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Rubber-modified polystyrene compositions

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The physical and mechanical properties of polystyrene compositions, prepared by blending high impact polystyrene (HIPS) with different types of elastomer, are studied. The results obtained show a considerable increase in HIPS impact strength when modified with isoprene and butadienestyrene elastomers. This increase in impact strength is due to factors such as low T_g and the flexibility of macromolecules of the elastomer phase and adhesion at the interphase boundary. An optimal elastomer concentration of 12.5 parts per hundred of resin is observed. A multi-directional influence of the elastomer additive on the impact strength and on the tensile and flexural strength has been found, due to different mechanisms of fracture.

1. Introduction

A number of investigations, dedicated to the problem of increasing the impact strength of the brittle polymers such as polystyrene, have been carried out [1–3]. To date, the most effective and most popular method, aimed at achieving this, utilizes the modification with elastomers. On the industrial scale, the modification of polystyrene with elastomers in the process of polymerization is widely applied. As a result a high impact polystyrene (HIPS) is obtained. This may be low, medium or high impact [4]. Depending on its initial type, the polystyrene's impact strength can be increased two- to fivefold. The HIPS impact strength is determined by factors such as the elastomer particle size, the distribution of these particles by size, the degree of adhesion between the polystyrene and elastomer phases, glass transition temperature, T_g, of the elastomer, the molecular mass of polystyrene, etc. [5]. Along with the impact strength, the modification of polystyrene with elastomers changes other strength properties as well, such as tensile strength, relative elongation and flexural strength [6].

In several cases, HIPS doesn't respond to specific exploitation requirements, such as achieving a very high impact strength and its preservation under low temperatures. One of the ways for attaining such a result is the additional modification of the commercially produced HIPS types with elastomers [7]. Because in this case the strength properties change to a different extent and multi-directional, a fuller investigation of the mutual dependence of composition properties is necessary.

The aim of conducting this investigation was to study some basic physical and mechanical properties of HIPS-based compositions, modified with different elastomer types.

TABLE I Elastomer compositions

Composition	Elastomer type
1. Composition 1	isoprene
2. Composition 2	butadienestyrene
3. Composition 3	α-methylstyrene
4. Composition 4	butyl
5. Composition 5	nitrile

2. Experimental procedure

2.1. Materials

The investigations were carried out with HIPS type BS 793, produced by NEFTOCHIM, Bulgaria. The elastomers given in Table I were used as modification additives.

Considering the recommended quantities of elastomer additive [8] with which high impact strength may be achieved while preserving the mechanical characteristic features of the matrix polymer, for our initial investigations we decided on a mean quantity of 10 p.h.r. (parts per hundred of resin).

2.2. Specimen preparation and tests

The preparation of the compositions was carried out on extruder with $L/D = 20$, outfitted with high shearing mixing screw. Each composition was extruded three times to ensure the uniform mixing. From the granulate thus obtained tiles 4 and 2 mm thick were pressed, under a pre-optimized regime of pressing. The test samples were cut out of these tiles. Before conducting the tests, the samples were treated under the respective temperature conditions for 2 h.

Charpy unnotched impact strength was determined according to Bulgarian State Standard (BSS) 7680-75, the tensile strength according to BSS 2991-75, the Dinstat flexural strength according to BSS 8819-71.

The reversible strain was determined by using the following formula:

$$\varepsilon_{rev} = 100(\Delta l_1 - \Delta l_2)/l_0 \ (\%) \qquad (1)$$

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where

$$\Delta l_1 = l_1 - l_0 \quad (2)$$

$$\Delta l_2 = l_2 - l_0 \quad (3)$$

l_1 is the length of the sample at the moment of tearing with tension; l_2 is the length of sample 24 h after testing; l_0 is the initial length of sample.

The relaxation of the stress was determined by using a relaxometer ZP-10, while the samples designed for testing their form and dimensions conform to BSS 2991-75. The determination of the mean relaxation time, τ_m, was achieved according to the method suggested by Pavlov *et al.* [17].

The determination of the gel fraction was carried out according to the method described in [9], by using benzene as extracting agent.

3. Results

The investigations for determining the Charpy unnotched impact strength (σ_i) were conducted in the + 20 to − 40 °C temperature range.

It can be seen from the relations, $\sigma_i = f(T)$, presented in Fig. 1 that with all compositions the impact strength in the temperature range studied is higher than that of the HIPS. With the latter, σ decreases with the reduction in temperature, this reduction being most significant within the + 20 to − 20 °C range. With temperatures lower than − 20 °C there was a fairly significant change in impact strength. With compositions 3, 4 and 5, impact strength also decreased with the drop of the temperature, even though to a lower extent. Compositions 1 and 2 possessed significantly higher impact strength, as compared to the rest. Moreover, σ does not change in the + 20 to − 30 °C range.

Further investigations were carried out with compositions 1 and 2, which showed higher impact strengths in the temperature range studied.

With both of them, an increase in elastomer additive gave an increase in impact strength up to the upper limit of 12.5 p.h.r. concentration. However, with 15 p.h.r. elastomer content, impact strength was slightly reduced (Figs 2 and 3). In addition, with an increase in elastomer content the change in temperature did not have significant effect upon impact strength. When modifying the HIPS with 5 p.h.r. butadiene-styrene elastomer, the increase in impact strength was greater than with the same quantity of isoprene elastomer.

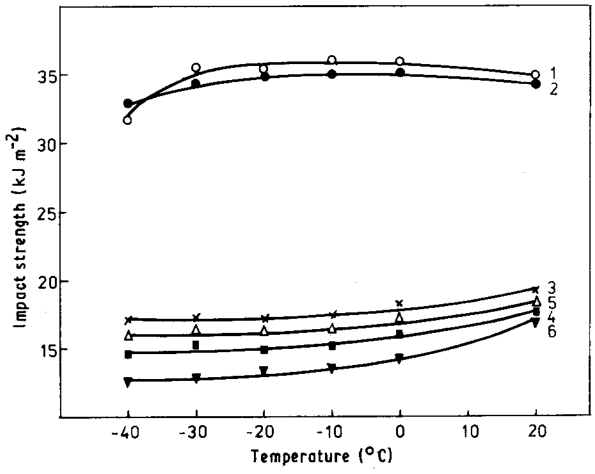

Figure 1 Plot of unnotched Charpy impact strength against temperature for: composition 1 (curve 1, ○); composition 2 (curve 2, ●); composition 3 (curve 3, ×); composition 4 (curve 4, ■); composition 5 (curve 5, △); unmodified HIPS (curve 6, ▼).

Besides the impact strength, the tensile strength, σ_t, and flexural strength, σ_f, were also determined for the compositions 1 and 2. It was found that with the modification of HIPS using elastomers, the tensile strength decreased (Fig. 4). This reduction in σ_t was highest with the initial concentration of 5 p.h.r. elastomer. Further increase in elastomer additive quantity did not significantly change the tensile strength.

The flexural strength of compositions 1 and 2 was also lower than that of HIPS, as flexural strength decreased with the increase in elastomer content. Note

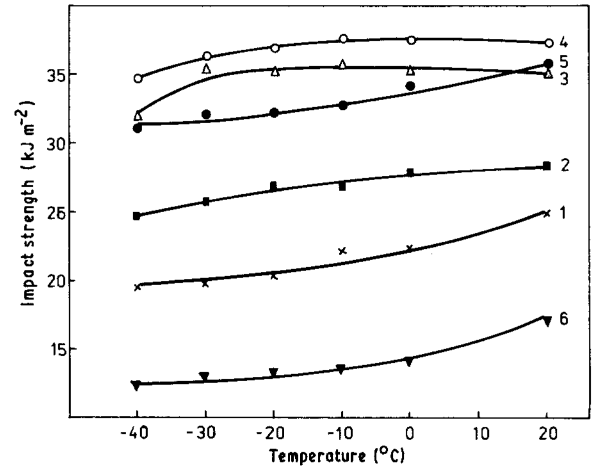

Figure 2 Plot of unnotched Charpy impact strength against temperature for composition 1: 5 p.h.r. (curve 1, ×); 7.5 p.h.r. (curve 2, ■); 10 p.h.r. (curve 3, △); 12.5 p.h.r. (curve 4, ○); 15 p.h.r. (curve 5, ●) and unmodified HIPS (curve 6, ▼).

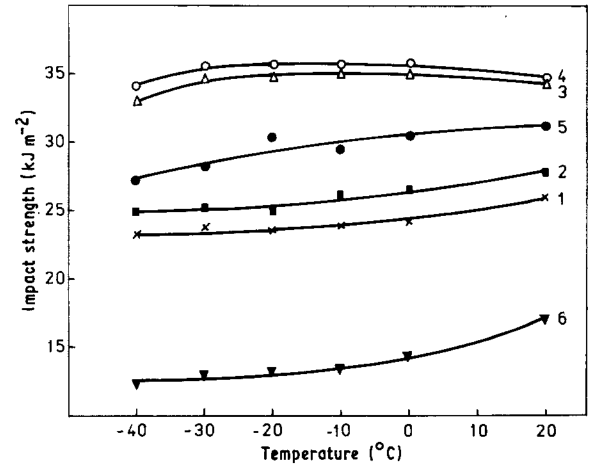

Figure 3 Plot of unnotched Charpy impact strength against temperature for composition 2: 5 p.h.r. (Curve 1, ×); 7.5 p.h.r. (curve 2, ■); 10 p.h.r. (curve 3, △); 12.5 p.h.r. (curve 4, ○); 15 p.h.r. (curve 5, ●) and unmodified HIPS (curve 6, ▼).

that in general a drop in temperature caused σ to decrease as well, but with temperatures lower than 0 °C σ did not change, as with HIPS and with compositions 1 and 2 (Figs 5 and 6).

The study of the reversible strain, ε_{rev}, shows that, with both types of compositions, it increased with the increase in the quantity of elastomer, just as the impact strength reaches an optimal value with 12.5 p.h.r. elastomer concentration, above which it decreased (Fig. 7).

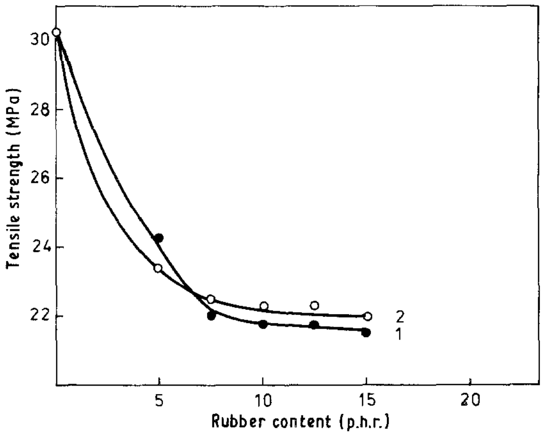

Figure 4 Plot of tensile strength against rubber content for composition 1 (curve 1, ●) and composition 2 (curve 2, ○).

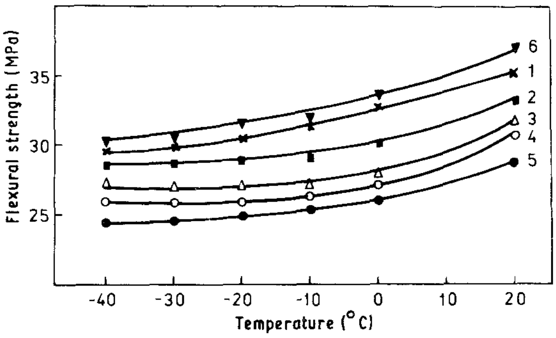

Figure 5 Plot of flexural strength against temperature for composition 1: 5 p.h.r. (curve 1, ×); 7.5 p.h.r. (curve 2, ■); 10 p.h.r. (curve 3, △); 12.5 p.h.r. (curve 4, ○); 15 p.h.r. (curve 5, ●) and unmodified HIPS (curve 6, ▼).

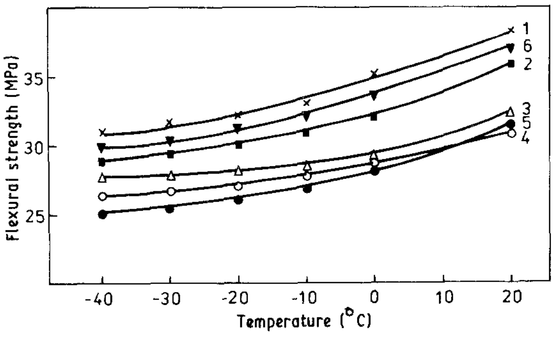

Figure 6 Plot of flexural strength against temperature for composition 2: 5 p.h.r. (curve 1, ×); 7.5 p.h.r. (curve 2, ■); 10 p.h.r. (curve 3, △); 12.5 p.h.r. (curve 4, ○); 15 p.h.r. (curve 5, ●) and unmodified HIPS (curve 6, ▼).

As is well known, polymer strength properties are closely related with the relaxation indices. In connection with this, the relaxation of the stress with ε a constant for HIPS and compositions 1 and 2 was studied (Figs 8 and 9).

As could be expected, the modification of HIPS with elastomers led to a significant acceleration of the relaxation processes, as with the increase in elastomer

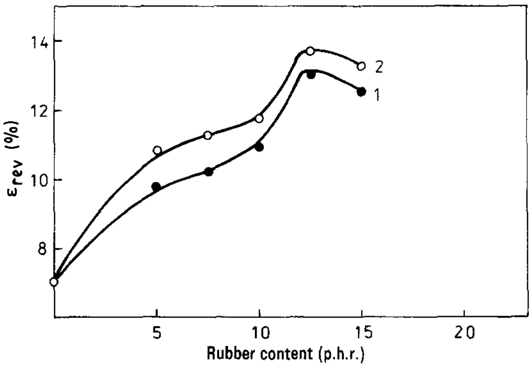

Figure 7 Plot of reversible strain (ε_{rev}) against rubber content for composition 1 (curve 1, ●) and composition 2 (curve 2, ○).

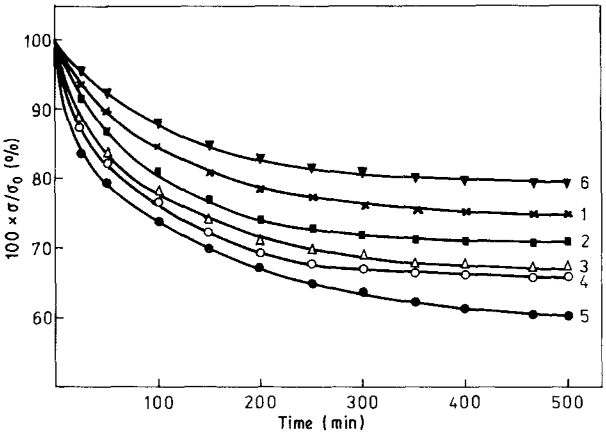

Figure 8 Stress relaxation curves of composition 1: 5 p.h.r. (curve 1, ×); 7.5 p.h.r. (curve 2, ■); 10 p.h.r. (curve 3, △); 12.5 p.h.r. (curve 4, ○); 15 p.h.r. (curve 5, ●) and unmodified HIPS (curve 6, ▼).

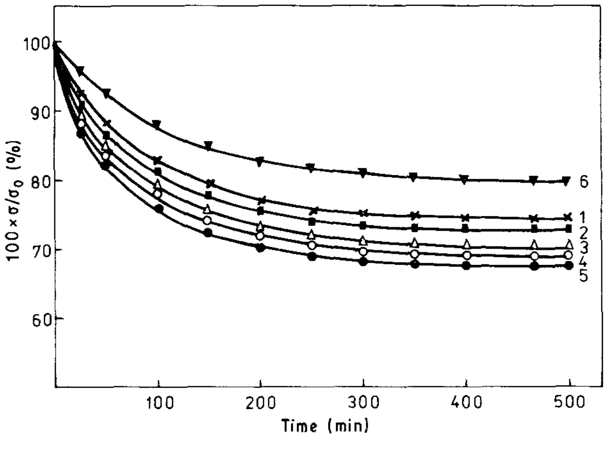

Figure 9 Stress relaxation curves of composition 2: 5 p.h.r. (curve 1, ×); 7.5 p.h.r. (curve 2, ■); 10 p.h.r. (curve 3, △); 12.5 p.h.r. (curve 4, ○); 15 p.h.r. (curve 5, ●) and unmodified HIPS (curve 6, ▼).

quantity the mean relaxation time, τ_m, decreased (Table II). Relaxation is quicker with composition 1, as compared to composition 2.

We investigated if and to what extent a chemical bond formed between HIPS and the elastomer additive in the process of mixing. We determined the gel fractions of the compositions 1 and 2 (with 10 p.h.r. concentration) with one-, two- and three-fold extrusion, as well as the gel fractions of the unmodified HIPS, the isoprene and the butadienestyrene elastomers. A gel fraction was found solely in composition 2 in the following quantities: single-fold extruding (7.54%); two-fold extruding (6.14%); three-fold extruding (4.22%).

4. Discussion

Our results show that the greatest strengthening effect is obtained with isoprene (composition 1) and butadienestyrene (composition 2) elastomers. These results can be explained by considering the T_g of the elastomers used (Table III).

The compositions manifesting highest impact strength along the whole temperature range studied contain elastomers with a lower T_g than the rest. Composition 4 is an exception, having lowest impact strength, despite the fact that the butyl elastomer has a comparatively low T_g. The cause for this has to be looked for in the low compatibility of the butyl elastomer with HIPS, which probably leads to the elastomer's non-homogeneic distribution in the polystyrene matrix, on one hand, and to a low adhesion on the interphase boundary, on the other. According to Bragaw [10, 11], when modifying brittle thermoplastics with elastomers, the T_g of the latter has to be within 60 °C of the temperature of testing so that maximum reinforcement is achieved. Hence, elastomers with T_g not higher than -40 °C have to be used. In addition, a role is played by the greater flexibility of the isoprene and butadienestyrene elastomer macromolecules. As a result of this, in compositions 1 and 2 fracture of type III is observed, according to the classification of Bucknall [12] (plastic fracture accompanied by a significant whitening of the fracture surface), up to $T = -20$ °C, while for the rest of the compositions this type of fracture is observed up to -10 °C, and with HIPS up to $T = 0$ °C.

As shown, the impact strength increased under the effect of growing quantities of isoprene and butadienestyrene elastomers. A maximum at 12.5 p.h.r. concentration was likely to appear with both investigated compositions, after which the further increase in the modifier quantities worsened this property. Such an effect has been observed by Silberberg and Han [15], who investigated polystyrene modified with elastomers. We believe that the phase inversion in the process of polymerization was incomplete to the extent that enough rubber was tied up in the uninverted parts of the resin to seriously reduce the level of reinforcing rubber.

In our particular case, the reduction in impact strength was due to the uneven distribution of the elastomer in the HIPS matrix and its localization in significantly large zones.

Unlike impact strength, which passed through a maximum with the increase in elastomer content, the tensile and flexural strengths continuously diminished. The monotonous drop in tensile strength with the increase in elastomer content has been observed by other authors [14, 16]. The explanation must be sought in the different mechanisms of fracture by testing with low intensity fracture, such as those for tensile and flexural strengths, and in tests with high intensity fracture, such as impact strength.

Silberberg and Han [15] compared the results from the tensile and impact strengths for several types of HIPS with different particle sizes. They have come to the conclusion that the reduction in the particle size with the same quantity of elastomer used favours an increase in tensile strength, while the increase in particle size favours an increase in impact strength. Thus different mechanisms of reinforcement act in the tensile and the impact tests.

The results from the determination of the reversible strain confirm the optimal concentration of 12.5 p.h.r. found in the tests. The increase in reversible strain with the acceleration of the relaxation processes was observed with the modification of HIPS with elastomers. The decrease in ε_{rev} with 15 p.h.r. concentration may be due to the fact that in lower concentrations the elastomer particles take part in the strain process and facilitate the conformity changes of HIPS under mechanical stresses. The formation of large elastomer layers with the increase in elastomer concentration led to their breaking away at the phase boundary from the polystyrene under the effect of mechanical stresses, as a result of which the plastic strain increased.

TABLE II Relaxation times

Composition (p.h.r.)	Mean relaxation time (min)
1. Composition 1	
5	125
7.5	118
10	115
12.5	110
15	104
2. Composition 2	
5	139
7.5	131
10	121
12.5	116
15	113
3. HIPS	170

TABLE III T_g for various elastomers

Elastomer type	T_g (°C)
1. Isoprene	-74
2. Butadienestyrene	-60
3. α-methylstyrene	-54
4. Butyl	-68
5. Nitrile	-32

The high impact strength is determined to a great extent by the possibilities for rapid relaxation [13]. With the modification of HIPS with polyisoprene and polybutadienestyrene, the relaxation processes accelerated with the increase in elastomer concentration. This acceleration was due to the low T_g of the elastomer phase, resulting in an increase in the mobility of the kinetic elements in the composition. The smaller acceleration of composition 1, as compared to composition 2, may be due to the lower T_g of the isoprene elastomer. As a result, it could be expected that the composition containing isoprene elastomer (composition 1) possessed higher impact strength than the composition containing butadienestyrene elastomer (composition 2). However, this was not observed practically. The two compositions had similar impact strengths throughout the whole temperature range examined. Most probably, besides T_g, an important role is played by the flexibility of the macromolecules of the elastomer modificator.

Another explanation of this fact is the assumption that for the high impact strength of composition 2, besides T_g, the adhesion at the interphase boundary has an effect; it is known that one of the conditions for achieving a high impact strength is good adhesion between the polystyrene and elastomer phases. Only in composition 2 was a gel fraction found. Most probably, in the process of mixing and as a result of mechanical destruction, a certain chemical bond formed at the interphase boundary, which contributed to the increase in impact strength of composition 2.

5. Conclusion

With the modification of HIPS by different elastomers, the effect of an increase in impact strength is most strongly manifested by the compositions containing isoprene and butadienestyrene elastomers (compositions 1 and 2). An optimal elastomer concentration of 12.5 p.h.r. was observed in them, which was the highest increase in impact strength achieved. A multi-directional effect of the elastomer additive upon the impact strength, on one hand, and on the tensile and flexural strengths, on the other hand, has been found, this being due to the different mechanisms of fracture. To explain the considerable increase in HIPS impact strength with the modification by isoprene and butadienestyrene elastomers, one must consider the increase in the number of possibilities for rapid relaxation due to the low T_g and to the flexibility of the macromolecules of the elastomer phase. With the composition containing butadienestyrene elastomer, a significant role is probably played by adhesion at the interphase boundary.

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