

Chlorobutyl Rubber-Based High-Impact Polystyrene

TERRY HUFF, *Exxon Chemical Company, Plastics Technology Division, Baytown, Texas 77520*

Synopsis

High-impact strength polystyrenes have been prepared which contain an included phase of polystyrene-grafted chlorobutyl rubber microgel. By use of a technique which involved precrosslinking the elastomer, monomer imbibement, a gel dispersal step, and a final suspension polymerization of the styrene monomer, products are produced having a high elastomer phase-to-elastomer ratio and suitable microgel particle size. These products have properties equivalent, in most respects, to commercial polybutadiene-based high-impact polystyrenes and have much improved resistance to outdoor aging.

INTRODUCTION

Two polystyrene-based plastic materials are important low-cost engineering plastics; these are the impact polystyrenes (HIPS) and the ABS family. The best of both of these types require a substantial amount of grafting of the matrix phase polymer to an included rubbery phase polymer. This grafting is achieved by conducting the polymerization of the monomer(s) destined to become the matrix phase in the presence of a preformed polybutadiene (or butadiene-containing copolymer) using as initiator a compound yielding radicals capable of abstracting allylic hydrogens to initiate the grafting reaction.¹ A continuing problem with both HIPS and ABS is their inferior stability to outdoor aging.² Degradation of the composites is related to the residual unsaturation in the polybutadiene phase, and at least two new products have been announced based on ethylene-propylene-diene (EPT) rubber to overcome this deficiency.^{3,4} The mechanism by which grafting occurs with this elastomer, which is very low in allylic hydrogen concentration, is not clear.

We have grafted polystyrene to chlorobutyl rubber, Cl(Bu)R, depending on the enhanced chain transfer activity of the allylic chlorine^{5,6} to compensate for the reduced concentration of potential grafting sites, in order to produce an impact polystyrene of improved outdoor aging stability.

This report will describe work to adjust the nature and particle size of the included elastomer phase of Cl(Bu)R-based HIPS and the effect of these adjustments on mechanical properties of the materials.

EXPERIMENTAL

Unstirred Bottle Polymerization and Preparation of Precrosslinked Cl(Bu)R

Solutions of chlorobutyl rubber in styrene monomer were made up in a stirred 2-liter resin kettle under nitrogen. The solution was then poured into

several 4-oz wide-mouth, nitrogen-purged bottles which were then loosely capped and placed in an oven under 4 psig of nitrogen pressure and run through a heating cycle, as indicated in Table II, to polymerize the styrene. The bottles were then cooled, broken open, and the contents chopped to small pieces for subsequent use.

When precrosslinked Cl(Bu)R was desired, pieces of Exxon-grade HT 1066 were placed on a Teflon pad in the vacuum oven (20 mm Hg) and heated to 150°C for 24 hr.

Preparative Scale Polymerization for Mechanical Property Determination

These runs were made in a stirred 2-liter resin kettle, under nitrogen. Temperature control was by a West Model JE controlled heating lamp. The reactor was topped by an efficient reflux condenser to prevent loss of monomer or solvent. The first step in these preparations was to suspend or dissolve the chopped rubber sample (cf. Table II) in the monomer and solvent (if any). This solution or imbibement step was allowed to proceed ≥ 16 hr with gentle stirring. The elastomer particle size was then set using one of the following techniques:

1. Dropwise addition of a polystyrene in styrene solution (75 g polystyrene, Dow 66 M crystal grade, in 179 g SM) to the elastomer in styrene solution (39 g elastomer in 216 g SM) to induce phase inversion followed by a high shear blending operation (under nitrogen and with external cooling) to set the particle size⁷ (cf. Table III).

2. A high shear blending operation (under nitrogen and with external cooling) on the solvent-swollen crosslinked elastomer (39 g)/monomer (474 g)/hexane (68 g, if present) mixture to reduce the elastomer particle size to the desired range (cf. Table III).

Polymerizations were finished in suspension using the following recipe (all weights per 100 parts by weight styrene):

1. After inversion or imbibement step and high shear blending operation: add 3 parts styrene containing 0.005 parts lecithin, 0.02 parts bisphenol A, and 138 parts of suspension system containing water and 0.3 parts GH-20 (Nippon Gobsei, high molecular weight poly(vinyl alcohol), 0.08 parts KH-17 (Nippon Gobsei, low molecular weight poly(vinyl alcohol), and 2.8 parts Na acetate.

2. Heat additional 2 or 3 hr at 90°C stirring at 300–350 rpm.

3. Add 0.15 parts benzoyl peroxide (wash in with water). Raise temperature to 95–100°C.

4. Add additional 0.15 parts benzoyl peroxide if beads do not appear to be hardening.

5. Usually leave stirring overnight at 90°C.

6. Filter, wash, and dry.

Determination of the Weight Per Cent and Particle Size of the Elastomer Phase in the Composites

The weight-% of elastomer phase in the composites was determined by shaking ~2-g sample of the dried beads with 60 ml of a 1:1 methylethyl ke-

TABLE I
Testing Procedures for Polymer Evaluation

Test for:	ASTM Testing Procedure	Comments
Flexural Modulus	D-790	Procedure A
Tensile, yield (% Elongation, fail)	D-638	Crosshead speed = 2"/min
Izod Impact	D-256	Method C
Melt Flow Rate (MFR)	D-1238	Condition P

tone (MEK)-acetone mixture for ≥ 16 hr. This slurry was then washed with MEK/acetone into two stainless-steel centrifuge tubes and centrifuged 10 min at 11,500 rpm. The residue was dried overnight at 70°C (15 mm Hg) and reweighed.

The weight-% of grafted and occluded polystyrene in crosslinked Cl(Bu)R-polystyrene grafts was determined by a ≥ 16 -hr Soxhlet extraction of weighed samples of the material with xylene. The residue was dried overnight at 70°C (5 mm Hg) and reweighed.

Particle size of the elastomer phase in the composites was estimated by pressing a single bead from the suspension polymerization between two thin glass slides at 200°C and viewing with a Spencer AO light microscope at 537 \times magnification. In cases where the elastomer phase particles were too small to be clearly distinguished at this magnification, they were assumed to be < 5 μ in diameter.

Mechanical Property Evaluations

Injection-molded specimens for mechanical property evaluation were prepared from the beads on a Frohring Minijector using a barrel temperature of $\sim 400^\circ\text{F}$. The mold was maintained at room temperature. Samples were held ≥ 2 days at room temperature prior to testing. Conditions for the various tests are shown in Table I.

MATERIALS

The chlorobutyl rubber used was Enjay Butyl HT 1066 (1.2 wt-% chlorine, ML1+8 at 212°F = 55, $\bar{M}_v \approx 450,000$) containing the normal stabilizer package.

Styrene monomer was Dow polymerization grade (12T) used without removal of the inhibitor.

Normal heptane was Phillips commercial grade used as received.

All other solvents, i.e., MEK, acetone, xylene, etc., were reagent grade and were used as received.

The stabilizers used, i.e., ionol (BHT), calcium stearate, and AO 2246 [2,2'-methylenebis(4-methyl-6-*t*-butylphenol)] were the standard high-purity grades normally supplied for polymer stabilization.

The styrene-butadiene copolymer used was Goodyear Pliolite 1006 R (23.5% styrene, Mooney, ML 1 & 4 at 212°F = 50) containing the normal stabilizer package.

TABLE II
Pretreatment of Elastomers

Elastomer Designation	Pretreatment	Wt-% Sol. MEK/Acetone	Wt-% Sol. Boiling Xylene
SBR-I	None	~0	100%
Cl (Bu)R-I	None	~0	100%
Cl(Bu)R-II	1. 28.4 wt-% Cl(Bu)R solution in styrene monomer 2. bottle polymerize at: 100° C (48 hr) 120° C (75 hr)	51.6	100%
Cl(Bu)R-III	1. 28.4 wt-% Cl(Bu)R solution in styrene monomer 2. bottle polymerize at 100° C (48 hr) 120° C (75 hr) 150° C (24 hr)	56.2	54.6
Cl(Bu)R-IV	Heat crosslink 24 hr at 150° C	~0	<5%

RESULTS AND DISCUSSION

Impact polystyrenes and ABS-type materials have been well characterized over the past several years, and the parameters which require control in order to obtain a desirable balance of properties have been carefully studied. The materials consist of a matrix phase of essentially nongrafted polymer, polystyrene, or styrene-acrylonitrile copolymer respectively for impact polystyrenes and ABS; contained in this matrix is a rubbery included phase to which is grafted some matrix phase polymer. The rubbery included phase also contains a considerable proportion of included but nongrafted matrix phase polymer; in fact, the total fraction of occluded but nongrafted matrix phase polymer in the rubbery phase is frequently greater than the fraction of matrix phase polymer grafted to the elastomer.⁸ The rubbery phase elastomer must be crosslinked to render the rubbery phase permanent to melt processing; it is not entirely clear whether this crosslinking also improves the properties of the composite by rendering the rubbery phase to a form which can, itself, more effectively elongate to absorb energy, but this might well be so.⁹

To summarize, then, among the known requirements for the reinforcement of polystyrene or styrene-acrylonitrile copolymer by elastomers are the following:

A. Requirements on the Rubbery Phase. (1) incompatibility with the rigid phase^{10,11,12}; (2) good adhesion between the elastomer and matrix phases^{11,12}; (3) optimum rubbery-phase particle size and distribution^{10,12,13,14}; (4) low T_g (i.e., $<-50^\circ\text{C}$)^{2,15}; (5) crosslinked to microgel^{10,12,16}; and (6) wt-% microgel $\sim 2-5 \times$ wt-% starting rubber.^{17,18}

B. Requirements on the Matrix Phase. High enough molecular weight to maximize mechanical properties; low enough molecular weight to confer good melt flowability^{16,17,19}.

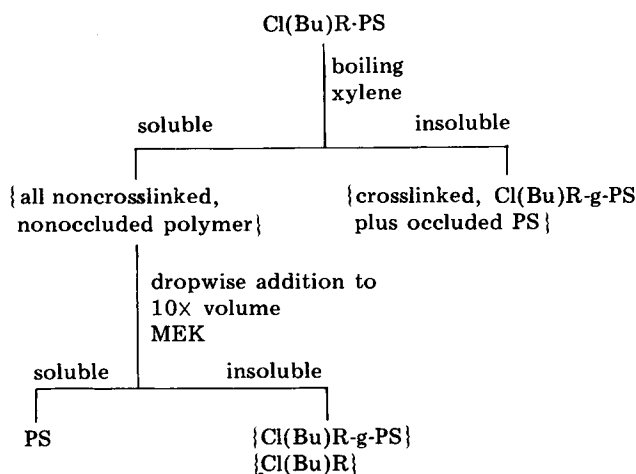
High-impact polystyrenes are normally produced in a tandem bulk and

suspension polymerization process wherein the size and composition of the included elastomer phase are set by controlled agitation^{20,21} during the bulk polymerization stage, and the complete conversion of styrene to polystyrene is accomplished in the suspension polymerization step.

Alternatively, it is possible to set the size and composition of the included elastomer phase by adding a polystyrene-in-styrene solution to an elastomer in styrene solution followed by a high shear blending operation.⁷ This mixture can then be suspension polymerized to complete conversion of the styrene to polystyrene to yield a suitable HIPS.

The latter technique was used to prepare an SBR-based and several Cl(Bu)R-based impact polystyrenes. Operations on the elastomer to prepare it for the suspension polymerization step are shown in Table II.

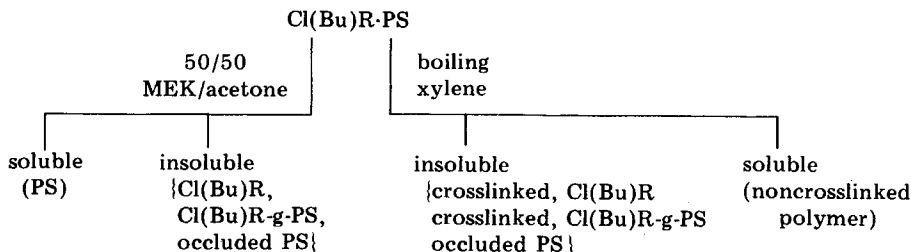
To determine the amounts of grafted and occluded polystyrene in the rubber phase of these materials, a separation scheme as shown below was envisioned:



From previous work⁸ on SBR-based HIPS, it was presumed that occluded PS would not be extracted from the elastomer gel phase. If this scheme were successful, comparison of equivalent crosslinked and noncrosslinked compositions (i.e., Cl(Bu)R-II and Cl(Bu)R-III, Table II) would allow accurate, separate determination of grafted PS and occluded PS in the gel phase, however, the final Cl(Bu)R-g-PS/PS separation was unsuccessful. Contrary to the case for simple melt blends, dropwise addition of the xylene solution containing the Cl(Bu)R-g-PS to 10× its volume of MEK resulted in a colloidal suspension which could only be separated by a lengthy centrifuge operation and which resulted in recovery of a minor amount of lightly grafted Cl(Bu)R fraction. The bulk of the Cl(Bu)R, being, presumably, more highly grafted, was soluble in the 1:10 xylene/MEK mixture and could not be separated from the polystyrene solution.

Because of the difficulty in obtaining the pure graft copolymer, a modified technique was adopted which allowed determination of the total elastomer phase concentration (i.e., Cl(Bu)R + Cl(Bu)R-g-PS + occluded PS) and/or

the total crosslinked elastomer phase concentration (i.e., crosslinked Cl(Bu)R + crosslinked Cl(Bu)R-g-PS + crosslinked elastomer occluded PS) as follows:



From the extraction data on the samples in Table II, it is inferred that the unstirred bottle polymerization for sample Cl(Bu)R-II results in formation of a Cl(Bu)R-polystyrene graft wherein ~40% polystyrene is grafted to (or occluded in) the elastomer phase. In sample Cl(Bu)R-III, a similar Cl(Bu)R-polystyrene graft is formed and the Cl(Bu)R moieties are heat crosslinked. Sample IV is the heat-crosslinked elastomer without grafted polystyrene.

These elastomer samples were then used to prepare impact polystyrenes as shown in Table III. In runs SBR-1, CB-1, and CB-2, the elastomer phase was rendered discontinuous by addition of polystyrene in styrene solution; in the latter instance, the polystyrene being derived from the nongrafted, styrene monomer-soluble portion of the Cl(Bu)R-II composition. In runs CB-3 through 7, the elastomer phase was discontinuous by virtue of being crosslinked and hence insoluble but highly swollen in styrene monomer. Particle size of the elastomer phase was adjusted, in all cases, by a high shear blending operation as indicated in Table III.

Direct use of unmodified chlorobutyl rubber to prepare impact polystyrene results in a product of poor mechanical properties and low in included elastomer phase relative to the SBR derived product (compare SBR-1 and CB-1, Table III). These results obtain because, although the chlorobutyl rubber-derived product contains a reasonable level of grafted polystyrene, it is not crosslinked and contains relatively little occluded but nongrafted polystyrene. A pregrafting step at higher elastomer concentration gives a product higher in elastomer phase concentration (i.e., grafted polystyrene) but still not crosslinked (cf. Table II, Cl(Bu)R-II) and, in the final product, still low in both impact strength and contained elastomer phase concentration relative to the SBR based material (compared SBR-1 and CB-2, Table III).

A considerable improvement in both elastomer phase concentration and in impact strength results for the chlorobutyl rubber-based materials when the elastomer is crosslinked before the final suspension polymerization. This crosslinking step can be carried out either on the pregrafted elastomer or on the pure chlorobutyl rubber (cf. Table II, Cl(Bu)R-III and IV), the latter operation being simpler and also yielding the more desirable final product (compare CB-3 and CB-4, Table III). The impact strength and stiffness of the materials clearly correlates with the concentration of contained elastomer phase independent of the Cl(Bu)R concentration. The increase in elastomer phase in the case of crosslinked relative to noncrosslinked Cl(Bu)R-based materials appears to derive from a large increase in occluded phase polysty-

TABLE III
 Impact Polystyrenes with Various Elastomer Bases

Run no.	Elastomer phase discontinuous by:	Elastomer particle size set by:	Elastomer base	wt-% elastomer	wt-% elastomer phase	MFR, (g/10 min)	Ty, psi	% Ef	Flex. mod. $\times 10^{-3}$, psi	Notched Izods	
										—	—
CB-1	Addition of polystyrene in styrene monomer to Cl(Bu)R in styrene monomer	Waring blender (3 min, high speed)	Cl(Bu)R-I	7.4	11.3	2.5	—	—	350	0.6	—
CB-2	ungrafted polystyrene from Cl(Bu)R-II in styrene monomer forms continuous phase	Waring blender (3 min, high speed)	Cl(Bu)R-II	7.1	13.4	—	7764	7	344	0.7	0.3
CB-3	elastomer phase cross-linked	Waring blender (3 min, high speed)	Cl(Bu)R-III	7.1	16.2	0.2	7034	8	338	1.1	0.5
CB-4	elastomer phase cross-linked	Waring blender (3 min, high speed)	Cl(Bu)R-IV	7.4	20.3	—	—	—	320	1.3	0.6
CB-5	elastomer phase cross-linked	Waring blender (1 min, low speed) gear pump (10 min.)	Cl(Bu)R-IV	7.4	—	1.4	5829	9	330	1.4	0.5
CB-6	elastomer phase cross-linked	Waring blender (1 min, low speed) Silverson Homogenizer (10 min.)	Cl(Bu)R-IV	7.4	—	1.5	5960	7	265	1.8	0.5
CB-7	elastomer phase cross-linked	heptane addition, Waring blender (1 min, low speed) Silverson homogenizer (10 min)	Cl(Bu)R-IV	7.4	—	2.4	3614	31	233	1.7	0.6
SBR-1	addition of polystyrene in styrene monomer to SBR in styrene monomer	Waring blender (3 min high speed)	SBR-I	7.4	15.2	0.6	5964	10	280	2.1	0.7
PBd-1	{ commercial sample, PBd-based HIPS }	—	PBd	7.3	—	2.0	4733	23	263	1.8	1.0

^a Assumed for CB-5-7 from CB-4.

rene with the former. For instance, in CB-1, the elastomer phase contains ~34.5% PS, while in the comparable crosslinked Cl(Bu)R case, CB-4, the elastomer phase contains ~63.5% PS. It is suggested that this difference represents styrene monomer imbibed and polymerized within the elastomer membrane in the crosslinked case.

Several high shear blending operations were tested for reduction of the elastomer phase particle size including use of the Waring blender, a recirculating gear pump, and the Silverson homogenizer; for lab-scale operations, the latter two devices required a short, low-speed Waring blender treatment to reduce the elastomer particle size to a level such that the slurry could be circulated. All of these techniques carried out as indicated in Table III, gave elastomer phase particle size reductions to $<5 \mu$ as indicated from optical microscopic examination. From mechanical property measurements, it is inferred that the Silverson homogenizer gives a slightly better dispersion of the rubbery phase than either the Waring blender or the gear pump treatment.

Commercial-range mechanical properties for Cl(Bu)R-based HIPS are thus obtained by precrosslinking the rubber, neat, followed by imbibement of styrene monomer, a high shear dispersal step, and the usual suspension polymerization to conclusion. Addition of *n*-heptane during the monomer imbibement step results in a more highly swollen rubber gel, presumably a smaller average particle size on high shear blending, and a final product of considerably improved surface gloss and elongation at fail (cf. Table III, CB-6 vs. CB-7). Properties of these products are compared to a commercial polybutadiene-based HIPS in Table III, CB-6 and 7 vs. PBd-1. With the exception of low-temperature impact strength, the Cl(Bu)R-based materials are equivalent in properties. Low-temperature impact strength of the materials depends on the glass transition temperature of the rubbery phase and, hence, an advantage should accrue to the polybutadiene-based HIPS (i.e., $T_g(\text{PBd}) \simeq -95^\circ\text{C}$, $T_g(\text{Cl(Bu)R}) \simeq -60^\circ\text{C}$).

A stabilizer package (0.5% A02246, 0.5% BHT, and 0.1% calcium stearate) was added to CB-7, and specimens were aged in a xenon Weatherometer along with the commercial polybutadiene-based sample. Data on the elongation at fail as a function of time in the Weatherometer are shown in Figure 1 for the samples in question along with data from the literature²² on an EPT-based HIPS and its associated polybutadiene-based control. The data show the excellent aging resistance of the Cl(Bu)R-based material relative to the other samples at least through 400 hr of exposure.

SUMMARY AND CONCLUSIONS

A procedure which allows the preparation of chlorobutyl rubber-based HIPS having a good balance of mechanical properties along with excellent outdoor aging stability has been developed. The technique requires:

1. A precrosslinking of the chlorobutyl rubber (to assure microgel in the finished product).
2. A monomer (solvent) imbibement step (to obtain a high level of occluded polystyrene and, hence, a high volume fraction of rubbery phase in the finished product).
3. A high shear blending operation (to reduce the monomer (solvent) swollen gel to the proper particle size microgel).

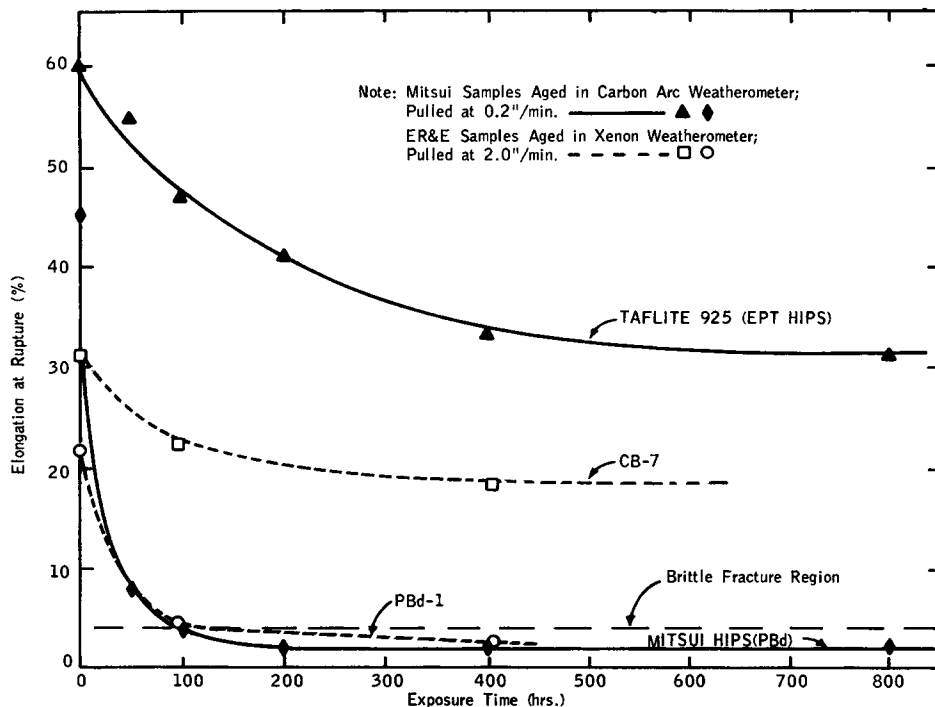


Fig. 1. Aging resistance of various high-impact polystyrenes.

4. A suspension polymerization of the styrene monomer/swollen microgel mixture during which grafting of polystyrene to chlorobutyl rubber takes place (to assure adequate adhesion between phases in the finished product).

The procedure appears to be relatively simple and direct and should be amenable to scale up to commercial-sized equipment.

Acknowledgment is due Dr. B. H. Johnson for suggestions and discussions during the course of this work; Professor R. W. Lenz for helpful discussions; Dr. S. H. Hastings for development of IR analytical techniques; and to Mr. C. N. Brawner who did a major portion of the polymer preparation and evaluation work described in this report.

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Received May 1, 1975