cycle time (injection time = 8 sec; holding + cooling time = 30 sec). The specular gloss of molded chips was measured using a 30° geometry.

Rubber Particle Size Analysis

The agglomerated and primary rubber particle sizes were measured quantitatively by a centrifugal photosedimentometer (CPSM; with the use of a Joyce Loebl type disk centrifuge). Details on the design and use of the CPSM have been written by Clark.[13] This process required that the rubber particles of the ABS molded part be dispersed in an acetone solvent at a 1% concentration, subjected to mild agitation using a wrist action shaker for approximately 16 h, and then analyzed. Care was taken to minimize breakdown of clusters while producing a colloidally dispersed grafted rubber cluster in the solvent. The solvent-dispersed rubber particles were then injected into the rotating disk centrifuge for measurement. A specific diameter was calculated using the Stokes' settling equation. This result was combined with the % light transmission and the use of MIE light scattering equations to obtain a calculated particle size and particle size distribution.[14]

An agglomeration index is defined as the number of primary particles (N_P) in the rubber particle agglomerate; i.e.,

$$N_P = V_A/V_P \approx D_{w,A}^3/D_{w,P}^3 \tag{1}$$

where V_A and V_P are volumes of agglomerated rubber particle and primary particle, respectively, and $D_{w,A}$ and $D_{w,P}$ are weight-average particle diameters for molded parts using condition C and for unmolded materials, respectively.

Weight-average particle diameters and agglomeration indexes are shown in Table I. The D_w/D_n ratio was measured to be 1.3–1.6 for pellet samples and was 1.3–4.2 for chip samples.

Morphology Study by Transmission Electron Microscopy

Selected samples were examined by a standard TEM technique. The specimens were microtomed sections stained by OsO_4. As shown in Figure 1, it became quite difficult to decide if rubber particle agglomeration was taking place for the studied systems that contained a large number of rubber particles. If the agglomeration was intensive, such as sample A4, rubber particle agglomeration could be observed by this standard sectioning technique [Fig. 1(e)].

However, in other cases, e.g., samples B6, C4, C5, and C6, where rubber particle agglomeration is not obvious, other techniques had to be used to determine the extent of rubber particle agglomeration. Consequently, a specific technique of preparing thin films of ABS for TEM was developed to examine rubber particle agglomeration.

The ABS was diluted from 17 to 1.7% rubber level by using a MEK solvent, and an additional amount of SAN polymer added to the solvent–ABS mixture.

Table I Effect of Molecular Structures on Rubber Particle Agglomeration and Molded Surface Appearance

Samples	GL (%)[a]	AN%[b]	M_w (kg/mol)	D_w (μm) (pellet)	D_w (μm) (C chip)	N_p	Gloss (30°) P chip	Gloss (30°) C chip
GL = ~ 30%								
A1	31.6	−0.6	53.6	0.194	0.648	37.3	54.5	6.9
A2	33.0	−1.0	72.9	0.194	0.339	5.3	68.0	35.0
A3	33.5	−1.9	68.3	0.194	0.537	21.2	58.0	9.6
A4	28.0	−2.6	57.6	0.194	0.883	94.3	44.0	3.0
A5	29.0	−5.8	93.8	0.503	0.526	1.1	53.0	47.0
A6	31.0	−8.9	70.7	0.503	0.577	1.5	56.0	49.0
GL = ~ 40%								
B1	39.6	−0.5	113.0	0.190	0.250	2.3	74.0	43.0
B2	44.1	−0.5	66.4	0.190	0.213	1.4	72.0	53.0
B3	40.2	−3.8	60.7	0.194	0.670	41.2	56.0	5.5
B4	41.0	−6.6	111.5	0.194	0.429	10.8	62.0	11.0
B5	44.0	3.3	131.5	0.194	0.317	4.4	60.0	15.8
B6	43.0	3.9	106.0	0.194	0.297	3.6	62.0	26.0
GL = ~ 50%								
C1	51.0	0.0	172.0	0.194	0.262	2.5	52.1	22.0
C2	53.0	1.0	146.5	0.194	0.227	1.9	57.0	41.0
C3	51.9	0.3	122.8	0.194	0.211	1.3	62.0	48.5
C4	53.2	0.4	87.8	0.190	0.195	1.1	72.0	57.0
C5	53.5	−4.3	111.5	0.194	0.242	1.9	68.0	42.5
C6	51.0	−9.8	96.9	0.194	0.509	18.1	57.0	11.0
GL = ~ 60%								
D1	57.7	0.3	85.8	0.190	0.193	1.1	72.0	57.0
D2	63.1	0.2	108.0	0.190	0.196	1.1	71.0	55.0
D3	59.1	0.2	121.0	0.190	0.194	1.1	68.0	52.0
D4	60.1	−3.7	153.5	0.194	0.226	1.6	59.0	41.0
GL ≥ 70%								
E1	70.0	−10.0	56.7	0.084	0.633	427.9	36.0	11.0
E2	72.0	0.5	74.5	0.084	0.276	35.5	62.0	39.0
E3	76.0	0.1	74.5	0.084	0.208	15.2	66.0	42.0

[a] GL, graft level (wt grafted SAN/wt rubber); M_w, weight-average molecular weight; D_w, weight-average particle size; N_p, agglomeration index; P, C, mild and severe molding conditions, respectively. The matrix SAN has acrylonitrile level of 26.5%. The rubber level of the final formulation is 17%.

[b] Graft − matrix.

The SAN was selected so that the AN copolymer composition matched the matrix SAN in the ABS. The sample–solvent mixture was gently shaken for about 16 h with a wrist action type shaker. The approach was to keep the energy input low so that the agglomerates were not broken.

A thin polymer film was prepared by slowly, vertically, and uniformly withdrawing a clean microscope slide from the solvent dispersion. The dried film was displaced from the slide and then mounted on a copper grid for staining by OsO_4.

For systems with more subtle levels of rubber particle agglomeration, the developed thin film technique (Fig. 2) differentiated the extent of agglomeration more clearly than the standard prepa-

ration technique (Fig. 1). The microscopy observations in Figure 2 were supported by the quantitative rubber particle analysis (see agglomeration index shown in Fig. 2) and correlated well with the molded specular gloss, especially for those molded by the severe molding condition C (Figs. 3 and 4 for gloss of molded chips by conditions C and P, respectively).

RESULTS AND DISCUSSION

Effect of Molecular Structures on Rubber Particle Agglomeration

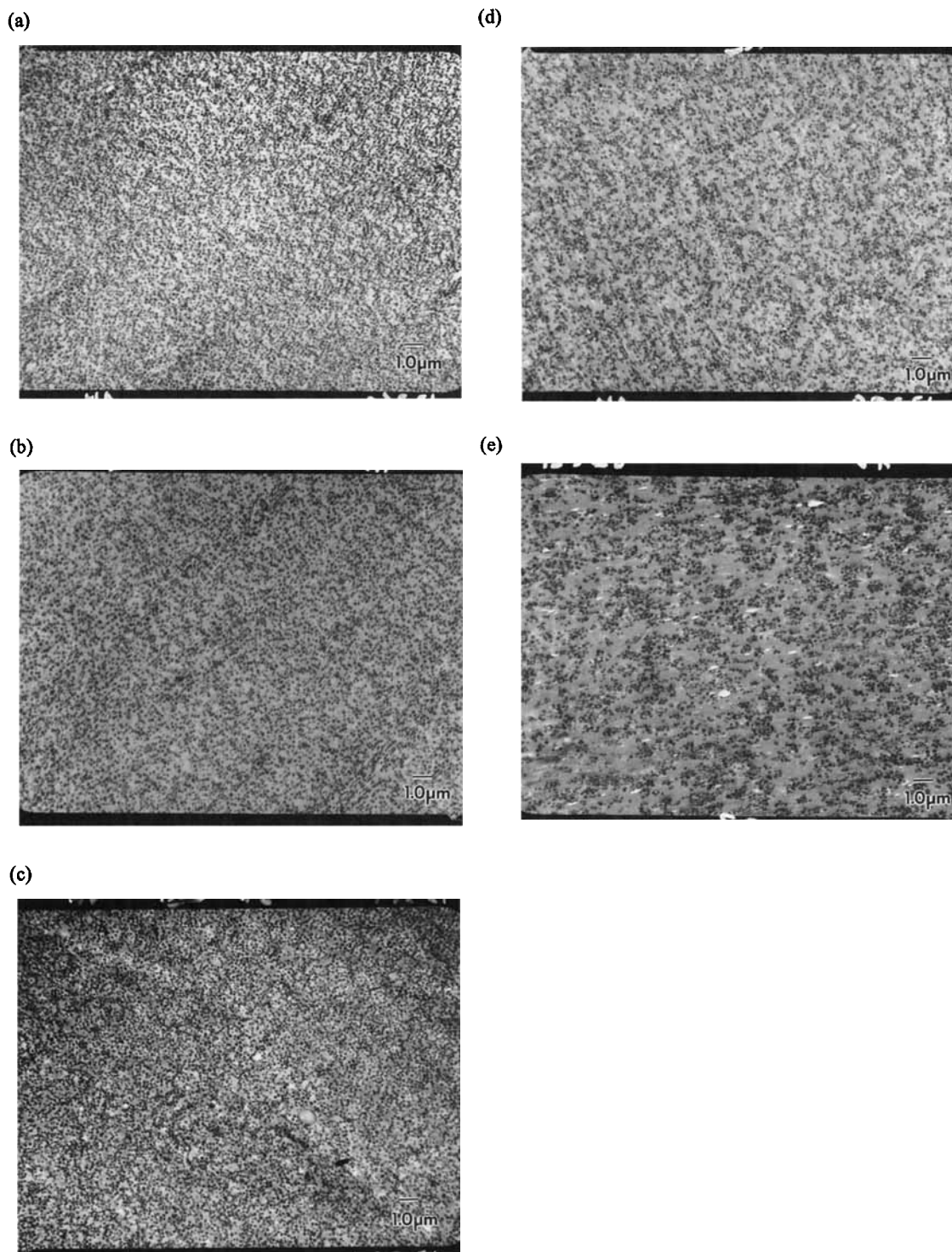Molecular structures of the ABS materials under investigation and the resulting rubber part-

Figure 1 Morphology of ABS samples prepared by the standard microtomed technique. Micrographs (a) to (e): samples C4, C5, B6, C6, and A4, respectively. The magnification is 4000.

icle agglomeration in the injection molded parts are shown in Table I. The effect of graft level and graft molecular weight is also shown in Figure 5. All the studied materials shown in those figures had a primary rubber particle size $D_{w,P}$ of 0.19 μm and compositional AN mismatch between the grafted and matrix SANs equal to or less than 1%.
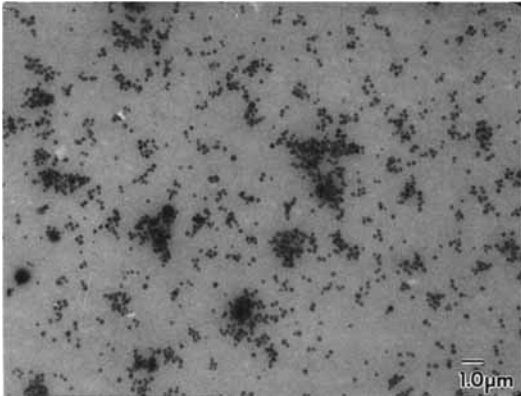
(a) N_p=1.1
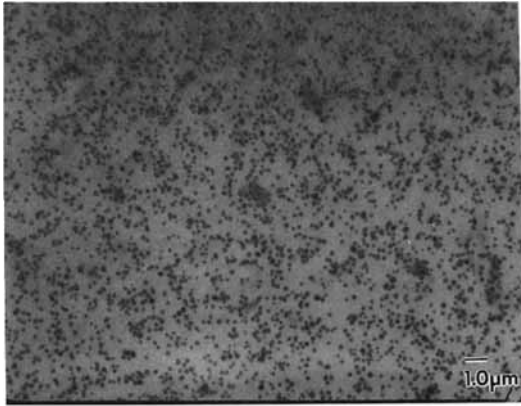
(d) N_p=18.1
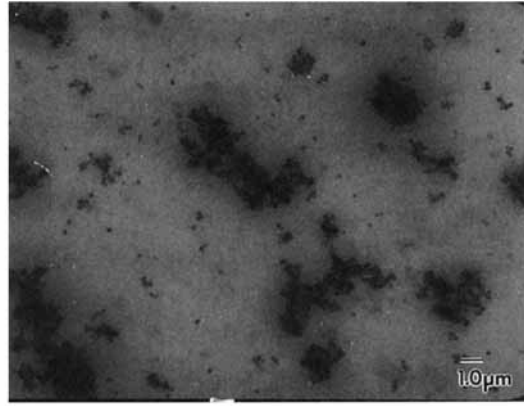
(b) N_p=1.9
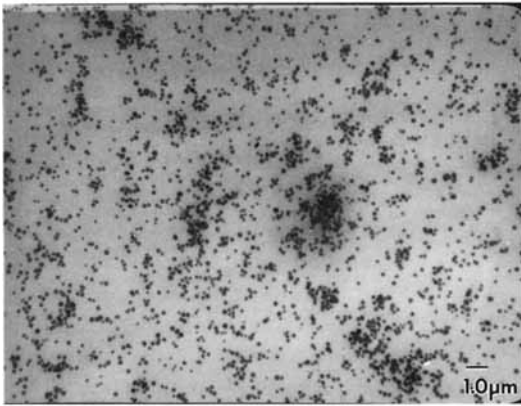
(e) N_p=94.3
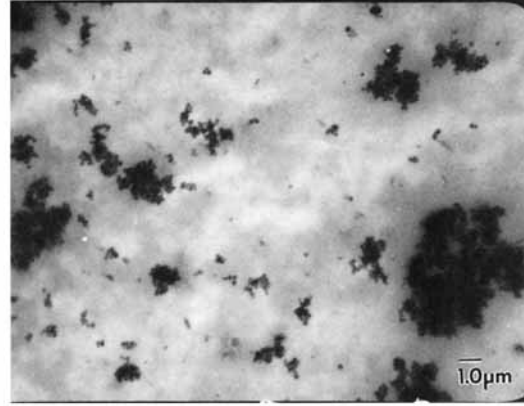
(c) N_p=3.6

Figure 2   Morphology of ABS samples prepared by the thin film technique. Micrographs
(a) to (e): samples C4, C5, B6, C6, and A4, respectively. The corresponding agglomeration
index (N_p) is shown in the top of each micrograph. The magnification is 4000.

As seen from Figure 5, at a high graft coverage
(60%), the rubber particles were stable with insig-
nificant agglomeration; i.e., the agglomeration index
N_P was close to 1.0. At intermediate graft levels (GL

= 40 and 50%), the degree of rubber particle ag-
glomeration increased with increasing graft molec-
ular weight. It is possible that a bridging phenom-
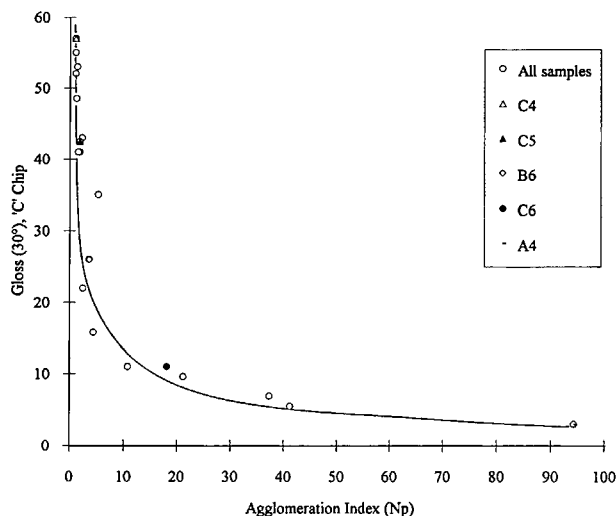enon occurred between the long graft molecular

Figure 3 Effect of rubber particle agglomeration on the gloss of molded chips produced under a severe molding condition, C. The primary particle size of rubbers is 0.19 μm. Micrographs for samples C4, C5, B6, C6, and A4 are shown in Figures 1 and 2 (a)-(e), respectively.

chains, which increases rubber particle agglomeration. On the other hand, at the lowest graft coverage (GL = 30%), N_P increased dramatically with decreasing graft molecular weight (Table I), although all systems at this coverage were quite unstable. Presumably, rubber particles with insufficient graft coverage tend to agglomerate owing to a driving force produced by the thermodynamic incompatibility between rubber and matrix. This agglomeration was enhanced by short graft chains which did not provide an effective steric effect.

Figure 5 also shows that lowering the graft level further increased the agglomeration, again a condition which could be caused by thermodynamic incompatibility. Rubber particles with a lower SAN graft level give an ABS having lower compatibility between the rubber and the matrix, hence leading to rubber particle agglomeration. Aoki[6] reported that with increasing graft coverage, rubber particle agglomeration (indicated by G) first decreased and then increased with a minimum located at a medium graft level. It should be noted that in his studied system, two factors, graft level and molecular weight, actually changed simultaneously; i.e., a higher graft level led to a higher graft molecular weight. In contrast, this study separates the effect of graft molecular weight from graft level and shows that they both have an effect on rubber particle agglomeration.

Table I shows that the degree of agglomeration increased as the particle size decreased. At the small particle size (0.08 μm), even with a high graft level

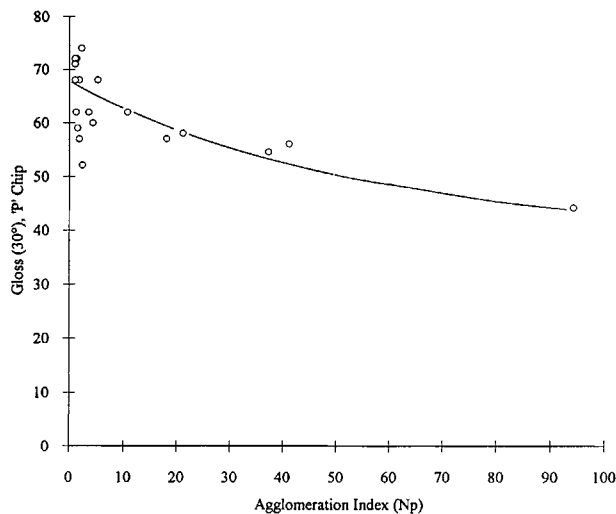**Figure 4** Effect of rubber particle agglomeration on the gloss of molded chips produced under a mild molding condition P.

(GL ≥ 70%), the particles were still agglomerated; whereas a low degree of agglomeration was found for materials with a rubber particle size of 0.5 μm. It is noted that a high graft level is needed for materials containing small particle size rubber that have a greater total surface area. A greater surface area increases surface free energy, which becomes a
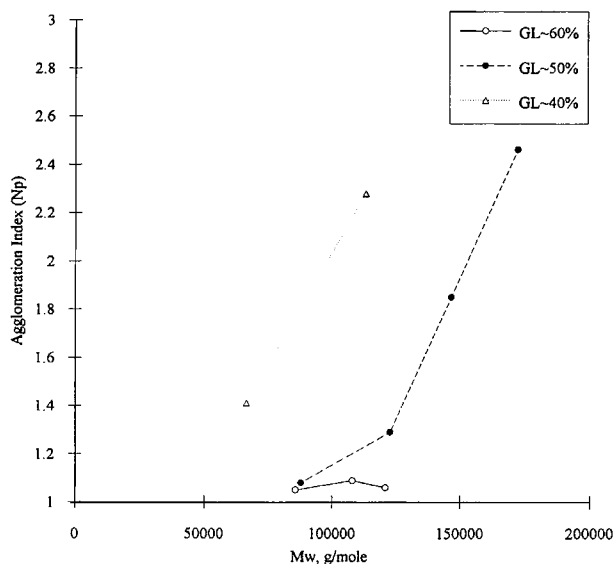

Figure 5 Effect of graft level and graft molecular weight on rubber particle agglomeration indicated by the agglomeration index. The compositional acrylonitrile mismatch between grafted and matrix styrene–acrylonitrile copolymers is equal to or less than 1.0%. The primary rubber particle size $D_{w,P}$ is 0.19 μm. The rubber level is 17%.

thermodynamic driving force for rubber particle agglomeration.

Table II, which is a subset of Table I, shows the effect of compositional acrylonitrile mismatch between the grafted and matrix SAN copolymers. Reducing the compositional AN mismatch decreased the tendency of grafted rubbers to interact with each other, thus minimizing rubber particle agglomeration.

Effect of Rubber Particle Agglomeration on Molded Surface Appearance

Rubber particle agglomeration phenomena decreased the specular gloss of the molded surface because agglomerates, which have a larger size than primary particles, increase surface roughness, which scatters more light and consequently leads to a lower gloss surface. As shown in Figure 3, the specular gloss (molded by severe condition C) decreased with an increasing agglomeration index. Hence, the molecular structures which affected rubber particle agglomeration affected the molded gloss in the same manner. It is also noted that with a slight increase in the agglomeration index, such as N_P between 2 to 10, the gloss dropped quite dramatically; whereas the molded gloss reached a plateau value at N_P greater than 10.

The gloss of molded chips produced under a mild condition P was shown to be relatively unaffected by the agglomeration index (Fig. 4). This observation is attributable to the agglomeration index with which particle agglomeration was evaluated for parts molded under condition C. Parts molded under this severe condition caused a rubber morphology near a thermodynamic equilibrium condition [having a
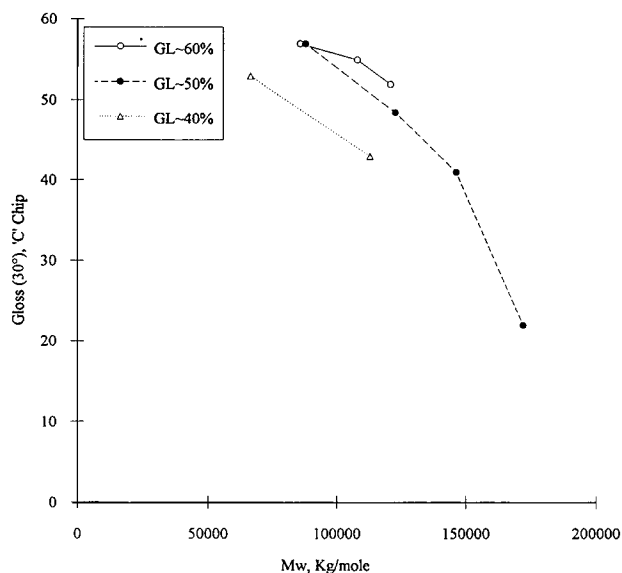

Figure 6   Effect of graft level and graft molecular weight on the gloss of molded chips produced under condition C. The compositional acrylonitrile mismatch between grafted and matrix styrene-acrylonitrile copolymers is equal to or less than 1.0%. The primary rubber particle size $D_{w,P}$ is 0.19 μm. The rubber level is 17%.

more complete phase separation (coalesced rubber particles) under a condition of higher temperature and longer residence time in a lower critical solution temperature (LCST) behavior]. In contrast, after being molded by a mild condition P, rubber particles of the materials did not reach thermodynamic equilibrium.

Figure 6 shows the effect of molecular structures on gloss, again indicating that the specular gloss (molded by severe condition C) decreased with an

Table II   Effect of Compositional Acrylonitrile Mismatch Between Grafted and Matrix Styrene–Acrylonitrile Copolymers on Rubber Particle Agglomeration and Molded Surface Appearance

Samples	GL (%)	AN%[a]	M_w (kg/mol)	D_w (μm) (pellet)	D_w (μm) (C chip)	N_p	Gloss (30°) P chip	Gloss (30°) C chip
A4	28.0	−2.6	57.6	0.194	0.883	94.3	44.0	3.0
A1	31.6	−0.6	53.6	0.194	0.648	37.3	54.5	6.9
B3	40.2	−3.8	60.7	0.194	0.670	41.2	56.0	5.5
B2	44.1	−0.5	66.4	0.190	0.213	1.4	72.0	53.0
B4	41.0	−6.6	111.5	0.194	0.429	10.8	62.0	11.0
B1	39.6	−0.5	113.0	0.190	0.250	2.3	74.0	43.0
C6	51.0	−9.8	96.9	0.194	0.509	18.1	57.0	11.0
C4	53.2	0.4	87.8	0.190	0.195	1.1	72.0	57.0

Abbreviations as in Table I.
[a] Graft − matrix.

increasing agglomeration index (also see Fig. 5). At a high graft coverage (GL = 60%), the rubber particles were stable with insignificant agglomeration; hence, the gloss was high at over 50. Higher graft molecular weight showed a slight decrease in the gloss.

At intermediate graft levels (GL = 40 and 50%), the degree of rubber particle agglomeration increased, and gloss decreased with increasing graft molecular weight. At the lowest graft coverage (GL = 30%), N_P increased dramatically with decreasing graft molecular weight (Table I). This change reduced the gloss. The gloss change correlated with the rubber particle agglomeration shown in Table I.

Figure 6 also shows that lowering the graft level decreased the gloss. This finding parallels an increased agglomeration index as shown in Figure 5.

Table I shows the effect of particle size on the gloss of the chips molded at condition C. For small particles with particle size equal to 0.08 μm, even with a high graft level (GL $\geq$ 70%), the gloss was at a medium level of 40. It is noted that, in general, rubber-modified materials containing small rubber particles, such as 0.08 μm, are expected to have a high gloss surface. The observed medium gloss value is caused by rubber particle agglomeration phenomena. On the other hand, materials with a rubber particle size of 0.5 μm obtained a fairly high gloss level at near 50 because low rubber particle agglomeration occurred (Table I).

The effect of compositional acrylonitrile mismatch between the grafted and matrix SANs on the gloss is shown in Table II. Reducing the compositional AN mismatch decreased rubber particle agglomeration, leading to an increased gloss of the chips molded at condition C.

CONCLUSIONS

Rubber particle agglomeration phenomena in ABS parts fabricated under a severe molding condition were examined by two useful experimental techniques: a TEM technique, which used thin film specimens qualitatively to examine agglomeration; and a rubber particle size measurement with which an agglomeration index, N_P (the number of primary particles in the rubber particle agglomerate), was applied to quantitatively determine the degree of rubber particle agglomeration. Rubber particle agglomeration was found to be caused by various molecular structures: large compositional acrylonitrile mismatch, insufficient graft coverage, high graft molecular weight, and small rubber particle size. The molecular structures which increased rubber particle agglomeration decreased the molded gloss.

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