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IMPROVEMENT OF IMPACT STRENGTH OF
POLYSTYRENE BY COMPOUNDING WITH
STYRENE-GRAFTED ETHYLENE PROPYLENE
ELASTOMERIC COPOLYMERS

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EXPERIMENTAL

Materials used

Amorphous ethylene propylene copolymer.—"Montecatini" product, obtained with soluble catalysts, having the following characteristics: intrinsic viscosity in toluene at 30° C 2.3 dl/g, molar percentage of propylene 72.

We used a copolymer rich in propylene, since polymers rich in ethylene have chain segments consisting only of methylene groups, which form zones, having a regular structure, that crystallize; this does not occur for the sequences of propylene monomeric units, because of the lack of stereoregularity of the polymers obtained with soluble catalysts.

Commercial polystyrene.—"Montecatini" *Stiroplasto* DL-AF, having an intrinsic viscosity in toluene at 30° C of 0.91 dl/g, corresponding to a mean viscosimetric molecular weight of 260,000.

tert-butyl peroxide.—Obtained by distillation of *Trigonex* A 75, a commercial product of "Noury & van der Lande", which is a mixture containing 25 per cent *tert*-butyl hydroperoxide and 75 per cent peroxide.

Cumyl peroxide.—Obtained by extraction with ethyl ether of the commercial product Di-cup 40 of Hercules Powder Company, which is a mixture of 40 per cent cumyl peroxide and 60 per cent calcium carbonate.

Toluene and methyl ethyl ketone.—Carlo Erba RP products.

Monomeric styrene.—"Montecatini" product, freshly redistilled.

Preparation of the Graft Product

The ethylene propylene copolymer, reduced to small granules, is placed in a flask together with an equal weight of styrene containing the peroxide used. The mass is agitated until a homogeneous dispersion is obtained; the flask is then sealed in an atmosphere of pure nitrogen, and allowed to stand 16 hours at room temperature, before it is heated to 135° C until complete polymerization of the monomer takes place.

In general, the polymerization is complete after 3–4 hours; after cooling, a viscous, elastic, apparently homogeneous mass of a grayish color is extracted from the flask; this is reduced to small particles by grinding in a mill. The grinding is carried out under an inert gas atmosphere; a copious amount of dry ice is added to the material. This, by hardening the material, favors the reduction into small particles by grinding. The material prepared in this way, which we shall call material A, consists of a mixture of polystyrene homopolymer, ethylene propylene copolymer which has not participated in the grafting reaction, graft polymer, and crosslinked and grafted polymer. Separately, and always under a carbon dioxide atmosphere, the commercial polystyrene is ground (material B).

The mixture of material B and of material A, reduced to granules, is homogenized for 8 minutes on a mill at 160° C, and the product compression molded at a pressure of 50 kg/cm² and a temperature of 160° C. The heat-molded flat sheets are cooled to room temperature, and from these are derived the samples for the mechanical tests. The same method of calendaring and molding was followed in the preparation of mechanical mixtures of polystyrene, and of the copolymer containing only ethylene and propylene prepared for purposes of comparison.

All the determinations of the mechanical properties on the molded samples were carried out in a constant-temperature room at a temperature of 23° C, with relative humidity of 45–50 per cent, following the ASTM standards indicated in Table II.

TABLE I
REACTION OF A 50/50 MIXTURE OF COPOLYMER AND STYRENE

Peroxide	phr	"Kumagawa" extract (24 hr)		% Styrene in extract (ir.)	
		with MEK	Toluene	MEK	Toluene
<i>t</i> -butyl	2	43	59	86	62.2
cumyl	4	46.5	60.5	83	59.5

The fractionation of the ground material A was carried out for analytical purposes by the following technique:

The separation of the styrene homopolymer and of the graft products having a high content of polystyrene was carried out by a Kumagawa extraction of the raw material of polymerization with methyl ethyl ketone for 24 hours;

The separation of the sum of the styrene homopolymer, of the ethylene propylene copolymer that has not reacted, and of the soluble graft products was carried out by a Kumagawa extraction of the polymerization raw material with toluene for 24 hours.

The polystyrene content in the extracted products was determined by infrared analysis, using, for analytical purposes, the band at 14.3μ .

Extraction with toluene can remove up to 50-60 per cent by weight of the initial mixture, and the extract contains up to 60-65 per cent polystyrene (see Table I).

The material remaining after the toluene extraction is present in the form of an insoluble gelatinous mass, which is characterized by a ratio (weight of swelled gel)/(weight of dry gel) = 20 - 30.

Proof of the existence of more than one phase in the graft polymer was obtained by extracting from the raw material A all the homopolymeric polystyrene, and submitting the residue, after molding, to measurements of the velocity of propagation of elastic waves and of the dissipation of elastic energy.

Results obtained by Baccaredda and Butta⁵ and kindly communicated to us have indicated the existence of two transitions, at -40 and $+90^\circ$ C, characteristic of the two homopolymers; this demonstrates the heterogeneity of the material.

DISCUSSION

The results obtained are given in Table II and illustrated in Figures 1-6, which are discussed in the following pages.

In Figures 1 and 2 are shown, as a function of the percentage by weight of elastomer, the breaking load σ_R by tension and σ_{Rf} by flexing, and the relative elongations ϵ_R and ϵ_{Rf} for mechanical mixtures of either rubber or graft polymer with commercial polystyrene.

The theory of the resistance of the polymeric materials and of their mechanical mixtures is far from perfect, and does not permit complete interpretation of the results illustrated in the Figures.

The breaking loads calculated on the basis of bond energy and of intermolecular forces generally have values that are approximately 100 times greater than the experimental values⁶. The discrepancies are generally explained by assuming, even invisible, inhomogeneities which lead to stress concentration, such as vacuoles, cuts, or inclusions. In the polystyrene-elastomer mixtures, the dispersed elastomer acts as a stress concentrator and thus reduces the breaking load of the material by

TABLE II
MECHANICAL PROPERTIES OF POLYSTYRENE BLENDS

% Copolymer ^a	Grafted ^h	Tensile strength, ^b kg/cm ²	Breaking elongation % ^b	Flexural strength, ^c kg/cm ²	Flexural elongation % ^c	Charpy resilience, ^d kg/cm	Hardness ^e	Flexural ^e modulus, 10 ⁸ kg/cm ²
0		263	—	423	1.4	1.5	75.3 ^f	30.4
3	no	318	11.8	499	1.9	1.58	74 ^f	26.2
6	no	349	5.7	425	2.8	6	62 ^f	28.1
8	no	212	6.7	473	4.7	8	60 ^f	28.0
9	no	—	—	495	4.3	10.5	62 ^f	28.0
12	no	168	5	451	4.7	13	58 ^f	24.2
15	no	—	—	423	6.5	14	54 ^f	21.5
17.5	no	128	4	370	6.0	11	36 ^f	20.8
20	no	113	3	355	4.9	8.7	31 ^f	18.8
35	no	97	3	168	0.4	4.5	97 ^g	7.68
50	no	17	21	246	3.5	6.6	91 ^g	—
100	yes	2.8	2250	rubbery	—	>100	42 ^g	—
10	yes	218	2.1	419	7	20	45 ^f	26.0
15	yes	178	2.0	355	—	20	34 ^f	—
20	yes	156	1.9	290	6	21	7 ^f	16.8
35	yes	40	0.0	85	0.34	>100	95 ^g	—
50 ^h	yes	27	6.5	rubbery	—	>100	87 ^g	—

^a $[\eta]$ in toluene, 30° C = 2.3 dl/g; mole % propylene 72. Polystyrene $[\eta]$ = 0.91 dl/g.

^b ASTM D 638-58T; tested at 9 mm/min.

^c ASTM D 790-58T; tested at 9 mm/min.

^d ASTM D 256-56; supports 5 cm apart.

^e ASTM D 785-51; D 676-49T.

^f Rockwell L; ^g Shore A.

^h Grafted rubber used for blends, prepared as in Table I, second example and defined in text as material A.

an amount increasing with its percentage. This is substantially in accord with the results shown.

Only in the case of elastomer-polystyrene mixtures have we studied the area of small percentages of elastomer; for low percentages of elastomer, there is observed a slight improvement in the mechanical properties. This was also observed in other cases, for example, on addition of small percentages of plasticizer to polyvinyl chloride and to polymethyl methacrylate⁷. Although a rigorous explanation of the phenomenon has not yet been given, we consider that the addition of small percentages of elastomer allows greater micro-brownian movement, and a better possibility of orientation of the macromolecules during stretching.

The elongations at break by tension (Figure 1) of the polystyrene-elastomer mixtures examined show scatter, but on the whole there is, after an initial maximum, a decrease in the values up to 35 per cent of elastomer, followed by a successive increase. The elongations at break by flexing (Figure 2) show an analogous course.

The curve stress (σ)-deformation (ϵ) derived from tension tests of the homopolymeric polystyrene (Figure 3A) is typical of a fragile material: it is observed from Table II that the work of deformation which can be absorbed, which is proportional to the area comprised between the curve and the axis of the abscissas, is small, the deformation at break being small.

The corresponding tension curve (Figure 3D) of the unvulcanized ethylene propylene elastomer is typical of a polymer that is highly deformable and notably capable of absorbing work of deformation, owing to its high elongation. The crude polymer derived from the grafting reaction, and consisting of half polystyrene and half ethylene propylene copolymer, shows a tension curve (Figure 3C) intermediate between that of the two homopolymers, but considerably different from that of the simple mechanical mixture of the two homopolymers having the same composition (Figure 3B). This latter is capable of absorbing a much lesser work of deformation, attaining lower elongations at break.

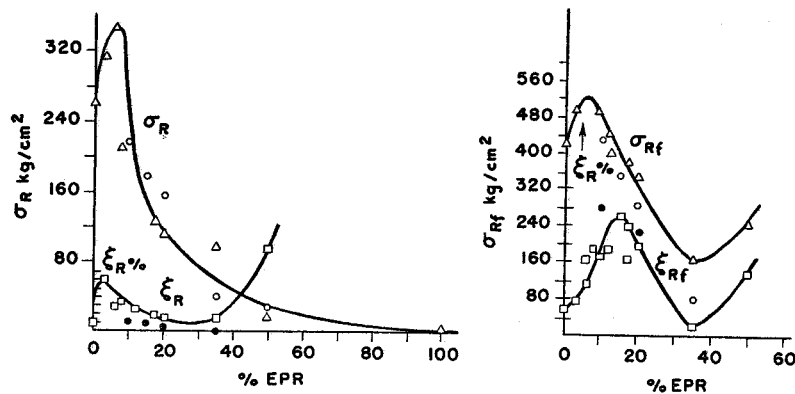


FIG. 1.—Influence of the percentage of ethylene propylene elastomer on breaking load σ_R and on elongation at break ϵ_R in tension tests on: a) $\Delta(\sigma_R)$; $\square(\epsilon_R)$ mechanical polystyrene-elastomer mixtures; b) $\circ(\sigma_R)$; $\bullet(\epsilon_R)$ mixtures of product A (see text) containing the graft polymer, and of polystyrene. Scale of elongation, ϵ_R , 2% per mark on abscissa scale.

FIG. 2.—Influence of the percentage of ethylene propylene elastomer on the breaking load σ_{Rf} and on the percentage elongation at break ϵ_{Rf} in flexing tests on: a) $\Delta(\sigma_{Rf})$; $\square(\epsilon_{Rf})$ mechanical mixtures of polystyrene-elastomer; b) $\circ(\sigma_{Rf})$; $\bullet(\epsilon_{Rf})$ mixtures of product A (see text) containing the graft polymer and polystyrene. Scale of ϵ_{Rf} 1% per mark on abscissa scale.

This shows that the method by which the dispersion of the vitreous polystyrene and of the elastic rubber is carried out has great influence on the properties; in mixtures containing graft polymer it is much easier to obtain a microscopically homogeneous distribution of the two phases, the grafted polystyrene being very compatible with the polystyrene matrix: consequently, better adhesion takes place between the phases, and increases the work of deformation necessary for break. The work of deformation derived from the tension curves can, as is known, only indicate the good or poor impact resistance of the materials examined, because conditions of test are quite different. In general, greater absorption of energy of deformation measured in the tension tests corresponds to higher values of impact strength, and *vice versa*.

The validity of this statement is confirmed by the impact strength measurements we carried out on mixtures containing the graft polymer, which show higher impact resistance than the corresponding mixtures, of equal composition, of the homopolymers (Figure 4).

The impact strength of the mechanical mixtures of the elastomer with polystyrene, as a function of the percentage of elastomer, gives a curve reaching a maximum (Figure 4), indicating a clear improvement in the impact properties in comparison with polystyrene alone. The use of the graft product in place of the unmodified elastomer allows impact strengths to be obtained that are higher for all compositions, indicating the existence of an extensive level portion of the curve before the curve begins to rise again, which occurs in compositions above 20 per cent of elastomer. A minimum is not observed as with the ungrafted elastomer, but instead very high values are attained.

According to modern theories⁸, the particles of elastomer concentrate stresses in the polystyrene phase, thus generating in it numerous microfractures in place of those few that might have existed in the pure homopolymer.

According to Griffith⁹, elastic energy absorbed in the propagation of the microfissures is proportional to the magnitude of the new surface developed by fracture and is therefore greater in the case of heterophase systems characterized by the existence of numerous microfractures.

According to other authors⁴, the reinforcing action might be due to the fact that, once a local vitreous fracture occurs in the polystyrene, the elastomer surrounded

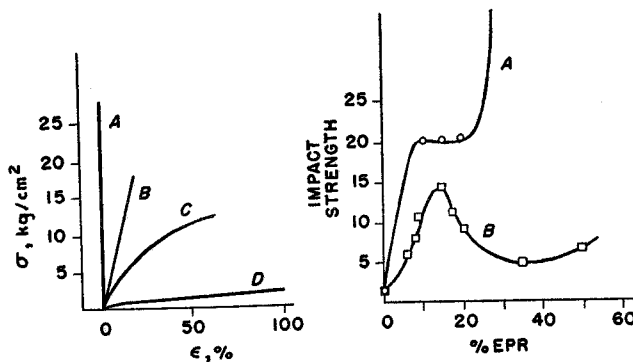


FIG. 3.—Stress-strain curves of (A) Polystyrene (incomplete); (D) Ethylene propylene rubber (incomplete); (C) Product A containing graft polymer; (B) mechanical mixture 50% polystyrene, 50% EPR.

FIG. 4.—Charpy resilience of (A) mixtures containing graft polymer; (B) mixtures of polystyrene and EPR; units kg cm/cm².

by it, and crossing the fissure, would be under tension, and would absorb energy of deformation until its separation from the surrounding matrix occurred. According to this theory, the force of the elastomer-resin adhesion is therefore determining; this is proportional to the interphase contact surface, and thus also to the product of the number of the particles of elastomer present in the system and the surface of each particle.

Both the preceding theories are good interpretations of the increase in impact strength with an increase in the percentage of elastomer, and also explain how, in mixtures of the ungrafted elastomer and polystyrene above a certain percentage of rubber, impact resistance of the mixtures again decreases. In fact, on increase of the number of particles of elastomer in the system, the possibility increases that these particles cohere, thus decreasing the number of microfractures (first theory) or the surface available for adhesion (second theory). When an elevated percentage of elastomer (approximately 35 per cent) has been exceeded (Figure 4), impact strength again increases. The system can in this case be considered as heterophasic, with macroscopically distinct phases, and the samples can be likened to rods, consisting of rigid extents (polystyrene zones), alternating with elastic elastomeric zones capable of absorbing a great deal of energy of deformation. The preceding theories, which presuppose the existence of a homogeneously, perfectly dispersed rubber phase, are then not applicable, and it is foreseeable that the polystyrene zones will remain practically undeformed.

The improved results, and the lack of a minimum, which are obtained by using the graft polymer in place of the unmodified ethylene propylene copolymer, can readily be interpreted in accordance with the second theory, on the basis of the improved adherence between the matrix and the elastomer, and of the impossibility of coalescence of large quantities of elastomer nuclei, owing to the perfect dispersibility of these nuclei due to the coexistence in the graft molecule of a polystyrene similar to the matrix, and of an elastomeric component similar to the rubbery phase.

The modulus of elasticity at bending of the polystyrene-elastomer and polystyrene-graft elastomer mixtures decrease continuously (Figure 5) with an increase in the percentage of elastomer. Among the most important theories that allow the modulus of elasticity of mixtures to be calculated, when the moduli of the

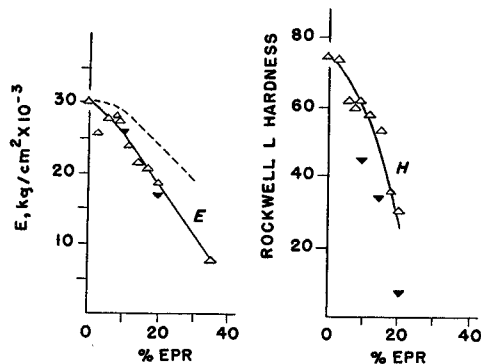


FIG. 5.—Flexural modulus of elasticity of elastomer-polystyrene mixtures Δ , and of mixtures of product A (see text) and polystyrene ∇ . Dashed curve = modulus according to Kerner.

FIG. 6.—Rockwell hardness, scale L, of: Δ elastomer-polystyrene mixtures; ∇ mixtures of product A (see text) containing the graft polymer and polystyrene.

substances constituting the mixture are known, we may cite those of Hashin¹⁰ and of Kerner¹¹.

We have applied the equations of Kerner in the simplified case of an elastomer having a torsional modulus $G = 10.2 \text{ kg/cm}^2$, which is very small in comparison with that of the polystyrene matrix.

For polystyrene, we assumed the experimental data $E = 30500 \text{ kg/cm}^2$ and γ (Poisson coefficient) = 0.3.

The theoretical curve of the Youngs' moduli shown in the dotted curve in Figure 5 is in rather good agreement with that of the experimental flexural moduli of elasticity.

The hardness of both types of mixture also decreases regularly with an increase in the percentage of elastomer (Figure 6). As is known, the hardness is not a fundamental property of the substance examined, but is a combination of various individual physical properties, and depends on the type of apparatus used for its determination. Using a sphere as penetrator, according to ASTM standards D 785-50, a property is measured which is principally determined by the modulus of elasticity of the material¹². It is observed, in Figure 6, that the values of the hardness decrease with an increase in the percentage of elastomer, that is, the curve is similar to that of the modulus of elasticity.

SUMMARY

Ethylene propylene copolymers having good elastomeric properties lend themselves very well to improving impact strength of fragile polymeric materials, such as polystyrene.

In order to obtain good results, the percentage of copolymer to be added should be chosen in such a way that the strength of the resulting mixture is as high as possible, but compatible, however, with the practically useful values of the hardness and of the modulus of elasticity, which decrease regularly with an increase in the percentage of elastomer.

The best results, for an equal percentage of elastomer, are obtained when the polystyrene is mixed with polystyrene grafted on the ethylene propylene copolymer, rather than with the ethylene propylene copolymer alone. This we attribute to the improved dispersion of the elastomer in the polystyrene matrix that is found in case of the use of the graft polymer. Thus, formation of vitreous and elastomeric microphases, rather than of macrophases, occurs, and there is a better adhesion between these.

The use of a graft polymer prevents, in practice, the phenomena of migration and sorting of the phases, and guarantees the maintenance over a period of time of a microphasic structure. The use of a saturated elastomer, such as that used by us, permits, additionally, an improvement in the resistance to aging, in comparison with the traditional materials consisting of mixtures of polystyrene and unsaturated elastomers.

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IMPROVEMENT OF IMPACT STRENGTH OF POLY- STYRENE BY COMPOUNDING WITH STYRENE- GRAFTED ETHYLENE PROPYLENE ELASTOMERIC COPOLYMERS*

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Certain practical applications of some thermoplastic resins in common use are limited by unsatisfactory mechanical properties, for example, brittleness. One of the methods most frequently used in industrial technology to improve impact strength of brittle resins is the incorporation of small percentages by weight of an elastomeric material having a modulus of elasticity lower than that of the resin. World production of resin elastomer mixtures has increased greatly during the past few years, the resins most frequently treated this way are polyvinyl chloride, polystyrene, and styrene acrylonitrile copolymers.

Another widely used method is that of adding plasticizers to the thermoplastic resins, so that their second order transition temperature, above which the polymer possesses elastomeric properties, is lowered.

Good results are also obtained by copolymerizing a monomer whose homopolymer is brittle with a monomer whose homopolymer has a low transition temperature.

The impact strength of thermoplastic resins depends to a great extent on the temperature, and for noncrystalline resins it is considerably lowered when they pass from the rubbery state to the glassy state, corresponding to the glass transition temperature T_g . Below this temperature the polymers become brittle, but not all polymers have the same impact strength. Polymers (for example, cellulose nitrate, or polycarbonates) which have secondary transitions below T_g behave better on impact¹.

In this paper, results of investigations carried out by us on polymeric products containing an amorphous ethylene propylene copolymer and polystyrene are illustrated.

In a polymeric product containing different monomeric units, two extreme typical cases can be distinguished, that is, a) the case in which the different monomeric units are contained in the same macromolecule and distributed in a random manner; the transition temperature then depends on the composition, and assumes values intermediate between those of the homopolymers² and in many cases is a linear function of the composition; and b) the case in which the different monomeric units are present only as homopolymers. Their mixtures then show both transition temperatures, each of which is slightly lowered by the presence of the other homopolymer, especially when the molecular weight is high. The presence of an elastomeric phase, even if immiscible with the other polymeric phase that is present, allows a greater deformability of the complex, and a consequent increase in impact strength.

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The best results, insofar as impact resistance is concerned, have always been obtained when the elastomer is present as a separate phase. One method of reducing the dispersibility, of the rubber in the brittle resin on a molecular scale, is to cross-link it, thus rendering it partially or completely unable to diffuse.

In order to obtain good impact resistance however it is necessary that a homogeneous distribution of the two phases be attained, so as to have a large number of particles of rubber well dispersed in the resin³, so that the system is, so to speak, pseudo-homogeneous. Optimum dispersions are generally obtained either mechanically, with suitable mixers, or by polymerizing the resin monomer in the presence of the rubber.

A grafting reaction that unites by a covalent bond a polymer of low impact resistance (for example, polystyrene) with a rubber incompatible with it allows optimum adhesion of the particle of rubber to a surrounding matrix consisting of the low-strength polymer to be attained.

Mixtures of polystyrene with various elastomers have been frequently studied^{3,4}.

Polymeric mixtures of polystyrene having high impact strength can, for example, be prepared by polymerizing monomeric styrene in the presence of small amounts of an unsaturated rubber, such as butadiene styrene copolymer. Some recent studies⁴ have shown that the polymerization reaction proceeds with formation of insoluble gels, determined by extraction of the material with a suitable solvent.

Microscopic examination of modified polystyrenes has shown that, in products having good impact strength, the rubbery phase is not molecularly dispersed in the polystyrene matrix in the gel state, but is dispersed in the latter in the form of discrete particles. In summary⁴, the conditions necessary for a polystyrene-elastomer composition to have elevated impact strength are the following:

- 1) the elastomer should have a glass transition temperature lower than the temperature at which it is to be used;
- 2) the elastomer should be intimately dispersed in the mass, and its particles should be small;
- 3) the elastomer should adhere sufficiently³ to the polystyrene matrix. This is possible if a molecular attractive interaction exists between the two polymers.

In the light of the preceding considerations, we prepared and studied a two-phase system consisting of a polystyrene matrix in which are dispersed discrete particles of a polystyrene-grafted ethylene propylene copolymer.

The grafted copolymer is partially crosslinked; in fact, although the crosslinking of the ethylene-propylene copolymer with peroxides takes place only at temperatures above 140–150° C, during the grafting reaction as carried out by us, a small amount of crosslinkage could be detected by examination of the solubility, without, however, any reduction in processability (which would be impossible for a vulcanized polymer with high crosslink density).

We used a saturated rubber instead of an unsaturated one both to reduce crosslinking and to obtain better aging resistance of the polymeric mixtures. The poor solubility of the ethylene propylene copolymer in the homopolymeric polystyrene is assured by the crosslinking reactions of the elastomer, which occur in the presence of the initiators we used. Good adhesion of the ethylene propylene copolymer to the polystyrene is assured by the grafting reaction, which permits a system to be obtained in which one passes continuously from the elastomeric phase to the resin phase. The ethylene propylene copolymer has a glass transition temperature much below room temperature. Therefore the conditions required to obtain a good impact resistant material exist.