

On the Graft Polymerization of Styrene and Acrylonitrile onto Polybutadiene in the Presence of Vinyl Acetate.

II. Properties of Graft Polymers

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SYNOPSIS

The properties of the graft polymers of styrene, acrylonitrile, and vinyl acetate onto polybutadiene rubber that were prepared for the modification of graft polymers of styrene and acrylonitrile onto polybutadiene (ABS polymers) by emulsion polymerization up to a high degree of conversion have been studied and discussed. Both the impact strength and notched impact strength of the graft polymers have been found to remarkably increase with a rising quantity of vinyl acetate, in particular, in the case of styrene substitution, whereas in the case of acrylonitrile substitution by vinyl acetate, the two characteristics become noticeably poorer. The effects of the vinyl acetate amount and the type of substituted monomers on bending strength, tensile strength, Vicat softening point, and glass transition temperature of the graft polymers are also clearly different. Furthermore, the properties of the above graft polymers blended with styrene/acrylonitrile copolymers have been studied.

INTRODUCTION

For modification of the properties of graft polymers of styrene and acrylonitrile onto polybutadiene rubbers (ABS) by changing the thermoplastic phase, the α -methyl styrene and methyl methacrylate monomers in particular, were largely used.¹⁻³ Because of their structure, the two monomers incorporate easily into the polymer.

The application of vinyl acetate in the graft polymerization of styrene and acrylonitrile onto polybutadiene rubber, however, is not as easy. As shown in a previous work,⁴ adequate vinyl acetate quantities in the graft polymer are expected at smaller degrees of conversion only for very high vinyl acetate amounts in the monomer mixture or only at a relatively high degree of conversion to distinctly influence the macroscopic properties. For this reason, graft polymers have been prepared by emulsion polymerization of styrene and acrylonitrile onto a polybutadiene latex up to a high degree of conversion

and with part of styrene, acrylonitrile, or styrene and acrylonitrile (in a nearly azeotropic composition in the mass ratio 3 : 1) being substituted by vinyl acetate. As a result, the graft polymers showed a higher styrene quantity and a lower acrylonitrile quantity in comparison to the theoretical data obtained from the Alfrey/Goldfinger equation. However, the theoretical and experimental vinyl acetate content are in relatively good agreement. This may be attributed to the considerably higher water solubility of the acrylonitrile in the polymerization system and the dominating presence of styrene in the inner grafted content of the polybutadiene particles.

The following will cover the properties of the graft polymers formed in this way⁵ as well as the properties of the products obtained by blending them with styrene/acrylonitrile copolymers.^{6,7}

EXPERIMENTAL

The graft polymers of styrene and acrylonitrile onto polybutadiene rubber latex with the number-average particle size of 54 nm have been prepared by batch-

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wise emulsion polymerization. The initiator has been redosed, and styrene, acrylonitrile, or styrene and acrylonitrile in the mass ratio of 3 : 1 have been substituted by vinyl acetate. The treatment to obtain the respective ABS/powder has been completed according to the procedure given in Ref. 4.

The powdery graft polymer formed has been homogenized and granulated by a Buss-Co kneader with the addition of common stabilizers and lubricants. The test pieces made of this graft polymer have been subjected to injection molding and the characteristics were tested under the conditions specified in TGL 25496. The average vinyl acetate quantity in the polymerized monomer mixture of the graft polymers is estimated according to that given in Ref. 4.

The glass transition temperatures of the graft polymers have been determined by a Perkin-Elmer DSC-2 within the temperature range of 230–450 K and/or 120–310 K using argon and/or hydrogen (heating rate 10 K/min).

For the ABS graft polymers blended with styrene/acrylonitrile copolymers, a graft polymer has been selected that was prepared by substitution of 10% wt of styrene by vinyl acetate in the monomer mixture according to the data given in Ref. 4.

The product used as styrene/acrylonitrile copolymer (SAN) was formed by bulk/solution polymerization and had a Fikentscher K value of 58 with the acrylonitrile content being 29% wt. The mixtures were also prepared by the Buss-Co kneader.

RESULTS AND DISCUSSION

Properties of Graft Polymers

The substitution of part of styrene or acrylonitrile by vinyl acetate in the emulsion graft polymerization system brings about different mechanical and thermal properties of the graft products.

The impact strength as a function of the vinyl acetate amount in the polymerized monomer mixture is shown in Figure 1. Although in the substitution of styrene by vinyl acetate the impact strength considerably increases with a rising amount of vinyl acetate, it shows only a slight increase if styrene and acrylonitrile are substituted in the mass ratio of 3 : 1. Considering the substitution of acrylonitrile alone, it decreases remarkably with a rising amount in the polymerized monomer mixture. A similar tendency has been shown for the number of test pieces that did not break in the impact strength test. In the styrene substitution, this number increases

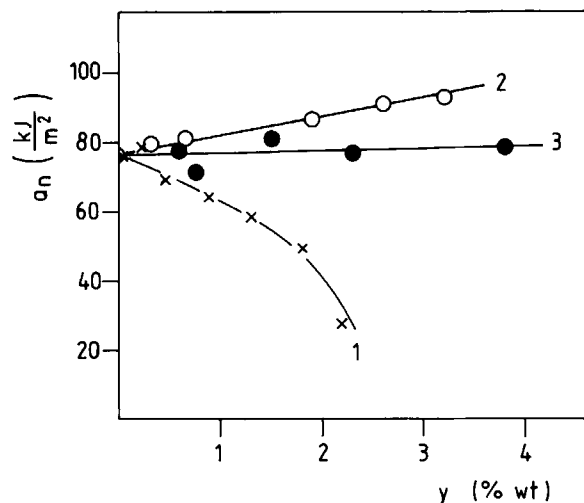


Figure 1 Dependence of the impact strength (a_n , 293 K) of the graft polymers on the vinyl acetate quantity in the polymerized monomer mixture (y): (1) substitution of acrylonitrile; (2) substitution of styrene; (3) substitution of styrene and acrylonitrile in the mass ratio of 3 : 1.

with a rising vinyl acetate amount up to more than 80%, whereas in the acrylonitrile substitution, nearly all test pieces with an amount of about 2.5% wt of vinyl acetate and more were broken.

With rising amounts of vinyl acetate introduced into the polymerized monomer mixture, the curve of the notched impact strength of graft polymers is similar to the impact strength curve (Fig. 2). The styrene substitution by vinyl acetate shows an increase in the notched impact strength with rising vinyl acetate content in the polymerized monomer mixture as against the ABS graft polymer that was not modified by vinyl acetate (see ordinate). The substitution of styrene and acrylonitrile by vinyl acetate in the mass ratio of 3 : 1 causes a smaller increase. The substitution of acrylonitrile only results in a very steep decrease in the notched impact strength, while the vinyl acetate content rises. When comparing the tendency of the specific viscosity data of the polymers separated from the elastomer phase with the rising amounts of acrylonitrile substituted by vinyl acetate (see Ref. 4) with the literature,⁸ ranges are reached where both the impact strength and the notched impact strength of the graft polymers decrease very steeply, with the specific viscosity of the separated styrene/acrylonitrile copolymers being somewhat lower.

The considerable reduction of the molecular weights of the graft polymers seems to be the main reason for the strong decrease in impact and notched impact strength of the products in the case of ac-

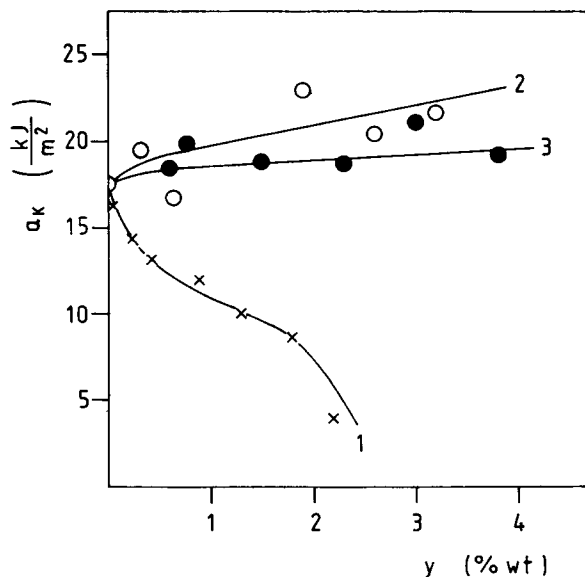


Figure 2 Correlation between notched impact strength (a_k , 293 K) of graft polymers and vinyl acetate quantity in the polymerized monomer mixture (y): (1) substitution of acrylonitrile; (2) substitution of styrene; (3) substitution of styrene and acrylonitrile in the mass ratio of 3 : 1.

rylonitrile substitution by vinyl acetate. This is confirmed by the notched impact strength that was as low as 7.6 kJ/m^2 for the pure graft polymer of styrene and acrylonitrile onto polybutadiene with a specific viscosity of the separated SAN of 0.2117. The pure graft polymer was formed under similar experimental conditions with a higher content of *tert*-dodecyl mercaptan.

Figure 3 indicates the correlation between bending strength and vinyl acetate amount in the polymerized monomer mixture. For the substitution of styrene as well as styrene and acrylonitrile in the mass ratio of 3 : 1, the bending strength slightly decreases the way the vinyl acetate amount rises. In case of acrylonitrile substitution, the bending strength strongly decreases.

The tensile strength as a function of the vinyl acetate content in the monomer mixture gives a similar result (Fig. 4). The decrease of tensile strength is small with rising vinyl acetate quantity for the substitution of styrene as well as styrene and acrylonitrile in the mass ratio of 3 : 1. However, for the substitution of acrylonitrile, it is considerable.

The dependence of the Vicat softening points of the graft polymers on the vinyl acetate quantity substituted in the polymerized monomer mixture is visible in Figure 5. As shown for the styrene substitution, the Vicat softening point of the graft products only slightly decreases with a rising vinyl

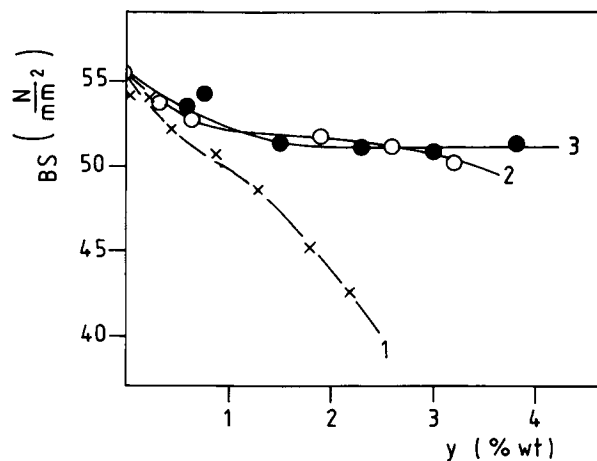


Figure 3 Dependence of the bending strength (BS) of the graft polymers on the vinyl acetate quantity in the polymerized monomer mixture (y): (1) substitution of acrylonitrile; (2) substitution of styrene; (3) substitution of styrene and acrylonitrile in the mass ratio of 3 : 1.

acetate amount. For the substitution of styrene and acrylonitrile in the mass ratio of 3 : 1, the decrease of the Vicat softening point becomes stronger with rising vinyl acetate quantity, whereas the substitution of acrylonitrile causes the most considerable drop.

The glass transition temperature of the rigid phase of graft polymers shows a similar dependence on the monomer substitution by vinyl acetate (Table I). For the styrene substitution, the glass transition temperature decreases only negligibly. If styrene and acrylonitrile are substituted in the mass ratio of

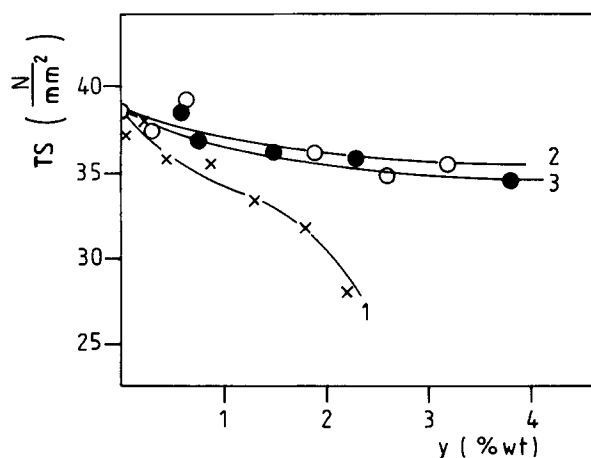


Figure 4 Correlation between tensile strength (TS) of the graft polymers and vinyl acetate quantity in the polymerized monomer mixture (y): (1) substitution of acrylonitrile; (2) substitution of styrene; (3) substitution of styrene and acrylonitrile in the mass ratio of 3 : 1.

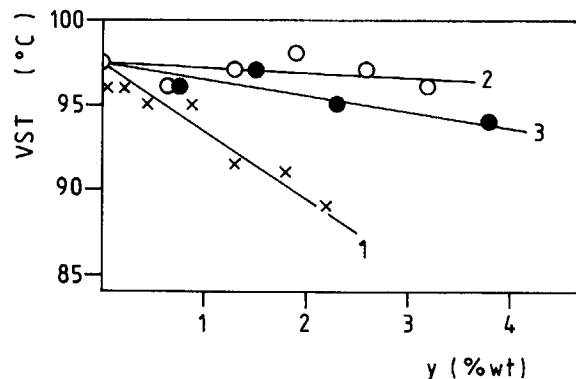


Figure 5 Dependence of the Vicat softening point (VST) of the graft polymers on the vinyl acetate quantity in the polymerized monomer mixture (y): (1) substitution of acrylonitrile; (2) substitution of styrene; (3) substitution of styrene and acrylonitrile in the mass ratio of 3 : 1.

3 : 1, the decrease becomes clearly visible, and for the substitution of acrylonitrile by vinyl acetate, it is the strongest.

The effect of the substitution of polymerized monomers by vinyl acetate is different in relation to the glass transition temperatures of the elastomer phase of the graft polymers. The results provided in Table I show that the substitution of acrylonitrile by vinyl acetate compared to common ABS does not cause any variation of the glass transition temperature of the elastomer phase. However, the substitution of styrene and particularly of styrene and acrylonitrile by vinyl acetate in the mass ratio of 3 : 1 makes the glass transition temperature of the elastomer phase considerably decrease. For the substitution of styrene and acrylonitrile, the lowering is up to 9 K. Similar effects on the glass transition temperature of the elastomer phase of ABS have been observed and studied thoroughly for the ad-

dition of dinonyl adipate.⁹ In this case, the reason for the drop of the glass transition temperature is the concentration of the additive in the elastomer phase and its lower softening range (<183 K). However, the drop of the glass transition temperatures of the elastomer phase in the substitution of styrene or styrene and acrylonitrile might be attributed to a changed graft structure and, consequently, to a better coupling of the rigid phase to the elastomer phase. Because of the different expansion coefficients of the two phases, the soft phase is necessarily dilated during cooling and subjected to a rising isotropic tensile stress. Thus, the main relaxation range of the rubber in the graft polymer is shifted toward lower temperatures as compared to pure rubber. This causes a decrease of the glass transition temperature.¹⁰ Also, this explains the different impact and notched impact strengths observed with the graft polymers. So, in case of substitution of only styrene by vinyl acetate, the larger modulus difference between elastomer and rigid phase affected by the decrease of the glass transition temperature of the elastomer phase and the matrix flow improved by vinyl acetate as well as the formation of shear bands rather than craze formation causes an increased fracture toughness of the graft polymers.¹¹

Obviously, in the substitution of styrene and acrylonitrile by vinyl acetate, the effects resulting from the decrease of the glass transition temperatures of elastomer and rigid phases largely compensate for the lower flow of the matrix in the sole styrene substitution. Thus, these effects bring about only a small increase of impact strength and notched impact strength. If acrylonitrile is substituted by vinyl acetate, the difference between the glass transition temperatures, and, thus, the modulus difference of the two phases as well as the flow of the matrix, is

Table I Glass Transition Temperatures (T_g) of the Graft Polymers for the Substitution of Styrene (ST) or Acrylonitrile (AN) by Vinyl Acetate

Vinyl Acetate Content in the Polymerized Monomer Mixture (% wt)	Monomer Substituted	T_g of the Rigid Phase (K)	T_g of the Elastomer Phase (K)
—	—	378.5	195
3.2	ST	378	192
3.8	ST : AN = 3 : 1	376	186
2.2	AN	372	195

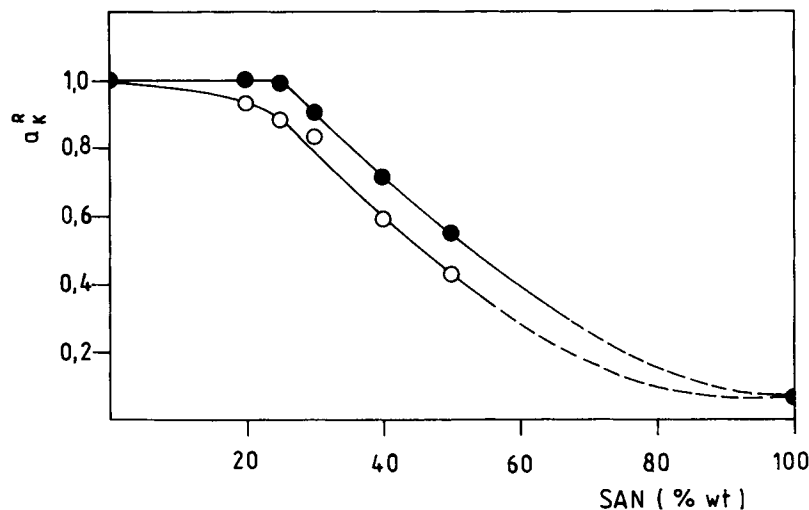


Figure 6 Dependence of the relative notched impact strength (a_K^R) on the composition of the polymer mixture consisting of graft polymer and SAN: (●) graft polymer of styrene, acrylonitrile, and vinyl acetate onto polybutadiene; (○) graft polymer of styrene and acrylonitrile onto polybutadiene.

smaller as against styrene substitution. This causes substantially poorer fracture toughness.

Properties of Blended Graft Polymers

Among the blends of graft polymers of styrene, acrylonitrile, and vinyl acetate on polybutadiene, the styrene/acrylonitrile copolymer blend is of particular interest.¹²

The results of blending a graft polymer of styrene and acrylonitrile on polybutadiene with a styrene/acrylonitrile copolymer (SAN) that has an acrylonitrile content of 29% wt are shown in Figures 6–8. In the polymerized monomer mixture of the graft polymer, 2.7% wt of styrene was substituted by vinyl acetate. The polymer mixture contains up to 50% wt of SAN.

Figure 6 indicates the dependence of the notched impact strength on the composition of the polymer mixture. The notched impact strength of the graft polymer/SAN mixture is compared with that of the ABS in the ABS/SAN mixture that has been prepared under similar conditions without using vinyl acetate. For the sake of clarity, the relative notched impact strength is plotted as the quotient of the current notched impact strength of the polymer mixture over the notched impact strength of the pure ABS test piece. Even with increasing SAN quantities in the polymer mixture by use of the graft polymers of styrene, acrylonitrile, and vinyl acetate on polybutadiene, the products formed show considerably

higher notched impact strengths in contrast to common ABS.

The bending strength (Fig. 7) and the tensile strength (Fig. 8) are in some degree lower in comparison to the blends with common ABS. They in-

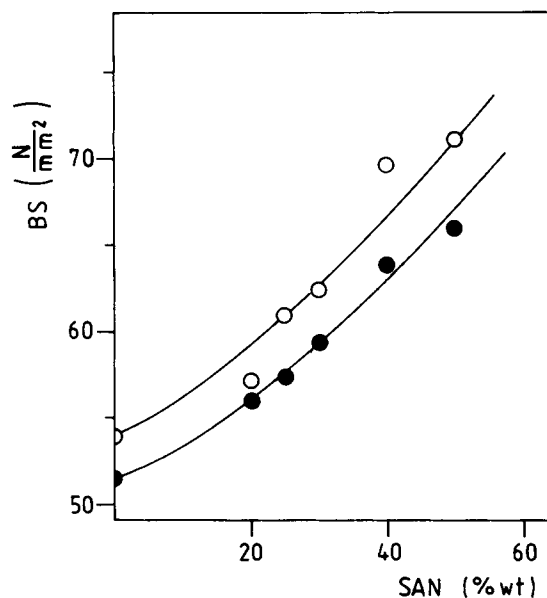


Figure 7 Dependence of the bending strength (BS) on the composition of the polymer mixture consisting of graft polymer and SAN: (●) graft polymer of styrene, acrylonitrile, and vinyl acetate onto polybutadiene; (○) graft polymer of styrene and acrylonitrile onto polybutadiene.

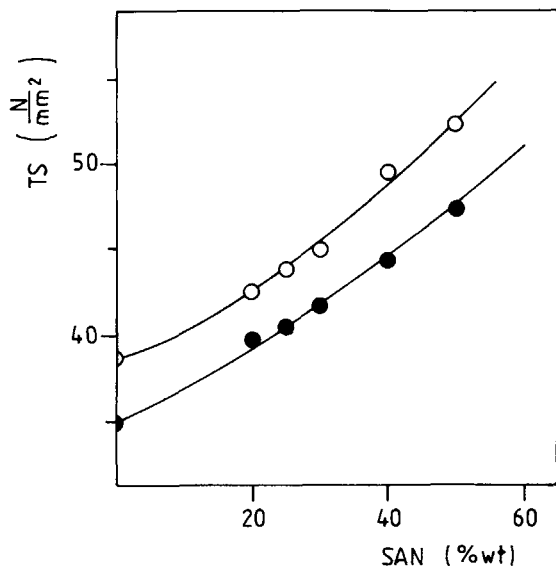


Figure 8 Dependence of the tensile strength (TS) on the composition of the polymer mixture consisting of graft polymer and SAN: (●) graft polymer of styrene, acrylonitrile, and vinyl acetate onto polybutadiene; (○) graft polymer of styrene and acrylonitrile onto polybutadiene.

crease, however, with rising SAN quantity in the polymer mixture as they do for ABS/SAN blends analogously.

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Received August 23, 1990

Accepted July 11, 1990