Modification of Natural Rubber Latex. III. Natural Rubber–Polystyrene Composite Latexes Synthesized Using Azobisisobutyronitrile as Initiator

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SYNOPSIS

Materials which may be classified as interpenetrating polymer networks have been prepared by the *in situ* polymerization of styrene in natural rubber latex using azobisisobutyronitrile (AIBN) as the initiator. The resulting materials have been characterized by electron microscopy, Soxhlet extraction coupled with proton nuclear magnetic resonance spectroscopy, dynamic mechanical analysis, and stress–strain analysis. The styrene polymerizes within the natural rubber latex particles to give a relatively fine phase-separated morphology with some evidence for a limited degree of segmental mixing. Moreover, it is clear that AIBN, despite what is stated in the literature, does lead to some grafting of polystyrene, and, in addition, causes significant degradation of the natural rubber molecules when the styrene content is low.

INTRODUCTION

Natural rubber, *cis*-polyisoprene, has an attractive range of physical properties and the backbone unsaturation makes it readily chemically modifiable to yield an even more diverse range. Among the modifications reported include ene reactions[1,2] and epoxidation. Modification of natural rubber (NR) in the original latex form has some obvious advantages. In the first two papers,[3,4] in this series the preparation and properties of latex interpenetrating polymer networks (IPN) and semi-IPNs were reported. The polymers used as the second component were polystyrene (PS) and poly(methyl methacrylate) (PMMA), which had been polymerized using a tetraethylene pentamine activated hydroperoxide initiator system. The resulting materials had a rather coarse morphology, but interesting property modifications were obtained without destabilization of the original latex. With a water-soluble activator and an oil-soluble hydroperoxide, the locus of polymerization was believed to be at the swollen particle interface, but the method of polymerization was such that in the case of the NR–PS materials some polymerization of the styrene (S) droplets also occurred. It was found that the hydroperoxide was not only polymerizing the methyl methacrylate or the S, but was also leading to the grafting of PMMA or PS chains to the NR. In an ideal IPN the two networks are not chemically attached.

Therefore, an initiator which does not produce grafting would be desirable. Azobisisobutyronitrile (AIBN) has been found[5,6] to be a particularly poor initiator in promoting the grafting of S onto NR. This is believed to be the result of its inability to abstract hydrogen atoms from the NR backbone.

In this paper the preparation of NR–PS composite latex particles using AIBN as the initiator is reported and the properties of these materials are discussed.

EXPERIMENTAL

Materials

Two NR latices were used. They were a centrifuged NR latex with a solids content of ca. 60 wt % and a

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precrosslinked NR latex of the same solids content, but which had been exposed to 5 m rad of ^{60}Co radiation. Use of the Flory–Rehner equation[7] yielded an average molecular weight between crosslinks of 55,000 g/mol for this rubber.

The styrene (BDH Ltd.) was destabilized in the conventional way by washing with a 5% aqueous solution of NaOH and then with distilled water until neutral. The crosslinking agent, divinyl benzene (BDH Ltd.), was similarly treated. The initiator, AIBN, and the stabilizer, oleic acid, were both supplied by BDH Ltd.

Polymerization

NR latex (250 g) was charged to a polymer reactor along with 70.5 g of a 2% NH_4OH solution and was deoxygenated by bubbling nitrogen for at least 30 min through the diluted, but still stable, latex. If necessary, ammonia was added to maintain the pH of the latex above 8.5. The nitrogen flow rate was then reduced to a low level and the temperature increased to 75°C before the addition, dropwise over 15 min, of the styrene monomer, the crosslinker, if present, the stabilizer at 0.5, and the AIBN at 0.3 wt % rubber, respectively. When this addition was complete, a further 15 min were allowed for transport from the droplet to the particle phase to occur. The reaction was then allowed to proceed for 24 h under continuous stirring to complete the polymerization. Samples were taken at intervals to establish, gravimetrically, the degree of conversion of monomer to polymer. To form sheet for subsequent mechanical tests, the latex was cast at room temperature in open glass trays to give a final opaque sheet thickness of ca. 1.5 mm. Once dry, the sheet was removed from the tray and transferred to a vacuum oven at 40°C to remove any last traces of monomer that may be present. The dried sheet was then leached in deionised water to remove any water-soluble impurities from the rubber. The leaching process took three days, during which period the water was changed several times. The sheet was then returned to the vacuum oven until it was thoroughly dry.

Techniques

(a) Sol/gel ratio determination. Soxhlet extractions were performed on pieces (ca. 0.5 g) of the cast sheets. A two-solvent process involving, first, petroleum ether, an NR solvent, and then THF, a solvent for both components, was employed. Relatively low boiling liquids were chosen to minimize the risk of

inducing degradation of the NR during the 24 h extraction periods. These extractions were for the same reason performed under nitrogen.

(b) Analysis of sol fractions. The sol fractions were analyzed by ^{1}H-NMR spectroscopy using a Jeol FX-100 100 MHz instrument.

(c) Mechanical tests. Dynamic mechanical data were obtained with a Polymer Laboratories DMTA apparatus using both the bending and the shear modes. The instrument was operated at a frequency of 10 Hz and at a heating rate of 2°C/min. Tensile testing on dumbbell testpieces was conducted using a microprocessor-based Nene 3000 tensometer controlled from an Amstrad 1512 computer. The test were performed at 20°C and at a strain rate of 20 mm/min. This tensometer was also used for the hysteresis measurements.

(d) Electron microscopy. Transmission electron micrographs were obtained with a model HU-11B Hitachi electron microscope. OsO_4 was used as a preferential stain for the NR component.

RESULTS AND DISCUSSION

Four IPN materials were prepared in this study (Table I). One started with the precrosslinked NR latex and the remaining three were synthesised from the uncrosslinked latex. The sample codes indicate the composition by weight and the number in brackets is the mole percentage of the crosslinker, divinyl benzene, with respect to S. The sample coded 100NR–0PS has undergone the full polymerization process, but in the absence of S. Because of the possibility of crosslinking the natural rubber while polymerizing the S, this material, rather than the received NR latex, was taken as the standard for comparison. The precrosslinked rubber is coded NR(P).

Conversion of monomer to polymer was virtually 100% in all cases and the long-term latex stability was reasonable. Film-formation was good and no film cracking[3,4] was apparent. The cast sheets were

Table I Composition Details

Sample	NR (wt %)	PS (wt %)
100NR–0PS	100	0
90NR–10PS(1.0)	90	10
80NR–20PS(1.0)	80	20
80NR(P)–20PS(1.0)	80	20
70NR–30PS(1.0)	70	30

Table II Weight Percentage of Soluble Material Extracted by the Indicated Solvents

Sample	Pet. Ether (wt %)	THF (wt %)	Total (wt %)
80NR–20PS(1.0)	14.3	5.1	19.4

transparent, but slightly darker in color than an equivalent NR sheet. The control (100NR–0PS) and the 90NR–10PS (1.0) material were very soft and tacky.

Particularly the softer members of this group of materials were difficult to microtome. Nonetheless, micrographs were obtained. The materials were phase-separated with light PS domains covering a range of sizes many of which were in the 50 nm region, but some were significantly larger with a typical diameter of about 360 nm. The original NR latex had an average particle diameter of 514 nm. It was concluded that the S was polymerized virtually completely within NR latex particles. This yields a markedly finer morphology than found for the NR latex-based composite particles prepared[3,4] using the *tert*-butylhydroperoxide–tetraethylene pentamine system. This is to be expected for an oil-soluble initiator. The enhanced film-forming behavior is directly attributable to this finer morphology.

A very limited amount of soxhlet extraction data are presented in Tables II and III. The amount of material extracted from this composition is much higher than for a compositionally identical material made using the *tert*-butylhydroperoxide–tetraethylene pentamine initiator system. In that case[3] only 3.1 wt % sol, in total, was found. The composition (Table III) of the sol as determined by ^{1}H-NMR spectroscopy was the same for both solvents, high in NR. The number average molecular weight of the sol was found, by gel permeation chromatography, to be ca. 50,000 and it had a polydispersity index of ca. 5.4. Both this increased levels of extraction compared with the already mentioned sample and the fact that the 100NR–0PS and the 90NR–10PS (1.0) materials were tacky indicates that this initiator is

Table III Composition of the Sol Fractions

Sample	Solvent	PS (mol %)	NR (mol %)
80NR–20PS(1.0)	Pet. ether	5	95
80NR–20PS(1.0)	THF	6	94

Table IV Dynamic Mechanical Data (10 Hz) for the NR Transition Region

Sample	T_g (°C)	Half-Peak Width (°C)
CNRL791[a]	−36	13
100NR–0PS	−36	12
90NR–10PS(1.0)	−36	12
80NR–20PS(1.0)	−36	14
80NR(P)–20PS(1.0)	−37	13
70NR–30PS(1.0)	−36	19

[a] As-received natural rubber.

causing degradation of the NR, but this becomes less significant as the amount of S present increases.

Table IV and Figure 1 show the NR glass transition (T_g) region for these materials. There is no shift in the peak positions, but the 70NR–30PS (1.0) sample has a somewhat broader transition indicative of a slight degree of enforced mixing. Table V and Figure 2 show the corresponding data for the PS T_g region. These data were obtained in the shear mode. At PS contents greater than 10% by weight the PS transition is well resolved, as is the β-transition[8] starting at around 67°C. There are significant shifts to lower temperatures of the T_g's of both the 80NR(P)–20PS(1.0) and the 70NR–30PS(1.0) blends. In the former material, the effect of pre-crosslinking the NR latex has been some enforced mixing of the two polymers. This is in agreement[9] with the findings in other work. These indicate that the tightness of the first-formed network in an IPN has a very influential effect on the morphology. The T_g shift shown by the 70NR–30PS(1.0) material
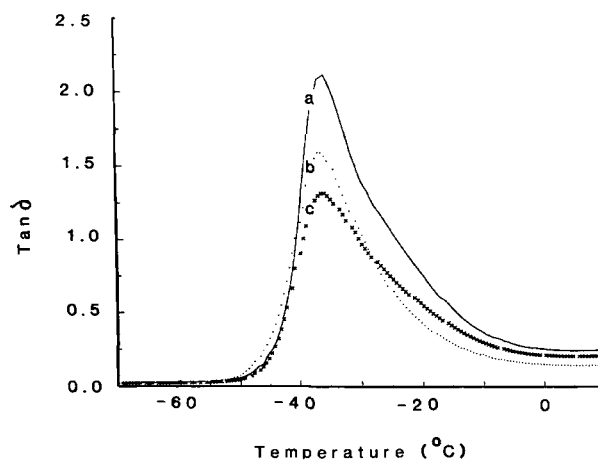

Figure 1 Tan δ–temperature plots (10 Hz; bending mode) of (a) the 90NR–10PS(1.0), (b) the 80NR–20PS(1.0), and (c) the 70NR–30PS(1.0) materials.

Table V Dynamic Mechanical Data (10 Hz) for the PS Transition Region

Sample	T_g (°C)
90NR–10PS(1.0)	—
80NR–20PS(1.0)	135
80NR(P)–20PS(1.0)	126
70NR–30PS(1.0)	128

confirms that there is some enforced mixing in this sample.

The stress–strain data for these materials are shown in Table VI and Figures 3 and 4. Comparison of the as received NR sample with the precrosslinked material (Table VI) shows the expected benefits of crosslinking, but quite unexpected was the dramatic loss in tensile properties shown by especially the 100NR–0PS material, but also by the 90NR–10PS blend. As mentioned earlier, both these materials were tacky to the touch. It is clear that AIBN is causing degradation of the NR. Increasing the PS content to 20 and 30 wt % results in significant reinforcement with strain hardening occurring at much lower strains than was the case for the NR which was not precrosslinked. The 80NR(P)– 20PS(1.0) material shows (Fig. 4) by far the best tensile properties in this set of materials with both a high tensile strength and a substantially unreduced elongation to break. This indicates that when there is a significant level of crosslinking in the NR, and possibly when the S content is greater than 10% by weight, the AIBN-induced degradation is not markedly dileterious.
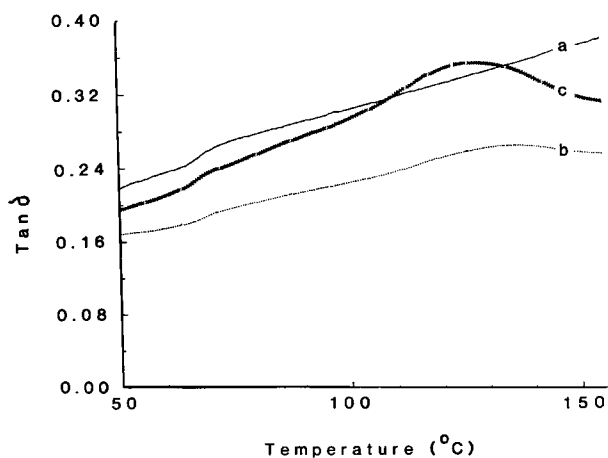
Table VI Stress–Strain Data

Sample	Initial Modulus (MPa)	Tensile Strength (MPa)	Elongation to Break (%)
CNRL791[a]	0.68	2.84	735
CNRL791(P)[b]	0.90	13.16	910
100NR–0PS	0.13	0.09	507
90NR–10PS(1.0)	0.50	0.30	435
80NR–20PS(1.0)	1.07	2.72	614
80NR(P)–20PS(1.0)	1.02	10.40	758
70NR–30PS(1.0)	1.08	3.55	618

[a] As-received natural rubber.
[b] As-received precrosslinked natural rubber.

The hysteresis loss data showed the expected decrease[10] on crosslinking the NR. However, the values for both materials containing 20 wt % of PS remained very low compared to the compositionally identical material prepared using the *tert*-butylhydroperoxide–tetraethylene pentamine initiator system. The presence of much smaller PS phases, and the consequent better film formation, is believed to be the reason for the dramatic improvement in hysteresis loss.

CONCLUSIONS

Although the mechanical properties of the IPNs produced with AIBN as the initiator of the second polymerization were not outstanding, some useful
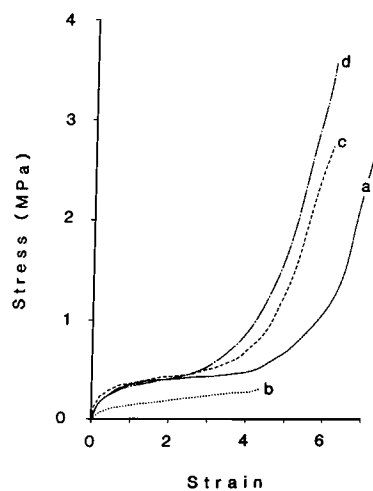

Figure 2 Tan δ–temperature plots (10 Hz; shear mode) of (a) the 90NR–10PS(1.0), (b) the 80NR–20PS(1.0), and (c) the 70NR–30PS(1.0) materials.

Figure 3 Stress–strain curves (20°C) of (a) the as-received NR, (b) the 90NR–10PS(1.0), (c) the 80NR–20PS(1.0), and (d) the 70NR–30PS(1.0) materials.
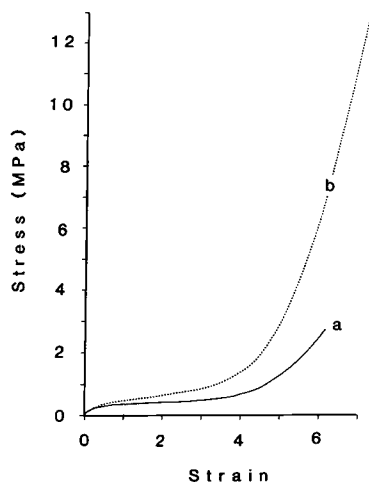
Figure 4 Stress–strain curves (20°C) of (a) the 80NR–20PS(1.0) and (b) the 80NR(P)–20PS(1.0) materials.

comments can be made about the use of AIBN as an oil-soluble initiator in the presence of NR.

First, it is widely claimed[5,6] that AIBN is a non-grafting initiator for diene rubbers. The soxhlet extraction and ^{1}H-NMR spectroscopy work reported in this paper indicate that some grafting does occur.

Second, it is clear that under the conditions of the polymerization used AIBN causes degradation of NR. Pchelintsev et al.[11] found that cis-1,4-polyisoprene in the presence of AIBN and oxygen experienced oxidative degradation of the NR backbone. He also showed that this degradation process occurred to a lesser extent in a nonoxidizing argon atmosphere. A mechanism was not proposed, but

his results are consistent with the findings from this study.

In the presence of the monomer the degradation process is in competition with polymerization and the consequences of degradation are less dramatic.

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