Graft copolymerization of styrene and acrylonitrile on to polybutadiene in the presence of n-butyl acrylate

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The preparation of graft copolymers of styrene, acrylonitrile and n-butyl acrylate on to a polybutadiene rubber by emulsion polymerization and up to high degrees of conversion are described and investigated theoretically. The resulting graft copolymers have a higher styrene content and a lower acrylonitrile content than predicted by theory, whereas the n-butyl acrylate has the expected content. Impact and notched impact resistances, bending and tensile strengths, ball-puncture resistance, Vicat softening temperature and glass transition temperatures of the graft copolymers have been measured and are discussed.

(Keywords: graft polymer; emulsion polymerization; polybutadiene)

INTRODUCTION
The properties of acrylonitrile/butadiene/styrene graft copolymers (ABS) have been modified by the incorporation of other comonomers capable of graft copolymerization. So α-methyl styrene and maleimides1-3 and vinyl acetate4 have been used and, in the presence of methyl methacrylate, transparent impact-resistant polymers have been obtained. Acrylates, in particular, have been used as a component of the elastic phase in products which have been on the world market since the early 1970s. These show good thermal and weather stability, high ultraviolet (u.v.) resistance and high ageing resistance5-7.

In the following paper we have investigated n-butyl acrylate as a modifier for the rigid thermoplastic phase of the ABS polymers, prepared by the emulsion graft copolymerization of styrene and acrylonitrile on to a polybutadiene latex, and taken to high degrees of conversion. The properties of the graft copolymers obtained have also been studied.

THEORETICAL MODEL FOR GRAFTING
CALCULATED GRAFT COMPOSITION
In the graft copolymerization of styrene (ST), acrylonitrile (AN) and n-butyl acrylate (BA) on to a polybutadiene rubber, the composition of the graft can be seen in a first approximation as the result of a terpolymerization. A two-parameter model has proved to be applicable to the copolymerization of ST and AN as well as to that of ST and BA8. Therefore, the validity of the Alfrey and Goldfinger equation9 has been assumed for the corresponding terpolymerization. As copolymerization parameters, those computed and verified by Kelen and Tüdös8 if available have been used (see Table 1).

In the investigation of the ST/AN/BA system no ternary azeotrope was found in accordance with the criteria of Tarasov et al.13 and Valvassori and Sartori14. The two binary azeotropes were calculated to consist of 61.2 mol% of ST and 38.8 mol% of AN or 77.3 mol% of ST and 22.7 mol% of BA respectively.

The terpolymerization behaviour of the system has been studied at different degrees of conversion by integrating and solving the Alfrey/Goldfinger equation according to the Runge/Kutta method. This study has been made for a batch reaction at equidistant conversion stages using a computer program.

At low degrees of conversion (2 mol%), Figure 1 shows the dependence of the terpolymer composition calculated from the monomer feed for the ST/AN/BA system. As can be seen, significant quantities of BA are incorporated into the terpolymer. This increases with rising BA quantity in the monomer feed at constant ST or AN quantity. A polymer composition is obtained which is closer to the connecting line of the two azeotropic points of the binary copolymerizations of ST/AN and ST/BA than the monomer composition. This tendency is the stronger, the greater the distance of the monomer feed composition from the connecting line of the two azeotropic points. At this point, the influence of the ST/AN azeotrope is essentially stronger than that of the ST/BA azeotrope.

For higher degrees of conversion, the result of theoretical computations gives a more varied behaviour for the terpolymerization system.

An azeotropic composition of ST and AN in the monomer feed (see Figure 2) yields ST/AN/BA terpolymers of similar composition at lower degrees of conversion. When the degrees of conversion are higher and the ST is consumed to a large extent, the difference between the composition of monomer mixture and the polymer is greater. Finally, the yielded polymers change to AN/BA copolymers with a maximum of AN in the differential terpolymer composition. This maximum is shifted towards smaller degrees of conversion with
increasing BA quantity in the monomer feed (20 mol% of BA: maximum at about 96 mol% of conversion; 30 mol% of BA: maximum at about 90 mol% of conversion). For 15 mol% of BA and smaller quantities in the monomer feed, no maximum of the AN incorporated was observed.

Deviations from the ST/AN azeotrope towards higher AN quantities in the monomer feed cause, at lower degrees of conversion, ST/AN/BA terpolymers of an increasingly heterogeneous composition. After the ST is used up, AN/BA copolymers are yielded. Similarly, the maximum of AN in the differential terpolymer composition shifts, for example at constant AN concentration in monomer feed (40 mol%), to lower degrees of conversion with an increasing quantity of BA in the monomer feed (10 mol% of BA: maximum at about 96 mol% of conversion; 20 mol% of BA: maximum at about 90 mol% of conversion; 30 mol% of BA: maximum at about 80 mol% of conversion; 5 mol% of BA: no maximum obtained).

Deviations from the ST/AN azeotrope towards higher ST quantities in the monomer feed lead to terpolymers which show relatively constant compositions, at higher degrees of conversion, too. This may be due to the approach of monomer feed composition to the connecting line between the binary azeotropic points in the triangular diagram. Thereby, especially with increasing quantities of BA in the monomer feed (for example at constant ST concentration of 60 mol%), at high degrees of conversion in the differential polymer composition, the ST and AN quantities in the polymer decrease more whereas the BA quantity substantially increases.

**EXPERIMENTAL**

The graft polymers were prepared by emulsion polymerization using the following basic formula.

<table>
<thead>
<tr>
<th>Rubber content</th>
<th>18.5 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic to aqueous phase ratio</td>
<td>1:2</td>
</tr>
<tr>
<td>E 30 emulsifier (Leuna-Werke)</td>
<td>2 wt% (based on the monomers)</td>
</tr>
<tr>
<td>t-Dodecyl mercaptan</td>
<td>0.6 wt% (based on the monomers)</td>
</tr>
<tr>
<td>Potassium persulphate</td>
<td>2 x 0.1 wt% (based on the monomers)</td>
</tr>
</tbody>
</table>

| ST to AN mass ratio      | 3:1      |

**Table** 1 Selected copolymerization parameters for the styrene/ acrylonitrile/n-butyl acrylate system

<table>
<thead>
<tr>
<th>Monomer 1</th>
<th>Monomer 2</th>
<th>$r_{12}$</th>
<th>$r_{21}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>Acrylonitrile</td>
<td>0.41</td>
<td>0.07</td>
<td>10</td>
</tr>
<tr>
<td>Styrene</td>
<td>n-Butyl acrylate</td>
<td>0.75</td>
<td>0.15</td>
<td>11</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>n-Butyl acrylate</td>
<td>1.2</td>
<td>0.89</td>
<td>12</td>
</tr>
</tbody>
</table>

**Figure 1** Dependence of terpolymer composition on the composition of the monomer mixture for the styrene (ST)/acrylonitrile (AN)/n-butyl acrylate (BA) system at low degrees of conversion. (---) connecting line between the binary azeotropes

**Figure 2** Dependence of the monomer composition (A), differential (B) and integral terpolymer composition (C) on the degree of conversion for the styrene (ST, 42 mol%)/acrylonitrile (AN, 28 mol%)/n-butyl acrylate (BA, 30 mol%) system.
When using BA in quantities up to 12.5 wt% (based on the monomers), the corresponding ST and AN quantities were substituted by BA at a mass ratio of 3:1. The number average particle size of the emulsion polybutadiene latex used as the base for grafting was 54 nm. The polybutadiene rubber contained 15% cis 1-4, 18% 1, 2 vinyl and 67% trans 1-4. The gel content was 92.0%.

After feeding the charge, graft polymerization was initiated by heating in an autoclave to 363 K. After about 1 h, at the above temperature, K$_2$S$_2$O$_8$ was added to reinitiate and complete the polymerization within 1 h at 363 K.

The graft latex obtained in this way was precipitated into magnesium chloride solution at 343 K. The product was washed several times, stabilized with 0.5%, 2,6-di-tert-butyl-p-cresol and 0.7% trisnonylphenolphosphate and oven-dried at 333 K to constant weight.

The powdered graft polymer was homogenized and granulated in a Buss-Co kneader in the presence of stabilizers and lubricants. The specimens were injection moulded and their characteristics tested in accordance with the conditions specified in the TGL 25496 standard.

A Perkin-Elmer differential scanning calorimeter, model DSC-2, was used to determine the glass transition temperatures of the graft polymers in argon (heating rate: 10 K min$^{-1}$). The residual monomer content of the graft latices was determined by gas chromatography, either directly in the latex or by removing the monomers by steam distillation.

**RESULTS AND DISCUSSION**

In the preparation of the graft polymers, ST and AN were substituted in the mass ratio, ST:AN = 3:1, approximately corresponding to the azoetrop and the BA quantities in the monomer mixture increased progressively.

The dependence of the residual styrene content and the residual BA content in the ABS latex on the BA content in the monomer mixture is depicted in Figure 3. Both methods, direct gas chromatography of the residual monomer contents and the gas chromatography of the composition of the organic phase following the steam distillation of the ABS latex, confirm a definite decrease in the residual ST content at increasing residual BA content with increasing BA quantity in the monomer feed at constant reaction conditions.

Figure 4 shows the composition of the graft polymers formed in emulsion polymerization. The composition is related only to the three-component system (ST, AN and BA) and plotted as a function of the BA quantity in the monomer feed. From the figure, it can be seen that in qualitative agreement with theory the ST and the AN quantities in the polymer decrease with increasing BA in the monomer feed. Further, this figure illustrates that the increasing BA content in the polymer is in good agreement with the value calculated for each degree of conversion. However, for ST, an increase in composition observed experimentally over that calculated and for AN, a decrease in composition in the polymer of the order of magnitude of 2–3 mol% has been observed. These
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Figure 5 Relationship between notched impact resistance ($\sigma_{ik}$) of the graft polymers and quantity of n-butyl acrylate (BA) in the monomer mixture. Test temperatures: (●) 293 K; (▲) 273 K; (○) 253 K

deviations from theory are considered to be due primarily to the different solubility of the monomers either in the aqueous or in the various organic phases. While under normal conditions at 293 K, AN (with 7.35 wt%15) may be largely regarded to be water-soluble in the system, ST (with 0.032 wt%16) and BA (with 0.16 wt%17) are largely insoluble in water at 298 K.

The findings from the emulsion polymerization system of ST and AN18,19 and that of ST, AN and methyl acrylate20 among others, are similar. A description is possible taking into account the various monomer solubilities or the monomer concentration in the aqueous phase, the monomer droplets and the swollen polymer particles in the emulsion for the ST/AN system at constant reaction conditions, for example on the basis of the actual monomer concentrations found in the swollen polymer particles as the main location of the polymerization21 or by introducing a specific parameter into the Mayo/Lewis equation which is, in particular, a function of the distribution coefficient of AN and of the water/monomer ratio22. The latter makes the amounts of ST in the copolymer 0–3% larger than the normal data. This also applies at high degrees of conversion within the range of 90–100% and is in agreement with the experimental data. The data obtained for the ST/AN/BA system with various polymerization conditions are also consistent with this interpretation and in the range of values observed.

The substitution of ST and AN by BA in the emulsion graft polymerization on to a polybutadiene considerably alters the mechanical and thermal properties of the graft polymers produced.

The dependence of notched impact resistance of the polymers on composition for the substitution of ST and AN at a 3:1 mass ratio by increasing amounts of BA in the monomer feed is shown in Figure 5 at high degrees of conversion (see Figure 3) and at different temperatures of measurement. They are compared directly with graft polymers of ST and AN on to polybutadiene (see ordinate), free of BA. As can be seen from the figure, the notched impact resistance increases with increasing BA content and reaches a maximum at about 2.5 wt% of BA. On further substitution, the resistance drops below the initial value. The effects observed at the test temperature of 293 K are considerably greater than those observed at 253 K. A similar dependence of the impact resistance on the BA quantity in the grafted polymer has been found for different test temperatures and is shown in Table 2. In contrast with the notched impact resistance, a relatively high level of the impact resistance is maintained compared with the initial value once the maximum of about 2.5 wt% is exceeded.

The relationship between the bending strength and the tensile strength of the graft polymers and increasing amount of BA substituting for ST and AN is shown in Figure 6. Both the bending strength and the tensile strength drop slightly with BA in the polymer. However, with increasing amount of BA, they remain relatively constant and only at large content do they again decrease. A similar shape has been found for the ball-puncture resistance with increasing BA in the polymer, as shown in Figure 7.

Table 2 Impact resistance of graft polymers at different test temperatures as a function of n-butyl acrylate in the monomer mixture

<table>
<thead>
<tr>
<th>X (mol%)</th>
<th>Impact resistance (kJ m(^{-2})/% of unbroken specimens)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>293 K</td>
</tr>
<tr>
<td>0</td>
<td>77.8/50</td>
</tr>
<tr>
<td>0.164</td>
<td>100/90</td>
</tr>
<tr>
<td>0.822</td>
<td>-/100</td>
</tr>
<tr>
<td>1.65</td>
<td>-/100</td>
</tr>
<tr>
<td>5.04</td>
<td>-/100</td>
</tr>
</tbody>
</table>

Figure 6 Dependence of: (○) bending strength (BS); and (●) tensile strength (TS) of the graft polymers on the n-butyl acrylate quantity in the monomer mixture.
The emulsion graft copolymerization of ST, AN and BA on to a polybutadiene carried out up to high degrees of conversion has been considered as terpolymerization of monomers to simplify matters. The composition of the graft copolymers has been compared with the theoretical results of the Alfrey/Goldfinger equation. The BA computed and experimental quantities contained in the copolymer are in good agreement. However, the copolymers have a higher ST content and a lower AN content than found in the calculations. This is attributable to the high water solubility of AN.

The substitution of ST and AN by BA at azotropic ratios gives graft copolymers whose bending strength and tensile strength decrease steeply in the presence of BA compared to the unsubstituted copolymer. With increasing BA quantity, the bending strength and tensile strength remain relatively constant and decrease considerably only at higher concentrations. The curve of the ball-puncture resistance shows a similar shape. In contrast, the notched impact resistance has a maximum also at lower temperatures at about 2 mol\% of BA in the monomer mixture. Both the Vicat softening temperature and the glass transition temperature of the graft copolymers decrease considerably linearly with rising BA quantity. Thus, graft copolymers prepared from BA show better properties in specific ranges than polymers prepared from the ST and AN monomers only.

**CONCLUSIONS**

The emulsion graft copolymerization of ST, AN and BA on to a polybutadiene carried out up to high degrees of thermal stability and flowability. Graft polymers prepared by use of BA provide improved resistance for about 2 tool\% of BA. In addition, the higher fracture toughness of the graft polymers, particularly with relation to the notched impact resistance for about 2 mol\% of BA. In addition, the graft polymers prepared by use of BA provide improved thermal stability and flowability.

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