Rubber phase dispersion in polypropylene

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Impact properties of rubber-modified blends are significantly dependent on particle size and size distribution (dispersion). Past work has shown strong variations in these particle parameters with different processing conditions and these variations reflect, in part, different shear fields developed during melt extrusion and moulding. A major problem ensues involving property variability because of process variability. It is neither practical nor economical to place stringent controls on process variability in a plant. Instead, our current research has indicated that lightly crosslinking the rubber reduced drastically the sensitivity of dispersion to processing conditions, and, with the correct rheology between the rubber and the resin, the same dispersion could be maintained through both the extrusion and moulding stages resulting in finished parts with increased chance of dispersion and property consistency. Four rubbers of different degrees of crosslinking and three polypropylenes of different melt flow and structure were blended at six rubber levels. Mixing was carried out with two twin-screw configurations and the blends were cast or injection moulded using a ram or a screw moulder representing six different processing shear histories. Dispersion was quantitatively characterized by scanning electron microscopy (SEM). Spherical rubber particles revealed on the fracture surface were counted and measured to determine particle size and size distribution for the individual blends. Correlation of the results indicated how particle size and size distribution was influenced by crosslinking and the rubber/resin rheology. This provided some understanding of the mechanics of soft-phase dispersion in these blends.

(Keywords: polypropylene; EPDM rubber; blends; morphology; toughening; dispersion)

INTRODUCTION

Physically blending two existing polymers to obtain a new material with improved mechanical, thermal and processing properties is an important concept in polymer science and technology. Rubber-modified thermoplastics, in particular, seem to offer added impact resistance while maintaining stiffness, strength, thermal stability and processability at a desired level. Past work showed strong dependence of blend properties on particle size and size distribution. Baer[1] found mechanical and dynamic properties to be determined mainly by particle size, independent of the processing method used to obtain such size. In general, the rubber particles are thought to have a dual role. They act as stress concentrators that initiate craze formation and as craze arrestors that prevent craze extension by branching[2,3]. Speri[3] found impact strength to favour small particle size (0.5 μm) and a narrow distribution (0.1 μm to 1.0 μm and centred around 0.5 μm). Toughening mechanisms were correlated quantitatively with particle size and size distribution in the work of Riew and co-workers[4]. For instance, crazing (later found to be cavitation) is dominant in epoxy resins toughened with large particles (1–5 μm), shear banding prevails in systems with small rubber particles (>0.1 μm), and optimum toughening is obtained under yield conditions that involve both shear and cavitation in blends that have both large and small particles (a bi-modal distribution).

Possible impact property improvements, achieved by controlling particle size and size distribution (dispersion), have stimulated recent development efforts in tailoring these particle parameters by varying processing conditions and rubber/resin rheology. The general conclusions are that strong shear fields developed during intense melt extrusion and moulding will produce fine dispersion[3,5,6] and large disparity in viscosity between rubber and resin and low-viscosity rubbers will also result in small particles[1,7]. Recent investigations in our laboratory[8–10], however, revealed some subtle exceptions to these rules. For example, intense melt extrusion in a twin-screw extruder can degrade the matrix and cause particle recombination. Subsequent screw injection moulding can also cause particle coalescence. Additionally, low-viscosity dispersed phase and large rubber/resin viscosity disparity result in smaller particles only in low rubber concentrations. At increasing rubber loading the trend is reversed due to reagglomeration.

Scission and reagglomeration of the dispersed phase both occur during a given process, and an equilibrium between large and small particles establishes the final dispersion. This dispersion, therefore, can be controlled both by the conditions of blending and moulding and by the rheological characteristics of the polymers. Twin-screw extrusion produces intense shear, often higher than more conventional mixing techniques. Extensive dispersion occurs first. Then the matrix is degraded and its viscosity, as well as the overall blend viscosity, is reduced. Two cases arise: low molecular weight rubbers coalesce much more readily due to rapid intermingling of macromolecules when they are brought into contact by forces of laminar flow; high molecular weight rubber particles, on the other hand, have more tenacity and may flow away from each other before significant recombination occurs. Reagglomerations of the lower molecular weight rubbers

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in reciprocating screw injection moulders are also evident. These particle recombination effects in processing also have been observed by other workers[5,11].

If process variability in a factory causes dispersion variability, a problem involving variations in the properties of the finished parts follows. It is neither practical nor economical to place stringent controls over blending and moulding conditions in a manufacturing plant. Instead, in our current research we have employed lightly crosslinked rubbers with increased molecular weight and viscosity to study their effects in reducing the sensitivity of dispersion to processing conditions.

This paper describes the materials selected and the techniques employed in compounding, moulding and characterizing a series of rubber-modified polypropylenes. The results will show how particle size and size distribution are influenced by composition, crosslinking, rubber/polypropylene rheology, and processing conditions, and provide some understanding of the mechanics of soft-phase dispersion in these blends.

EXPERIMENTAL

Materials

Polypropylenes. In our current investigation, three materials from Hercules Inc. were used as matrix resins. They offer a range of structure and melt behaviour and their properties are listed in *Table 1*. H65 and H63 are polypropylene homopolymers having different molecular weights, that of H65 being higher. H63 has, as a result, a higher melt flow rate and a lower viscosity. C75 is a terminal block propylene–ethylene copolymer, an impact grade that has significantly higher Izod and Gardner impact energies. All three materials show marked notch sensitivity and low temperature brittleness.

Rubbers. In our previous study[8–10] un-crosslinked EPDM (ethylene–propylene non-conjugated diene terpolymer) rubbers were used and rubber/polypropylene blends were prepared in two stages. First, 50:50 rubber/polypropylene masterbatches were blended in an internal mixer, then milled and diced into small cubes. Second, the rubber cubes and additional polypropylene were melt blended in a co-rotating twin-screw extruder. These blends, which contained un-crosslinked rubber, exhibited particle recombination and dispersion dependence on processing shear history as previously described. For our current investigation, lightly crosslinked EPDM rubber/polypropylene pre-blends supplied by Uniroyal Chemical were used. These systems, being 50%–75% EPDM in polypropylene, were blended in a manner analogous to our earlier masterbatch preparation with added peroxide for different degrees of crosslinking[12]. The pre-blends were prepared subsequently with additional polypropylene (second stage) to obtain desired compositions, which refer to actual weight percentages of EPDM rubber in the blends. *Table 2* lists various properties of the EPDM rubbers.

Processing

Blending. A co-rotating, twin-screw 53 mm Werner-Pfleiderer compounding extruder was used to combine Uniroyal pre-blends with additional polypropylene to final compositions. The machine consists of two screws placed side by side to provide conveying and kneading actions. The screws are convertible and constructed of blocks for any desired configurations. Two screw designs were employed in this work to provide 'low' and 'high' mixing shear. The first arrangement, generating what is termed low mixing shear, consisted of a series of compression and decompression elements. The second configuration had kneading blocks and reverse pitch flights and provided high mixing shear. At the end of the screws, the blended material was extruded through a die plate into a water bath. The quenched strands were then chopped into pellets. Extruder temperature profiles were kept essentially constant for both screw geometries.

Moulding. Injection moulding of blends into test samples was carried out also under two rates, low and high moulding shear. The moulding shear rate is defined as that occurring in the plastication operation, and both shear rates are much lower than in the blending stage. The high moulding shear was provided by a reciprocating-screw injection moulder, the low moulding shear by a ram injection moulder. A third moulding shear condition, that of essentially zero rate, was also obtained by casting samples in small shallow trays in a vacuum oven.

Morphology and dispersion characterization

ASTM flex bars were notched, placed in a liquid nitrogen bath and broken to create a fracture surface. Because of the brittle fracture and difference in thermal expansion when the sample warmed to room tempera-

Table 2 Crosslinked rubbers used in blends

Designation	Type	Cross-linking*	Crystallinity†
A	EPDM-1	Low	High
B	EPDM-2	Medium	Low
C	EPDM-2	High	Low
D	EPDM-1	High	High

* Crosslinking ranges from 15% (Low) to 40% (High) of total available crosslink sites based on amount of peroxide added.

† Crystallinity is based on ethylene content which ranges from 48% (Low) to 72% (High).

Table 1 Polypropylenes used in blends

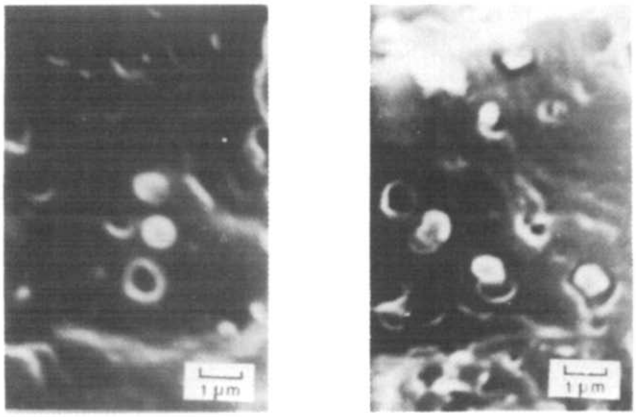
Polypropylene	Structure	Molecular weight	Melt flow, (g/10 min)	Notched Izod impact @ 23 °C, J/cm	Gardner impact J		Tensile properties @ 23°C	
					23°C	−34°C	Yield strength MPa	Modulus MPa
H65	Homopolymer	High	4	0.4	2.5	0.17	30	1580
H63	Homopolymer	Low	13	0.4	1.5	0.15	31	1800
C75	Copolymer[a]	High	3	1.3	36	4.1	23	1030

[a] Propylene—ethylene terminal block copolymer.

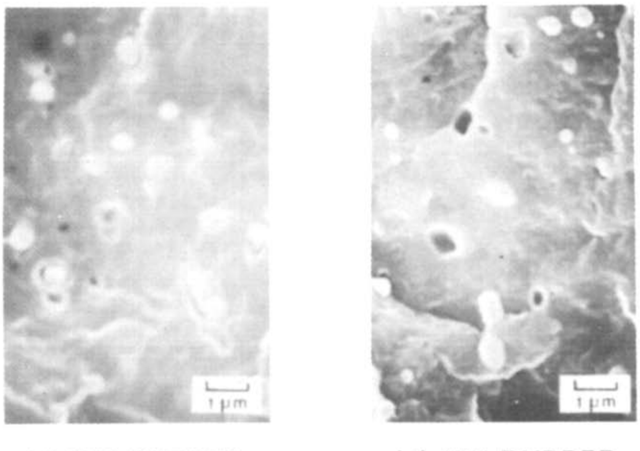
ture, the rubber particles were distinguishable on the fracture surface and were well resolved under the scanning electron microscope. Dispersion measurements involved photographing random areas of the fracture surface at various magnifications using SEM. The particles were then measured and counted to determine particle size and size distribution. The measurements were sometimes based on surface chord diameters instead of true particle diameters. On a comparative basis, the uncorrected results should not affect our conclusions.

RESULTS AND DISCUSSION

Figure 1 represents scanning electron micrographs of some of the blends prepared to study influence of composition on dispersion. The amount of discrete rubber evidently increases with increasing rubber concentration as expected. The particle size, shape and size distribution are qualitatively similar for all compositions. They are essentially spherical in shape and, under the SEM, appear white in a darkened polypropylene matrix. The interface is well defined and the rubber seems to adhere well to the matrix. In cases where rubber particles fall out of their sites in fracture, the sites are also spherical and well defined. To provide a quantitative assessment of composition effects on dispersion, representative rubber particles were measured and counted using scanning electron micrographs at magnifications from 1250 to 10 000 × . Typical results are presented in *Figure 2*. Three parameters—namely the average size (diameter), D_a; the median size, D_m; and the most frequently occurring size, D—are important descriptors of the population. A comparison of these parameters in *Figure 2* indicates that rubber phase dispersion changes very little with composition. The results may not be entirely unexpected in these low rubber concentrations. In high shear fields and for low concentrations, the extent of dispersion and the probability of particle contact and subsequent coalescence probably remains independent of composition. The tenacity of the crosslinked rubbers additionally prevents the particles from continually shearing apart or reagglomerating, thus establishing an equilibrium and standard size range.



(a) 5% RUBBER (b) 7.5% RUBBER



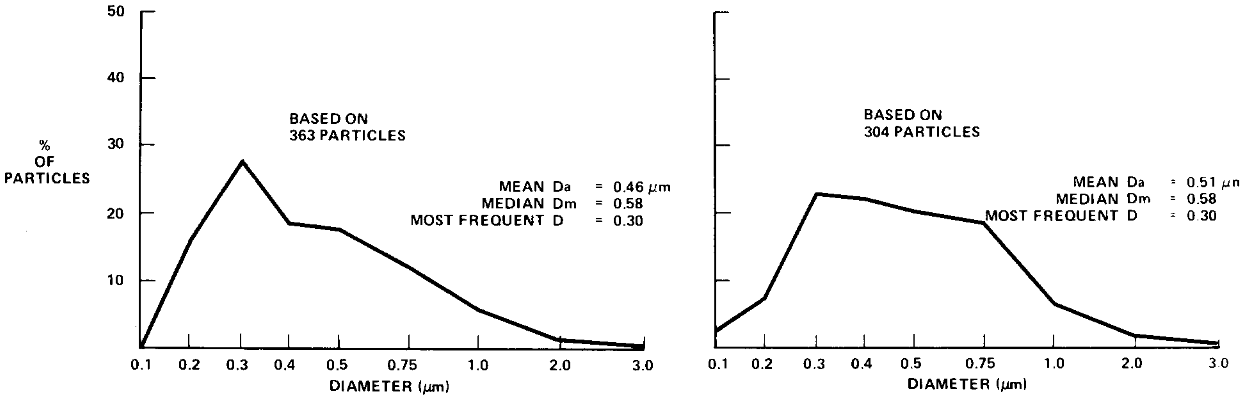
(c) 10% RUBBER (d) 15% RUBBER

Figure 1 Typical dispersion vs. composition in rubber A/polypropylene C75 blends

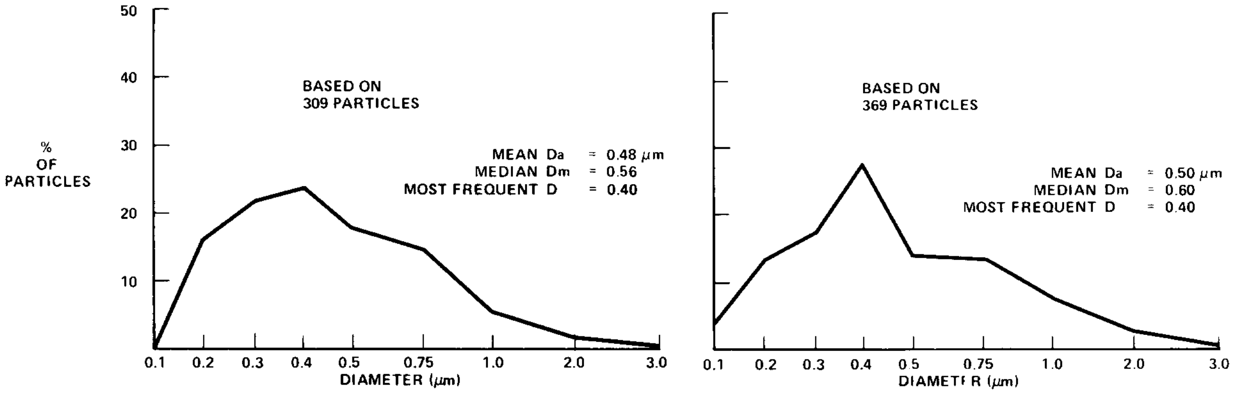
Figure 3 shows typical blend dispersion as a function of polypropylene type. The relative ranking appears to be H65 > H63 > C75 in terms of particle size. The difference in particle population is significant in both average and median sizes. The rubber modifier seems to be least effective in the higher molecular weight homopolymer, H65. Both average and median particle sizes are largest and the population is broad. This reduced dispersion efficiency in H65 is probably related to marked matrix degradation in H65 as compared with H63 and C75 resins. When H63 and C75 are compared, the higher molecular weight and melt viscosity in C75 copolymer seems to result in more effective dispersion of the rubber phase. In addition, increased compatibility of EPDM rubbers with C75 copolymer may also be partially responsible for the enhanced dispersion.

In previous work[8–10] where un-crosslinked EPDM rubbers were blended with polypropylenes, no clear correlation between mechanical properties and rubber type could be made. The rubbers, nevertheless, differed widely in molecular weight, crystallinity and viscosity. There was, however, some correlation between rubber type and the extent of dispersion in the final blends. In a highly degraded matrix, low molecular weight elastomers had a strong tendency toward recombination, resulting in poorly dispersed domains. Meanwhile, high molecular weight elastomers probably saw the same probability of particle contact, but their viscosity prevented any interfusion of reagglomeration before they were again separated. In a less degraded matrix, the trend was reversed: recombination effects were much reduced and low molecular weight rubbers dispersed more effectively. Rubber viscosity could also affect dispersion based on a constant shear stress criterion that assumes a continuous shear stress in the blend. The operating shear rate in the rubber was derived from the operating shear rate in the matrix through component viscosities. It was this operating shear rate in the rubber phase combined with its molecular weight and elasticity that determined the resultant dispersion[8].

Current results of effect of crosslinked rubbers are given in *Figure 4*. Although H65 has been prestabilized, mixing in the twin-screw extruder gave rise to degradation in the homopolymer, as indicated by a substantial increase in the measured flow rate. As a result, different rubbers exhibit different degrees of particle recombination induced by the degraded matrix. The effect of crosslinking on the extent of recombination can be best examined by comparing dispersion in blends with rubber A and D (*Figure 4*). The two rubbers are identical EPDM elas-

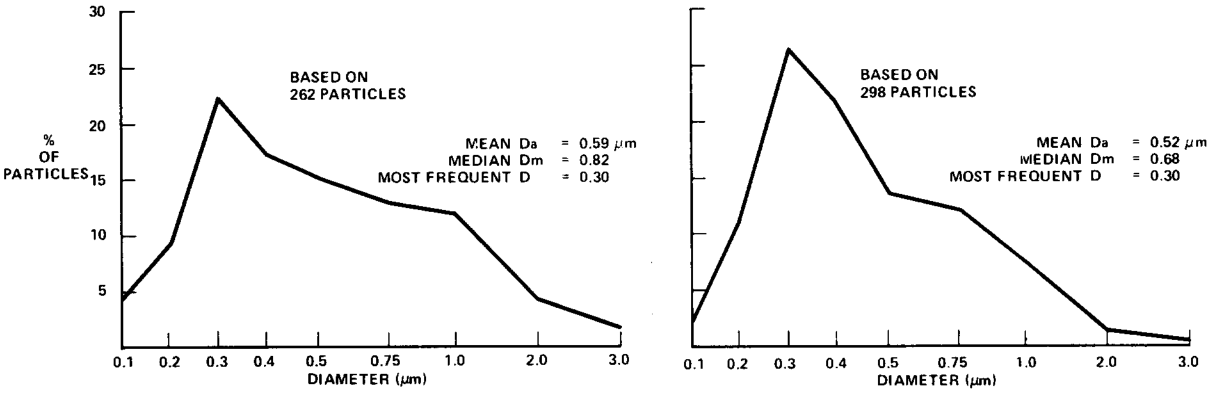


(a) 5% RUBBER **(b) 7.5% RUBBER**

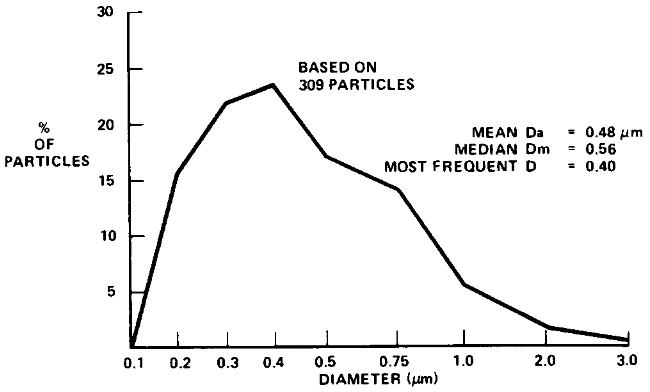


(c) 10% RUBBER **(d) 15% RUBBER**

Figure 2 Particle size distribution vs. composition in rubber A/polypropylene C75 blends

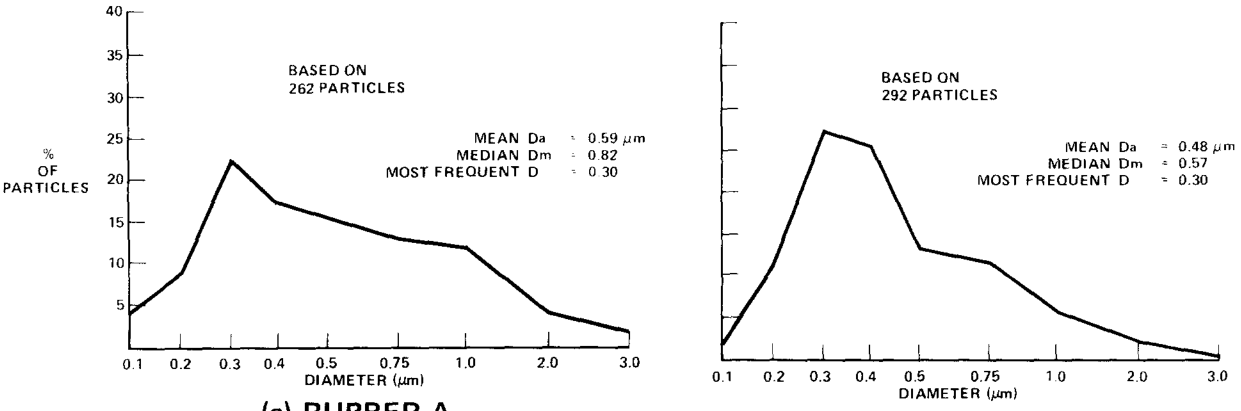


(a) H65 **(b) H63**

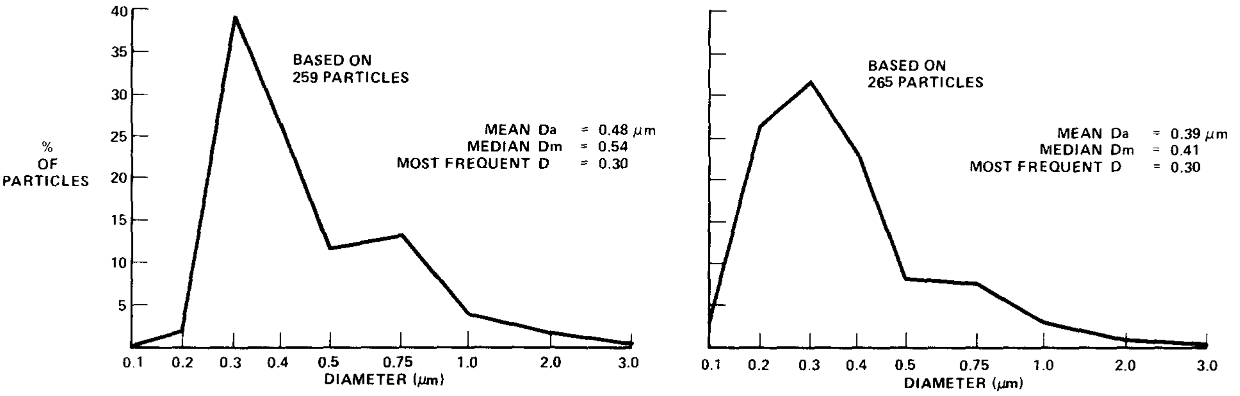


(c) C75

Figure 3 Particle size distribution vs. polypropylene type in 10 wt% rubber A/polypropylene blends



(a) RUBBER A **(b) RUBBER B**



(c) RUBBER C **(d) RUBBER D**

Figure 4 Particle size distribution vs. rubber type in 10 wt% rubber/polypropylene H65 blends

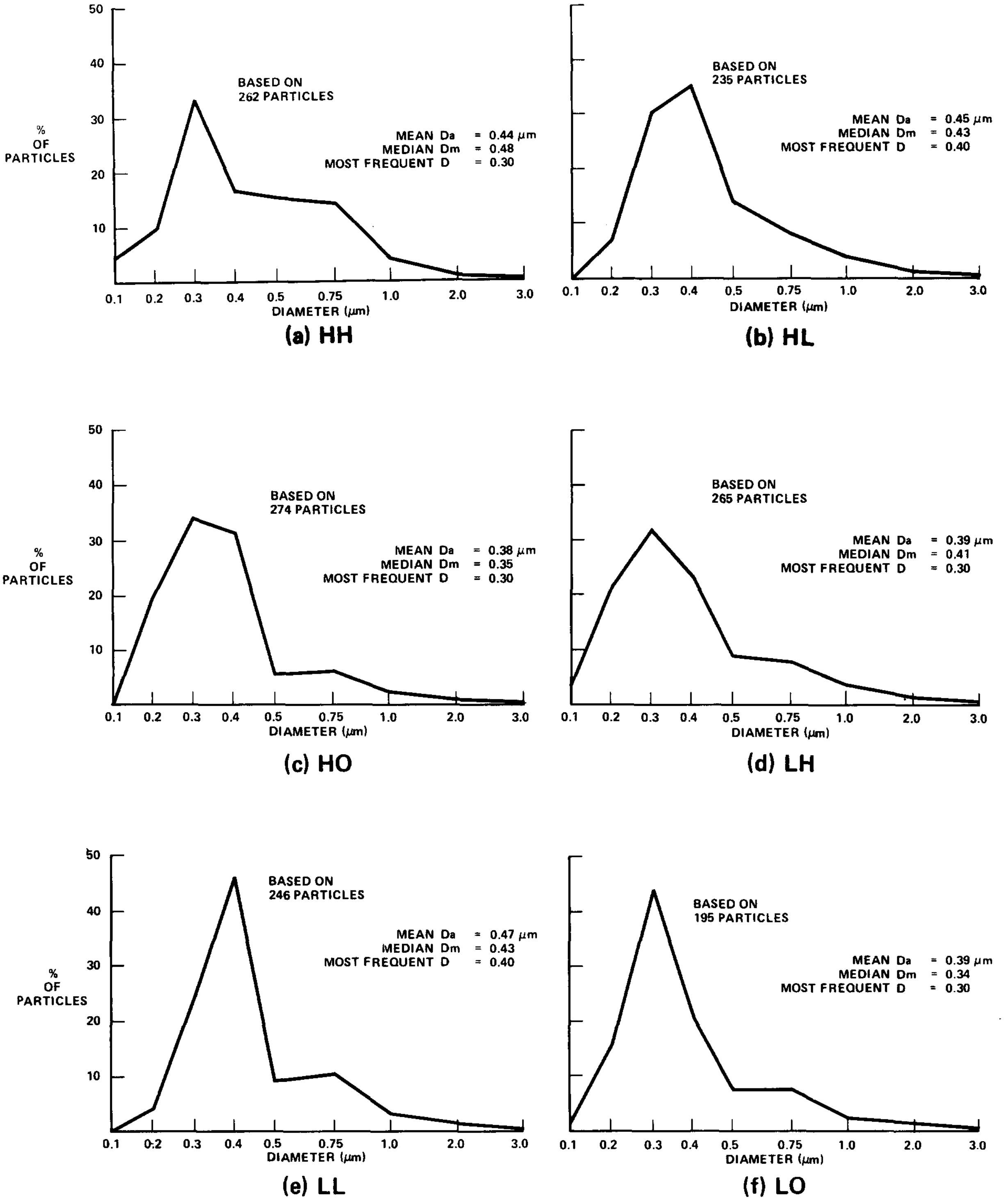
tomers, but rubber D has a significantly larger concentration of peroxide, and hence, contains more crosslinks. Better dispersed grade D rubber, compared with grade A, probably results from the added crosslinks effectively resisting particle reagglomeration. The influence of rubber crystallinity on particle recombination can be similarly studied by comparing blends with rubbers B, C and D. The high degree of crystallinity in rubber D, compared with rubbers B and C, seems to induce finer dispersion of rubber D.

It can be seen in the preceding paragraphs (on the effect of rubber type on dispersion) that rubber D, having a high crosslink concentration, results in the finest dispersion. This fine dispersion apparently results from the effective role of crosslinking in resisting particle reagglomeration. This same rubber system was chosen to study the influence of processing conditions, namely whether large variations in processing shear histories coupled with substantial matrix degradation would affect dispersion behaviour of this crosslinked material. *Figure 5* shows blends prepared with the six different processing conditions described earlier. Dispersion is typically fine and appears similar for all blends, irrespective of mixing and moulding conditions. Our current results differ from those found earlier for un-crosslinked rubbers[8–10] that exhibited strong dispersion dependence on processing conditions. Crosslinking the rubbers seems, therefore, to have succeeded in reducing this dependency rather significantly.

Table 3 provides average particle sizes estimated from SEM micrographs for all 10% rubber/90% polypropylene blends prepared to examine the merits of crosslinked rubbers. Several observations can be made: dispersion of the crosslinked rubbers appears to be independent of the processing conditions for any given resin/rubber combination. The poorest dispersion is found in blends with H65, probably because of the most severe matrix degradation and subsequent particle recombination as discussed earlier. The degree of rubber crosslinking is found to slightly influence dispersion in this resin, with increased crosslink concentrations favouring finer dispersions (rubber D, for example); increasingly fine dispersions are realized for blends with H63 and C75 where the effects of rubber type and degree of crosslinking progressively diminish, especially with the C75 copolymer.

CONCLUSIONS

One aspect of blend characteristics that appears not to have been investigated quantitatively is rubber-phase dispersion. Past work has revealed that rubber particle size and size distribution influence micromechanical yielding processes, such as crazing, shear banding, etc., that, in turn, affect macroscopic toughening characteristics of the blends. Dispersion has also been found to depend on composition, rubber and resin properties and processing conditions. The effect of processing conditions on dispersion is of particular interest because of the possible product property variations due to dispersion variability that arises from process variability in a manuf-



(a) HH **(b) HL**

(c) HO **(d) LH**

(e) LL **(f) LO**

Figure 5 Particle size distribution vs. processing conditions in 10 wt% rubber D/polypropylene H65 blends. Processing conditions:

		Moulding shear		
		High	*Low*	*Zero*
Mixing	High	HH	HL	HO
Shear	Low	LH	LL	LO

acturing plant. Our current investigation focuses on the use of lightly crosslinked elastomers in controlling dispersion. Specifically, possible changes in dispersion of these crosslinked systems with composition, polypropylene and rubber type, and processing conditions have been quantitatively studied.

Our measurements on blends with compositions ranging from 5% to 20% rubber reveal that crosslinked rubbers disperse very well in polypropylene and particle size and size distribution change very little with composition. In these low rubber concentrations that are customary in most impact modification work, the extent of dispersion in a given shear field and the probability of subsequent particle contact and reagglomeration probably remains the same for all compositions. Additionally, the tenacity of crosslinked rubbers probably prevents the particles from continually dispersing or coalescing, thus establishing an equilibrium and standard size range for all blends.

Our study of the effect of polypropylene type shows that

Table 3 Average particle size (D_a, μm) in various blends (10 w % Rubber/90 w % Polypropylene)

		Processing conditions*					
Polypropylene H65		*HH*	*HL*	*HO*	*LH*	*LL*	*LO*
Rubber	A	0.58	0.58	0.54	0.59	0.62	0.62
	B	0.41	–	0.47	0.48	–	0.48
	C	0.46	–	0.45	0.48	–	0.41
	D	0.44	0.45	0.38	0.39	0.47	0.39
Polypropylene H63							
Rubber	A	0.52	0.58	0.59	0.52	0.57	0.57
	B	0.40	–	0.45	0.48	–	0.40
	C	0.42	–	0.41	0.42	–	0.42
	D	0.39	0.44	0.39	0.42	0.42	0.39
Polypropylene C75							
Rubber	A	0.50	0.46	0.51	0.48	0.46	0.47
	B	0.47	–	0.48	0.48	–	0.40
	C	0.48	–	0.42	0.39	–	0.42
	D	0.43	0.46	0.44	0.42	0.51	0.49

* First letter stands for mixing, second letter for molding shear rate. For example: HL : high mixing, low molding; HO : high mixing, zero molding.

there is some influence of polypropylene properties on rubber-phase dispersion. For example, dispersion seems to be least effective in higher molecular weight homopolymer, H65. This is probably related to marked matrix degradation in H65 compared with other polypropylenes, resulting in substantial particle reagglomeration in the former. When H63 and C75 were compared, the higher molecular weight, higher viscosity C75 copolymer appeared to result in finer dispersions probably because of its melt strength and higher rubber solubility.

In our investigation of rubber type, crosslinking the rubbers apparently reduces the particle recombination tendency induced by a degraded matrix. The blends exhibit better dispersion with increasing crosslink concentrations.

The resistance to dispersion variability of crosslinked rubbers is also evident in blends prepared at six different processing conditions. In this study, dispersion has been found to change very little in all blends irrespective of mixing and moulding conditions. Our observations have, therefore, suggested some merits of lightly crosslinked elastomers in improving and stabilizing blend dispersion in various processing conditions that could conceivably arise in a factory.

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