

Modification of Poly(styrene) by Reactive Blending with Nitrified Rubber

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ABSTRACT: A possible way to obtain modified poly(styrene) (PS) with a new complex of properties: 2–3 times higher impact resistance in a combination with significantly increased tensile strength and bending strength, 6–8 times higher flowability and strongly increased adhesion is described here. It is established that the modified PS new properties complex is a result from an elastification, nitrification, structure modification, and "critical" phenomena in the two component system studied. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 638–645, 2001

Key words: poly(styrene); nitrified rubber; reactive blending; modified poly(styrene) with a new complex of properties

INTRODUCTION

There are a lot of commercial poly(styrene) (PS) grades but they cannot satisfy all specific requirements of all possible application fields. This motivates the development of new PS modifiers that, on the other hand, hide the potential possibility for the creation of new polymer compositions by blending with different polymers immiscible with the nonmodified PS. The reinforcement of the PS is usually made with elastomers, including the thermoplastic one.^{1–7} There are a lot of reinforcement theories but none of them explains fully this phenomenon. Nowadays it is known that the reinforcing effect depends on a lot of factors: the elastomer particles both the size and distance, the mixing conditions, the amount and degree of crosslinking of the elastomer, the adhesion between the reinforcing elastomer and PS, the thickness, structure, and properties of the interface layer, etc.^{8–12} One approach to overcome the instability of the phase morphology and poor adhesion at the interface due to the poor compati-

bility is to carry out reactive processing including *in situ* chemical reactions between components of the blend.¹³

Low nitrified elastomers are crosslinked, but are still high elastic products that contain significant amount of polar groups as well as unstable bounded nitro groups. The last one stipulates their chemical activity. These properties make them very suitable for reinforcing of brittle plastomers, because the interface interaction between the plastic matrix and rubber particles could be easily regulated by a change in the degree of rubber nitrification. Therefore our experiments are pointed at reactive blending of PS with nitrified rubber.

EXPERIMENTAL

Our experiments were carried out with polystyrene, Bustrene K-525, (Chemical Combine Nephtochim, Bulgaria), and nitrified styrene-butadiene rubber (NSBR), containing 0.5–2.3 wt % nitrogen, obtained as described in ref. 14. The reactive blending was performed on a lab rolls at a temperature of 378 ± 5 K in air.

Tensile and bending tests (before and after aging) were carried out on Instron TT-DM (USA) and the impact resistance on Sharp method according to the corresponding ISO standards.

The melt flow index was estimated according to ASTM-D-1238-57T at a constant $P = 50$ N and a temperature of 443 and 463 K using an IIRT-10 (Russia) apparatus; the kinematic viscosity, according to ASTM-D-445 at a temperature of 298 ± 0.1 K in toluene; the intrinsic viscosity, with a Bishoff viscosimeter at a temperature of 303 ± 0.1 K in toluene.

The light permeability was measured with a spectrophotometer ZV-type (Germany) at $\lambda = 693$ nm.

The adhesion was measured according to the thermoplastic adhesives requirements.¹⁵

The thermomechanical tests were performed with Kargin thermomechanical balance at a constant loading of 10^6 N/m² and a heating rate of 1 K/min.¹⁶

The dielectric parameters: specific volume electric resistance ρ_v , was measured using "Teraometer IS1" apparatus and the dielectric constant ϵ using an a. c. bridge 551, type "MIE" at a frequency of 1000 Hz.

X-ray analysis was made in the angle region of 2° – 30° , using "TuR-M-61" (Germany) apparatus with filtrated CuK_α irradiation. The electron micrographs were taken from fracture surfaces by the two-stage replica technique, using a Philips transmission microscope model EM 400. The samples were prefrozen in liquid nitrogen before breaking.

The IR spectra were taken down from tablets with KBr using IR-10 apparatus (Germany).

RESULTS AND DISCUSSION

Mechanical Parameters

Interesting changes in the basic mechanical parameters of the modified PS are observed as evident from Figure 1. The comparison of curves I–IV shows that the higher the rubber nitrification degree is, the higher mechanical parameters are. This is due to the stronger interaction and better compatibility of PS with the highly nitrified SBR as evident from Figure 2. The light permeability increases with increase of the rubber nitrification degree, indicating in this way the bettering of the compatibility with the increase of the nitrification degree of the rubber.

In all cases the maximum of the corresponding curve is the region of the low NSBR concentrations—under 1 phr. This course of the curves cannot be explained only with a reinforcing effect of the rubber particles. The 2–3 times increase of the impact resistance with simultaneously slight increase of the tensile and bending strength is also difficult for explanation from the point of view of the known reinforcement theories.

Rheological Characteristics

The flowability index increases sharply when small amounts of NSBR are added - under 1 phr and after that decreases (Fig. 3). Such effect of accelerated flowing could not be explained with a structural plastification in presence of small amounts of NSBR and molecular plastification after that. The NSBR has been crosslinked during the nitrification and its blending with PS was made in a solid phase. This means that a blending on molecular level is impossible.

The PS and NSBR blending on rolls is a mechanical-chemical process due to which changes in the molecular mass of the modifies could arise. Our results from estimating the intrinsic viscosity used as an indirect measure of the molecular mass are presented in Figure 4. The intrinsic viscosity increase at 0.4–1.2 phr NSBR is in correspondence with the mechanical parameters increase in the same concentration region but it cannot explain the strongly improved flowability of these modifies. The rheological characteristics' dependence on the NSBR concentration is another indication of the complicated NSBR action mechanism.

Adhesion

The bringing of polar —CO, —OH, —NO₂, and —ONO₂ groups in the PS during the blending with NSBR, accompanied with increased flowability, gives reason to expect an improved adhesion of the modified PS to polar substrates. As evident from Figure 5, the increase of NSBR amount up to 1 phr leads to sharp increase of the adhesion due to a simultaneous increase of the polar groups' content and the flowability of the modifies. The adhesion continues the improvement after that, slightly due to the lower flowability of the modifies.

From the same Figure 5, it is also evident that the adhesion tested at a hot-melt temperature of 463 K (curves I–III) or 473 K (curves

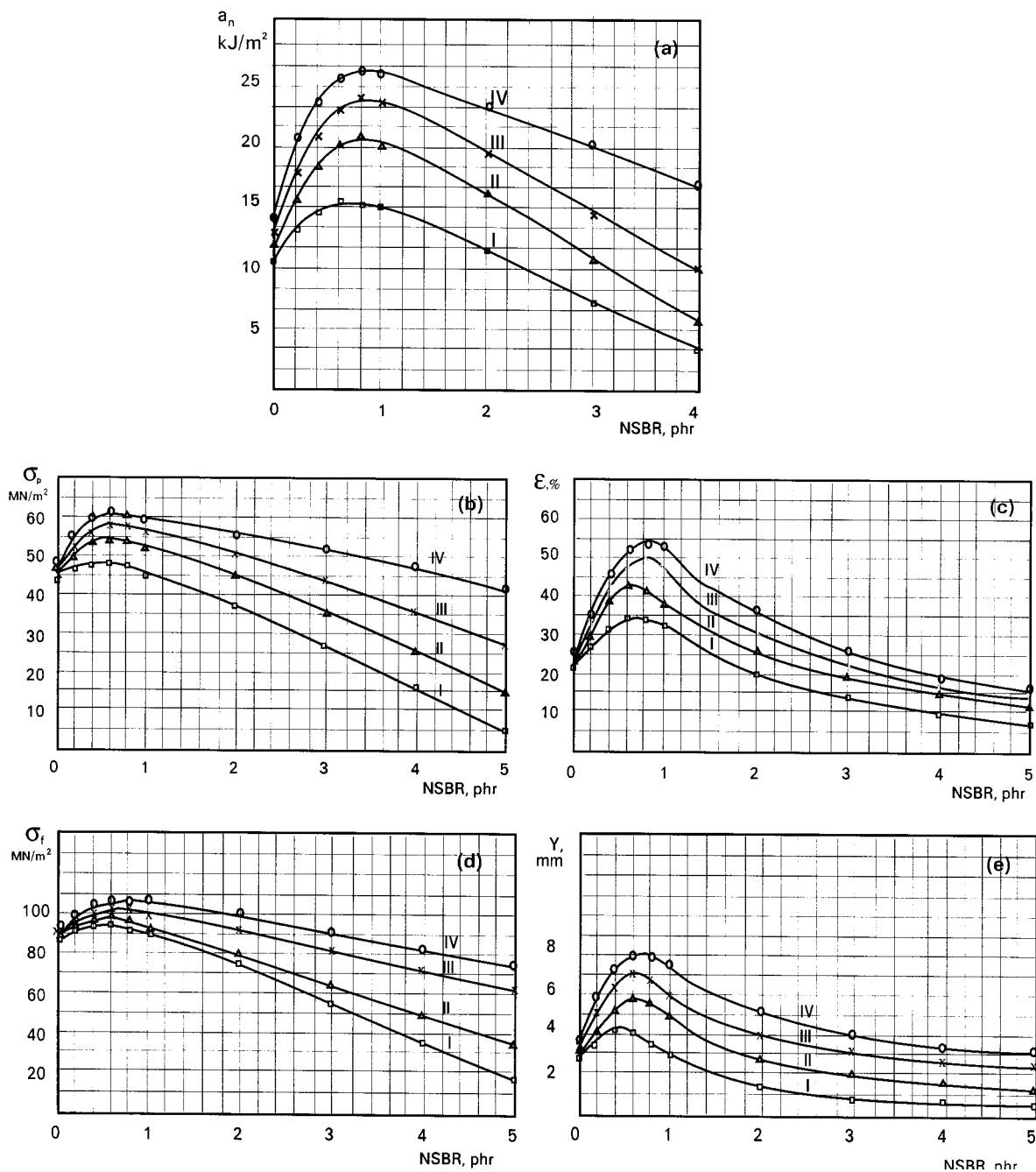


Figure 1 The mechanical parameters: impact resistance a_n (a), tensile strength σ_p (b), elongation at break ϵ (c), bending strength σ_f (d), and bending strain at break γ (e) as a function of the NSBR amount and degree of its nitrification. Nitrogen content in NSBR (wt %): (I) 0.5, (II) 1.3, (III) 1.8, and (IV) 2.3.

I'–III') is as high as the degree of nitrification of NSBR is.

Comparative Characteristic of the Modified and Some Commercial Types of PS

For fuller characterization of the modified polystyrene (MPS) with optimal properties, we esti-

mated some of its other parameters: aging resistance, impact resistance at low and high temperatures, specific volume resistance ρ_v , and dielectric constant ϵ . A comparison was made with nonmodified PS, Bustren K-525 (Bulgaria), and impact PS, Bustren U-825 (Bulgaria), available as commercial products.

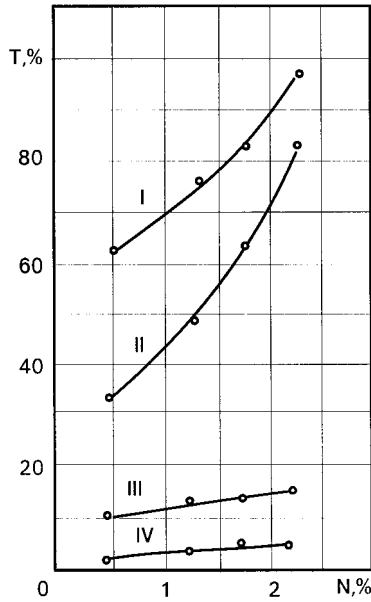


Figure 2 Optical transparency of the modified PS as a function of the degree of nitrification and the added NSBR amount (phr): (I) 0.5, (II) 1.0, (III) 2.0, and (IV) 5.0.

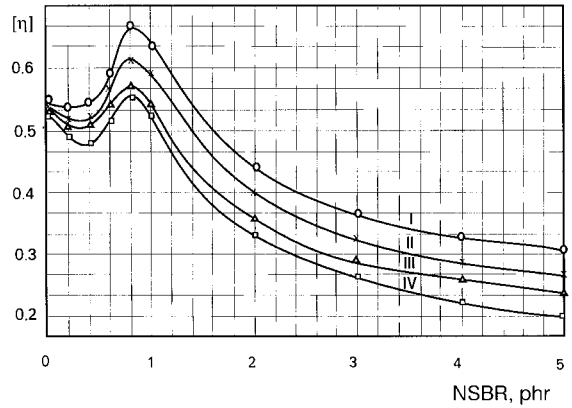


Figure 4 The intrinsic viscosity of modified PS as a function of the amount of NSBR and the degree of its nitrification. Nitrogen content in NSBR (wt %): (I) 0.5, (II) 1.3, (III) 1.8, and (IV) 2.3.

From Table I it is evident that the newly developed material surpasses the starting and the impact PS on tensile strength and flowability. It

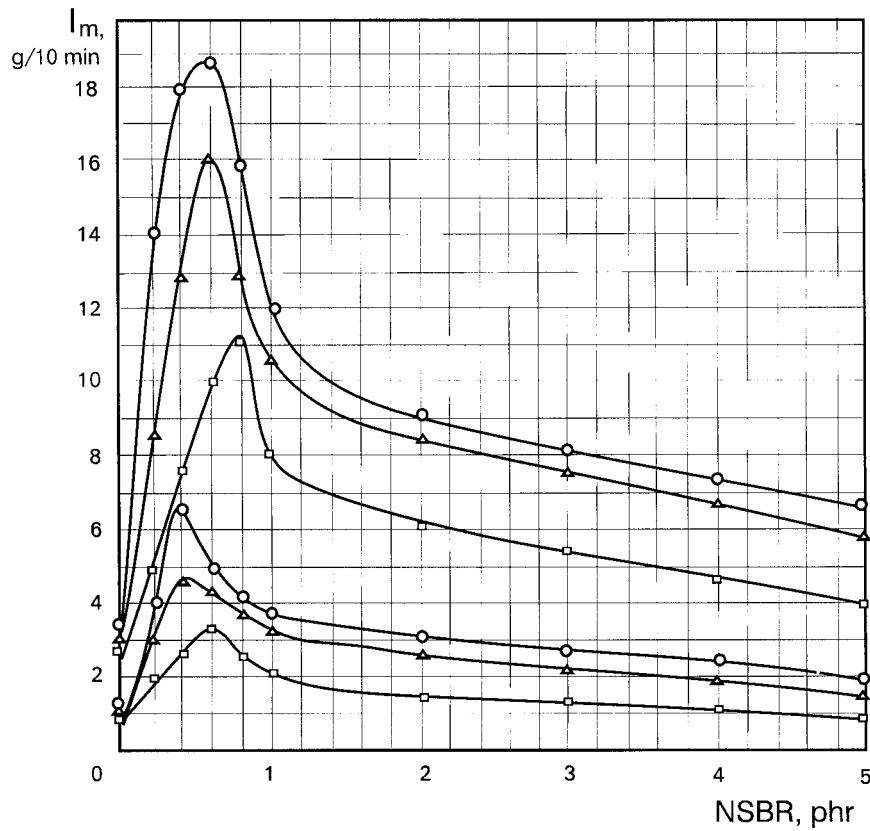


Figure 3 The flowability index of modified PS—at a temperature of 443 K (curves I–III) and 463 K (curves I'–III')—as a function of the amount of NSBR and the degree of its nitrification. Nitrogen content in NSBR (wt %): (curves I, I') 0.5, (curves II, II') 1.3, and (curves III, III') 2.3.

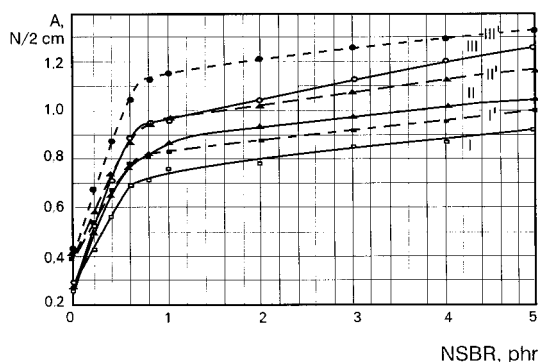


Figure 5 Adhesion in the system artificial sole-leather/artificial sole-leather at a temperature of the hot-melt 463 K (I–III) and 473 K (I'–III') as a function of the amount of NSBR and the degree of its nitrification. Nitrogen content in NSBR (wt %): (I, I') 0.5, (II, II') 1.3, and (III, III') 2.3.

does not differ significantly from the starting PS on Brinell hardness, Vica thermal resistance, and dielectric parameters. In impact resistance the modified PS is between the two commercial products, but after atmosphere aging it approaches the impact PS due to its better aging resistance. The improved adhesion to polar materials is a specific property of the modified PS.

Probable Mechanism of NSBR Action

The sharp increase (reaching to 2.5 times) of the impact resistance of PS by adding of small

amounts NSBR—under 1 phr—accompanied with a sharp increase of the flowability index (5–8 times) and a significant increase of the tensile and bending strength (25–30%) is an indication for a complicated mechanism of nitrified rubber action, including not only elastification but also other probable processes like chemical interaction, structural modification, etc.

The presence of —OH, —CO, —NO₂, and —ONO₂ groups in the nitrified rubber used in our experiments was proven by means of IR spectroscopy. As evident from Figure 6, in the spectrum of NSBR the following absorption peaks appear: at 1700 cm⁻¹ (ν CO); at 1550 cm⁻¹ (ν_{as} N=O) and at 1360 cm⁻¹ (ν_s N=O); 1640 cm⁻¹ (ν_{as} ONO₂) and 1280 cm⁻¹ (ν_s ONO₂); weak bands at 1040 and 1090 cm⁻¹ characteristic of p-substitute aromatic rings; a doublet at 860 cm⁻¹ indicating the presence of nitrogen groups at p place of benzene ring; increased general adsorption in the range of 3600–3200 cm⁻¹ that proves the presence of hydroxyl groups.¹⁷

Some of them are linked unstably and split off easily in the form of nitrogen oxides hydrolyzing to a nitrogen acid in presence of moisture. The nitrogen oxides and nitrogen acid could nitrificate the PS under the soft conditions of our experiments, most probably via an attachment of a nitrogen group to the place of destruction during the blending on rolls or a replacement of a ter-

Table I Comparative Characteristic of Some Types PS

Parameter	Materials		
	PS Bustren K-525	PS Bustren U-825	MPS (0.8 phr NSBR, 2.3 wt % Nitrogen)
Charpy impact resistance (kJ/m ²)			
At -20°C	9	70	23
+20°C	10	75	25
+40°C	11	79	25 ^a
After atmosphere aging,			
6 months	11	73	25 ^a
12 months	9	35	24
24 months	7	29	23
Tensile strength (MN/m ²)	44.0	23.5	60.2
Bending strength (MN/m ²)	84.0	46.1	102.6
Brinell hardness (MN/m ²)	210	160	207
Vica thermal resistance (°C)	99.5	97.1	98.5
Flowability at 190°C (g/min)	2.3	2.0	11.1
Specific volume resistance ρ_v , (10 ¹³ Ω · m)	19	10	4.3
Dielectric constant, ϵ 10 ³	2.42	2.59	2.79
Adhesion (MN/2 cm)	0.37	—	1.15

^a Twenty percent of samples were not broken.

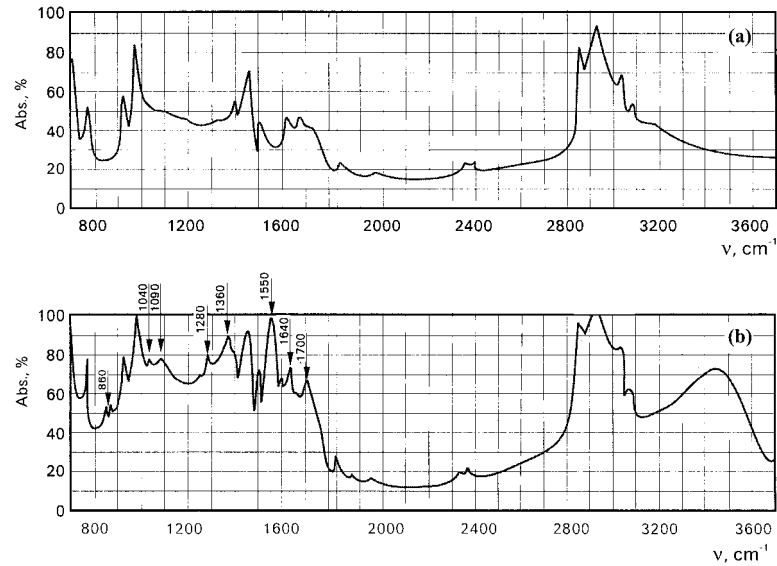


Figure 6 IR spectra of a non-nitrified (1) and nitrified SBR (2) containing 2.3 wt % nitrogen.

tiary hydrogen atom in the backbone PS chain.¹⁸ Although the nitrification of PS by NSBR was not proven directly, there are a number of facts confirming indirectly but unambiguously such an interaction: the blending heat effect (of about 20–30 K, measured by a thermocouple); the typical yellow color for nitrogen products of the modifies as well as the compatibility of PS and NSBR improvement with the increase the degree of nitrification of the latter.

A comparative electron microscopy observation showed indisputably that the adding of NSBR to the PS leads to a significant change of its primary globular structure. In all modifies we observed

chaotic suited “capsules” centered with NSBR on the background of the globular structure of the non-modified PS [Figure 7(a, b)]. This arrangement in capsules is in the frame of the amorphous phase state as proved by X-ray analysis.

The morphology of the modified PS gives us reason to suggest the existence of three phases in the studied two-component system. This suggestion of ours was verified by thermomechanical investigation. In Figure 8 is presented a thermomechanical curve of PS modified with 1 phr NSBR, containing 1.8 wt % nitrogen. There are two deflections on this curve corresponding to glass temperatures of two phases: at a tem-

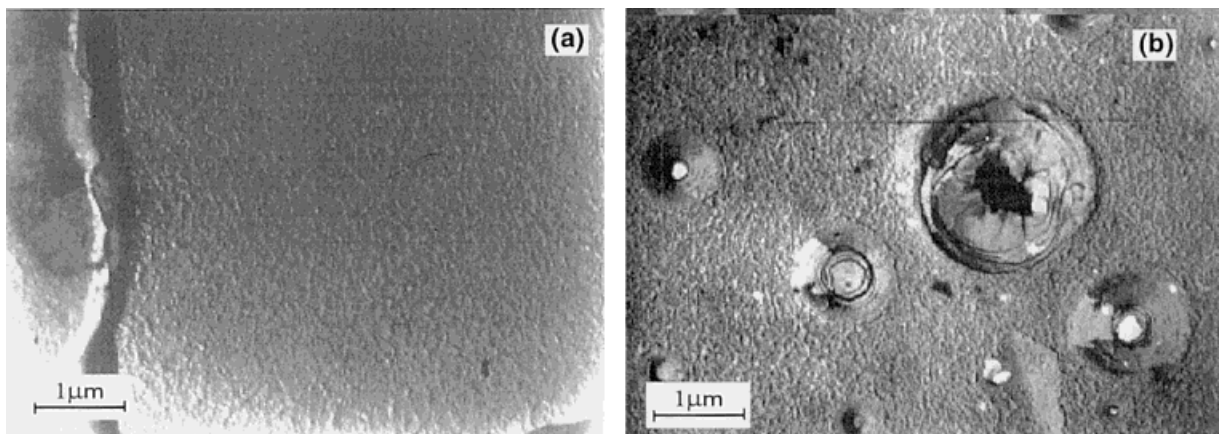


Figure 7 Electron microscopy photographs of two-step replicas from nonmodified (a) and NSBR modified (b) PS.

perature of 373 K corresponding to a T_g of the starting PS and at 363 K corresponding to a new, third phase in our polymer system (T_g of NSBR is in the range of the minus temperatures).

A presence of three phases in some two-component polymer systems has been observed by other authors, which suggests that the appearance of the third intermediate phase is a result of a reciprocal diffusion of the both polymers.¹⁹ In our case, the appearance of a third intermediate phase could be a result of a reciprocal diffusion and a chemical interaction of PS and NSBR.

From a point of view of the elastification, nitrification, and structural modification, it is difficult to explain the fact of simultaneously sharp increase of the flowability index and the intrinsic viscosity (irrespective of the molecular mass of the modified PS) in the range of the low NSBR concentrations—of about 0.8–1 phr. It could not be a result of a transition from structural to molecular plastification because our modifier is a crosslinked rubber. Kulesnev and co-workers²⁰ ascribe such phenomena to a critical state of the polymer blends just before their layering during the change of the ratio between the compounding polymers. The entire polymer system has special structure in the “critical” region providing for the sharp increase of its flowability and other properties. The polymer blends in a critical state are characterized by some slight turbidity whereas the homogeneous blends are fully transparent and the layered blends are fully nontransparent. In Figure 9 is shown the optical transparency of modified PS as a function of the added amount NSBR. It is evident that it decreases sharply in the region of a sharp change of a lot of parameters of the modified PS and this could be accepted as an indication of layering of our polymer blend in the NSBR concentration region of 0.8–1 phr.

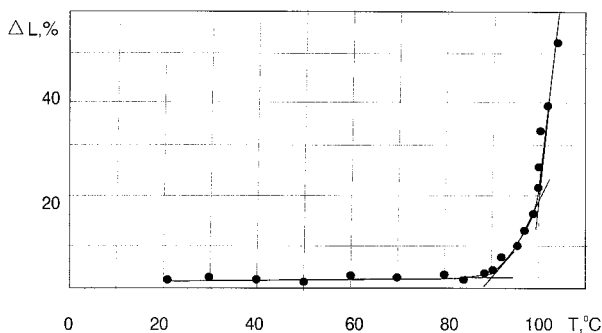


Figure 8 Thermomechanical curve of PS modified with 1 phr NSBR containing 1.8 wt % nitrogen.

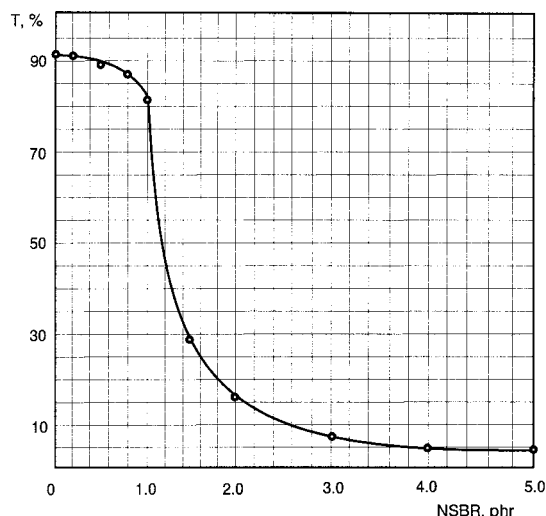


Figure 9 Optical transparency of the modified PS as a function of the added amount NSBR containing 2.3 wt % nitrogen.

CONCLUSIONS

The blending of PS and nitrified rubber is a possible way to obtain modifiates with a new complex of properties: sharply increased impact resistance (about 2.5 times) and flowability (about 5–8 times) combined with significantly increased tensile and bending strength (about 25–30%), improved aging resistance, and adhesion to polar materials, good dielectric parameters, and heat resistance.

The PS and nitrified rubber blending is reactive and leads to the formation of an intermediate phase of nitrified PS acting as compatibilizer in this two-component polymer system.

The modification of the starting PS properties is due to an elastification, nitriation, and structure modification effect of the nitrified rubber as well as critical phenomena in these two-component systems, based on the change of the interface forces in the studied polymer blend as a result of the change in the nitriation degree of the rubber.

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