

Synthesis and Thermal Stability of Bitumen–Polymer Ionomers

R. ENGEL,^{1,*} A. VIDAL,^{1,†} E. PAPIRER,¹ and J. GROSMANGIN²

¹Centre de Recherches sur la Physico-Chimie des Surfaces Solides, 68200 Mulhouse, France, and

²Compagnie Française de Raffinage, 75739 Paris, Cedex 15, France

SYNOPSIS

Road bitumens, when combined with polymers such as styrene–butadiene–styrene (SBS) block copolymers, show improved mechanical properties. The corresponding blends, however, are thermodynamically unstable, and phase separation quickly occurs at higher temperatures. A solution is proposed for improving the thermal stability of these blends: It is based on the formation of reversible, ionic interactions between the bitumen and the SBS, thereby leading to a mixed, ionomeric network. Both compounds are first chemically modified by the grafting of carboxylic acid groups, then mixed, and, finally, the available acid groups are partially or totally neutralized by adding zinc acetate dihydrate to the blends. Comparison of the thermal stability of the resulting ionomeric blends with that of the untreated blends is discussed. The use of ion–ion interactions to enhance miscibility, which, for the first time, has been extended to bitumen–polymer systems, is shown to be a means of obtaining stable blends.

INTRODUCTION

Bitumens are widely used, especially as binders in road paving, because of their excellent adhesive properties and good resistance to weathering, chemical attack, or radiation. Under standard conditions of traffic and temperature, these materials usually show acceptable mechanical properties, but binders with higher performances are sometimes needed.

One way of improving the mechanical properties of road bitumens is to modify them with polymers, among which styrene–butadiene–styrene (SBS) block copolymers appear particularly well suited. A better flexibility of the modified bitumens at lower service temperatures (-25°C) and a reduced tendency to creep at higher (50°C) service temperatures have been reported,¹ as well as a limited increase in the hot-melt (160°C) viscosity, so conventional

processing of the binders remains possible. The highest degree of improvement reportedly is due to the presence of a continuous, elastomeric network that is swollen by the maltenes constituting the dispersive medium of the bitumen.² The building of such a network, possible only if the styrene/butadiene (S/B) ratio of the copolymer is not too high, results from a microphase separation in which PS domains act as physical crosslinks. Zenke³ extensively and critically reviewed the literature pertaining to the modification of road bitumens with various polymers.

Unfortunately, road bitumens and SBS do not form thermodynamically stable blends. Consequently, a phase separation occurs that is particularly quick at higher temperatures (blends usually are stored at 160°C). Demixing not only has adverse effects on mechanical and aging properties, but also severely impairs the spraying or pumping of bitumen–SBS blends.

Several ways of solving this problem have been investigated. They generally consist of modifying one or both constituents of the blend, either by physical means (addition of solid fine particles, sur-

* Present address: Laboratoire des Substances Macromoléculaires, Institut National des Sciences Appliquées (INSA), BP 8, 76131 Mont-Saint-Aignan, Cedex, France.

† To whom correspondence should be addressed.

face-active compounds, . . .) or by chemical means. In the latter case, various attempts have been reported:

1. *Adjustment of the bitumen composition.* Stable blends, of bitumen and either SBS or styrene-isoprene-styrene block copolymers, were obtained by adjusting the aromaticity and molecular mass of specific constituents of the bitumen¹; however, this method has drawbacks from the economical viewpoint since it may preclude the use of commercial bitumens;
2. *Grafting of macromolecules on the bitumen.*⁴ The authors reported that they could find no evidence of a chemical reaction between the polymers (among which a SBS copolymer) and bitumens selected;
3. *Addition of stabilizing agents to bitumen-polymer blends.*⁵⁻⁷ An increase in blend stability was claimed but no details about the chemical reactions involved were given.

The approach we followed consisted in synthesizing mixed, thermally stable bitumen-polymer networks, starting from blends of reactive polymer and reactive bitumen. Ionomeric networks were selected for this purpose. Ionomers are defined as organic, uncrosslinked polymers, carrying a low proportion (up to 15 mol %) of ionic, or ionizable, pendant groups, partially or totally neutralized with counterions.⁸⁻¹⁰ The term "asphalt ionomer" was coined by Ciplijauskas et al. to designate asphalts on which reactive groups (e.g., sulfonate groups) have been grafted and subsequently neutralized with various metal oxides.¹¹ An interesting feature of ionomers is that the ionic reticulation produced by the neutralization is reversible on heating and shearing. This reversibility allows the viscosity of ionomers to be decreased down to such a level that these materials can be processed.

Numerous papers have been published on the role of specific interactions in enhancing polymer-polymer miscibility. Smith et al.¹² investigated blends of polyethers and poly(carboxylic acid)s and concluded to the existence of H-bonds between ether and acid groups. Otocka and Eirich¹³ reported that ion-ion interactions were responsible for the formation of stable intermolecular pyridinium-carboxylate links within blends of butadiene-lithium methacrylate and butadiene-methyl(2-methyl 5-vinyl)-pyridinium iodide copolymers. Sulzberg and Cotter¹⁴ reported on electron transfer between electron-acceptor polyesters and electron-donor poly-

mers from acryliminodiethanols. More recently, Eisenberg et al.¹⁵ compatibilized polystyrene with either poly(ethyl acrylate) or polyisoprene by sulfonating the former polymer and copolymerizing the latter ones with 4-vinylpyridine. Compatibility reportedly was due to proton transfer between sulfonic acid and 4-vinylpyridine groups. Hara and Eisenberg¹⁶ were the first to investigate the possibility of enhancing the miscibility of poly(alkylene oxide)s and polystyrene through ion-dipole interaction: This was achieved by using a polystyrene ionomer, e.g., lithium methacrylate-styrene copolymer. A review on the use of ionic interactions to control miscibility in otherwise incompatible systems has recently been published.¹⁷ However, to the best of our knowledge, ionic interactions of the ion-ion type have not yet been used to stabilize bitumen-polymer blends.

In this article, we report the synthesis of new ionomeric blends, based on a road bitumen and a SBS copolymer, and discuss the morphological stability of these ionomers, as compared with nonionomeric blends of the same materials ("regular blends").

The first step of this synthesis was to graft carboxylic groups on the starting materials. The bitumen and the SBS were treated separately with maleic anhydride (MA) to allow a better control of the chemical reactions involved. MA was selected because of its reactivity towards both SBS or styrene-isoprene-styrene (SIS) copolymers¹⁸⁻²² and bitumens or bituminous coals.^{23,24} Moreover, the bifunctionality of MA should increase the probability of forming intermolecular ionic associations. Azobisisobutyronitrile (AIBN) was chosen as the free-radical promoter for the modification of SBS since it allows a high conversion ratio, as well as a better control of the reaction.

In a second step, the chemically modified materials were then mixed. Finally, the acid groups grafted on the bitumen and the polymer were neutralized with zinc acetate dihydrate (ZAD), which was selected under the following considerations:

1. Studies of ionomer properties have shown that divalent cations are more efficient than monovalent ones in binding chains of the parent polymer together^{9,10};
2. Metal oxides have but a limited compatibility with bitumen;
3. The acetic acid formed during the neutralization with ZAD can be easily eliminated, which is not the case when using, e.g., fatty acids, the plasticizing effect of which brings about additional difficulties.

The degree of neutralization, which reportedly influences the viscosity of ionomers,^{8,11} was controlled as follows: (i) by the amount of salt added—two values were selected, the lower one corresponding to the neutralization of half the acid groups present, and the higher one to a large excess of ZAD; (ii) by the reaction time.

EXPERIMENTAL

Materials

The bitumen was a 80/100 penetration-grade, commercial road-bitumen (B80/100) from the Compagnie Française de Raffinage (Table I). The polymer was a linear SBS block-copolymer ("Cariflex TR1101") from Shell Chimie. Its general properties, as given by the manufacturer, are shown in Table II. MA from Fluka was used as received. Its partial hydrolysis to maleic acid probably occurred to some extent but, taking into account the conditions of the reaction, it was considered to bear no significant influence. ¹⁴C-labeled MA (specific activity: 5.1 TBq·mol⁻¹) was supplied by the Commissariat à l'Énergie Atomique in Gif-sur-Yvette, France. AIBN was purchased from Fluka. Analytical-grade ZAD was received from Prolabo.

Analytical Techniques

IR spectroscopy was performed with a Perkin-Elmer 580B spectrophotometer. All measurements were made on films, laid down on KBr wafers by evapo-

Table I General Characteristics of B80/100

Penetration at 25°C (0.1 mm) (NF T 66-004 standard)	84
Ring-and-ball temperature (°C) (NF T 66-008 standard)	45.6
FRAASS breaking point (°C) (IP 80-53)	-20.8
Specific gravity at 25°C (ASTM D 70-76)	1.03
Elementary analysis (%)	
C	84.75
H	10.05
S	4.10
O	0.40
N	0.10
Fractional composition (%)	
Asphaltenes	15.1
Saturates	10.7
Monoaromatic compounds	7.7
Other aromatic compounds	38.6
Resins	27.9

Table II General Characteristics of TR1101

S/B ratio	30/70
Specific gravity	0.94
300% modulus (GN/m ²)	2.76
Tensile strength (MN/m ²)	31.7
Elongation at break (%)	880
Shore A hardness	71

rating solutions of samples in CCl₄ or chloroform. ¹H-NMR spectra were obtained with a Bruker Spectrospin 80 MHz-spectrometer. The solvent was deuteriochloroform, and the internal reference was tetramethylsilane.

Analytical GPC was performed in tetrahydrofuran (THF) at 25°C, the flow rate being set at 1 cm³ min⁻¹ (Gilson pump). The injection volume was 50 nm³ for all runs. Samples of B80/100, with a concentration of 1 g dm⁻³, were separated on 3 Styragel columns with porosities 5, 10, and 100 nm. The fractions were detected with an UV spectrophotometer (Pye Unicam). For polymer samples, the concentration was 4 g dm⁻³, and we used 4 Styragel columns with porosities 10, 100, 10³, and 10⁴ nm, as well as a differential refractometer (Optilab) with a 1-cm optical path. Calibration was made with PS standards from Chrompack.

Thermal properties were examined with a Mettler DSC-30 thermoanalyser, which was interfaced to a microprocessor. Before each run, the cell was flushed with ultrapure nitrogen, flowing at a constant rate. The starting temperature was set at 140°C, i.e., some 40°C above the glass transition temperature of PS, to allow samples to reach thermodynamic equilibrium before being analysed.²⁵ Samples were first quenched down to -150°C at 50°C min⁻¹ so as to have comparable thermal histories,²⁶ and then heated to 150°C at a rate of 10°C min⁻¹. They were weighed before and after each run to the nearest 10 μg. Glass transition temperatures (*T_g*) and variations of the specific heat (ΔC_p) at *T_g* were automatically calculated from the heating curve by the microprocessor.

Measurements of β -radioactivity were performed on a liquid-scintillation counter (Prius PL Tri-carb from Packard).

The samples were observed in the transmitted-light mode, under a magnification of 200, with a Metallux-II hot-stage optical microscope from Leitz. Samples were prepared as follows: A drop of material was laid down on a glass slide and covered with a glass slip. The preparation was then put on the hot stage, and a 20-g load applied on the glass slip. Tem-

perature rises of 5°C were thereafter performed, followed by annealing steps of at least 35 min. This procedure was carried out until the dispersions could be observed.

Heat stability tests were then made every 30°C in the 60–190°C temperature range. At each temperature step, samples were annealed under the previously mentioned conditions, but this time without any load. Photomicrographs of the dispersions were taken with a Polaroid camera, loaded with 3000 ASA films.

Synthesis of Mixed Bitumen–SBS Ionomers

MA-Modified SBS

SBS was reacted with MA according to the procedure used by Meyer and colleagues for SIS.²¹ In a typical experiment, 10 g polymer, dissolved in 300 cm³ toluene, were treated with 5 g MA in an inert atmosphere. As soon as the reaction temperature (80°C) was reached, a 0.1 g L⁻¹ solution of AIBN in toluene was added in three fractions at 15-min intervals under agitation. The reaction medium was stirred continuously thereafter for up to 3 h at 80°C. Test samples were taken every 30 min. After completion of the reaction, the reaction medium was added to a tenfold volume of ethanol. The precipitate was filtrated, then repeatedly washed to eliminate the unreacted MA, and finally dried under vacuum at room temperature.

MA-Modified B80/100

The modification of B80/100 was performed in the bulk as follows: 500 g bitumen were treated in an inert atmosphere with 25 g (5 wt %) MA in a 1-L reactor. MA was added at room temperature. The reaction medium was then heated to 170°C, the agitation starting as soon as this temperature was reached. Test samples were taken every hour. The maximum reaction time was 5 h. The excess MA was eliminated from the agitation vessel by sublimation under vacuum and stirring for 2.5 h at 170°C.

B80/100-SBS Blends

SBS and B80/100 were mixed with a three-blade propeller in a baffle-free, cylindrical agitation vessel. Typically, 15 g SBS were added to 285 g molten B80/100. Mixing was carried out for 2 h at 165°C. The agitator speed was set at 515 rpm.

The same procedure could not be used to mix the maleated SBS and maleated B80/100 together be-

cause the polymer degraded under shearing. Instead, we resorted to solution mixing. In a typical experiment, 2.1 g maleated SBS were dissolved in 20–30 cm³ toluene. The solution was then added to 40 g maleated B80/100 in a 100 cm³ reactor and stirred in an inert atmosphere for 2 h at 80°C. After mixing, the excess solvent was distilled away under vacuum for 2.5 h at 170°C, the reaction medium being kept under nitrogen.

In all cases, the weight fraction of the polymer in the blends was set at 5%.

Ionomeric Blends

In a typical run, ZAD was added, generally in the solid state, to a blend of maleated B80/100 and maleated TR1101 under stirring at 170°C. In some cases, however, the salt was first dissolved in water, then incorporated to the reaction medium at room temperature under a flow of nitrogen. Water vaporized on heating to 170°C, and stirring started as soon as the viscosity of the medium was low enough. Table III summarizes the conditions under which the neutralization was conducted in each case.

RESULTS AND DISCUSSION

Composite Ionomer Synthesis

Chemical Modification of Starting Materials

SBS. TR1101 has a weight-average molecular mass of 220,000 g mol⁻¹. The microstructure of the polybutadiene (PB) sequence, as determined by ¹H-NMR spectrometry, is 93 mol % 1–4.

The IR spectrum of a sample of maleated TR1101 after a 4-h reaction time shows (Fig. 1) a new doublet at 1,780 and 1,860 cm⁻¹, which is characteristic of the absorption by the carbonyl groups of pentacyclic acid anhydride moieties.^{27,28} No significant evolution

Table III Synthesis of Bitumen–SBS Ionomers (Neutralization Conditions)

Sample	Salt Form	Mass of Salt Added (g)	Time of Neutralization (min)
A	Powder	0.45	40
B	Powder	0.45	210
C	Powder	4.5	40
D	Powder	4.5	210
E	Aq. sol.	0.45	40

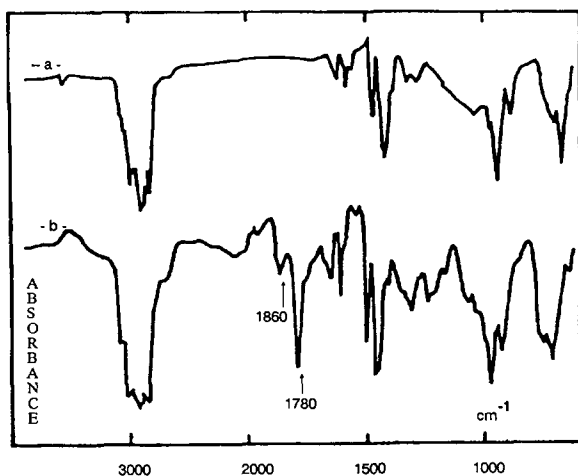


Figure 1 IR spectra of TR1101: (a), initial; (b), maleated.

can be observed for bands at 970 cm^{-1} (1-4 PB microstructure) nor at 995 and 910 cm^{-1} (1-2 PB microstructure).

The analysis of the maleated SBS with DSC reveals a statistically significant increase of the 1-4 PB glass transition temperature, which may be due to the enhancement of the interactions between the PB sequences, following the grafting of polar groups.

The amount of grafted MA increases with the reaction time, as shown by β -spectrometry of the samples treated with ^{14}C -labeled MA (Table IV). When this amount becomes too high, however, crosslinking of the elastomer occurs to some extent. To avoid this, the reaction time was kept under 30 min and the corresponding degree of modification under 1.5%.

B80/100. A comparison of the IR spectra of the initial and maleated bitumens (Fig. 2) shows that, after treatment with MA, five new bands appear at 920 , 1060 , 1220 , and 1860 cm^{-1} . These are due to absorption by pentacyclic acid anhydrides.^{28,29} Nor-

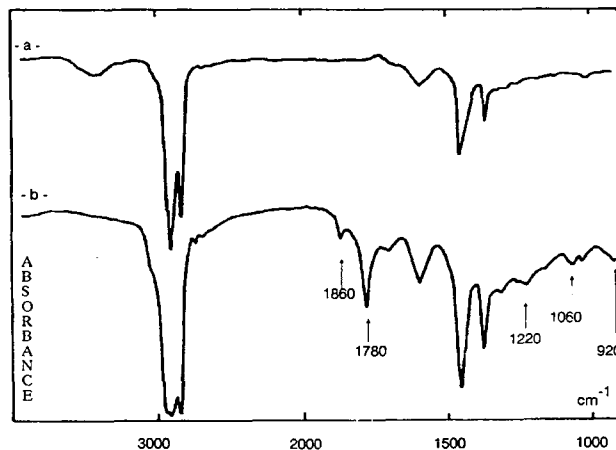


Figure 2 IR spectra of B80/100: (a), initial; (b), maleated.

malization of the 1780 cm^{-1} band (characteristic of MA) by comparison with the 2250 cm^{-1} one (characteristic of bitumen) indicates that the reaction between B80/100 and MA is complete within 1-2 h.

This view is supported by GPC analyses of the maleated B80/100, which show a shift of the molecular mass distribution toward higher values, the maximal shift (+20%) being reached after a reaction time of 2 h.

Blend Morphology

When necessary, solvent removal was checked by GPC and IR analysis of the blends.

We have verified that all dispersions remain stable at the temperature at which they become observable. Indeed, the morphology of a regular B80/100-TR1101 blend at 70°C [Fig. 3(a)] appears quite similar to that of the same blend after 30 min at 90°C [Fig. 3(b)]. Polymer-rich particles appear white. The higher contrast of Figure 3(b) results from an overall decrease in the thickness of the preparation with increasing temperature and annealing time; polymer-rich domains become more visible, but their relative positions are not modified. Similarly, the morphology of an ionomeric blend D (Table III) at 185°C [Fig. 8(a)] closely resembles that of the same blend after 45 min of annealing at that temperature [Fig. 8(b)]. Use has been made of the birefringence of ZAD to detect this salt in ionomeric blends by observing the dispersions through crossed polarizers; thus, the larger, whiter particles appearing in Figures 5(a), 6(a), and 8(a) have been identified as undispersed ZAD.

Table IV Kinetics of the Reaction Between TR1101 and MA

Reaction Time (min)	Reacted Anhydride (%)
30	1.24
60	1.93
90	1.98
120	1.84
150	1.96
180	2.50

The reproducibility of the blending procedure and of the ionomer synthesis was estimated by monitoring morphology changes occurring under comparable annealing conditions. For regular blends, a comparison of the photomicrographs of two batches, first at the temperature of possible observation [Figs. 3(a) and 4(a)], then at 100°C [Figs. 3(c) and 4(b)], and, finally, at 115°C [Figs. 3(d) and 4(c)], shows parallel evolutions of the morphology. The same conclusion can be drawn from photomicrographs of two batches of ionomeric blend A (Table III) by comparing morphologies first at the temperature of possible observation [Figs. 5(a) and 6(a)] and then at 165°C [Figs. 5(c) and 6(b)].

Figure 7(a) shows a typical photomicrograph of a blend of maleated B80/100 and maleated TR1101.

The dispersion seems homogeneous down to a scale of a few micrometers, except for the presence of larger particles, which probably are gel particles formed during crosslinking of the maleated polymer before its incorporation to B80/100. It is impossible to distinguish between the continuous and dispersed phase at that level of magnification, but observations of the same preparations at higher temperatures [Fig. 7(b)] indicate that the polymer has been extensively and randomly dispersed in the bitumen.

Photomicrographs of B80/100-TR1101 ionomeric blends at the temperature of first observation [Figs. 5(a) or 6(a) and Fig. 8(a)] show larger particles that correspond to ZAD, as well as smaller particles, that correspond to polymer-rich domains. The latter have ill-defined contours, which renders

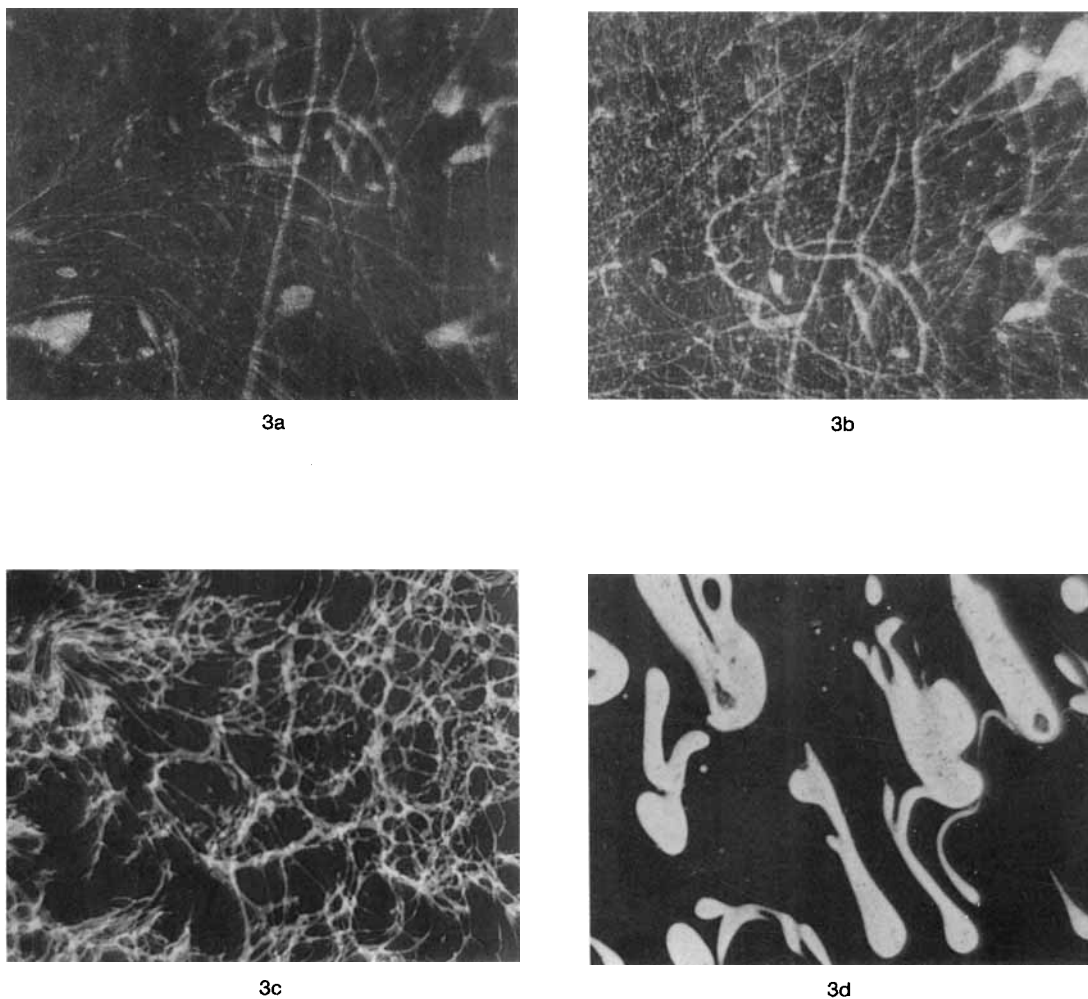
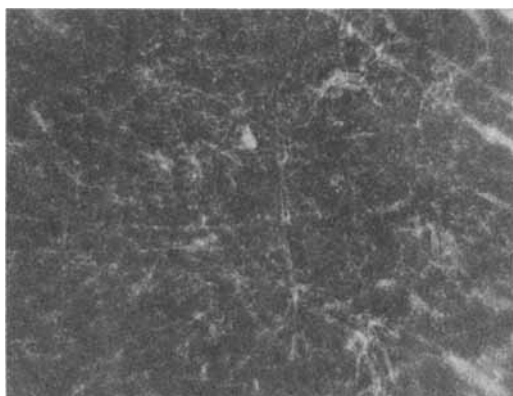
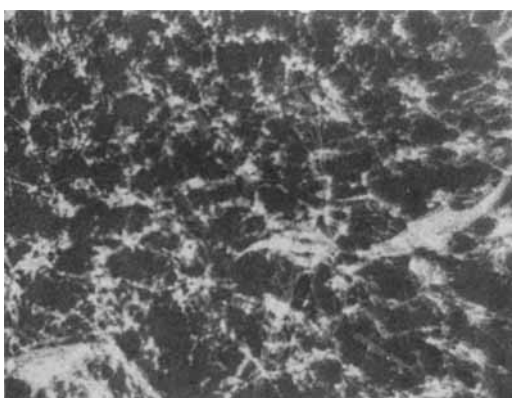


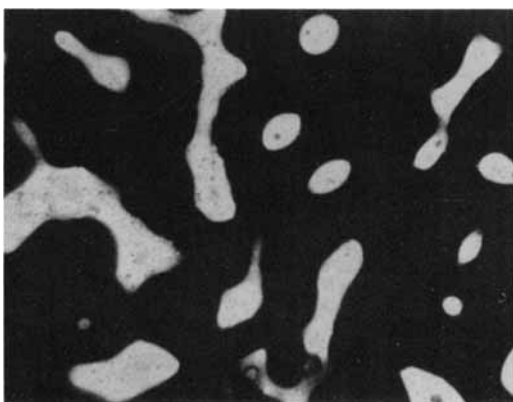
Figure 3 Morphology of B80/100-TR1101 blends: (a), at 70°C; (b), after 30 min at 90°C; (c), after 1.25 h at 100°C; (d), after 1.25 h at 115°C.



4a



4b

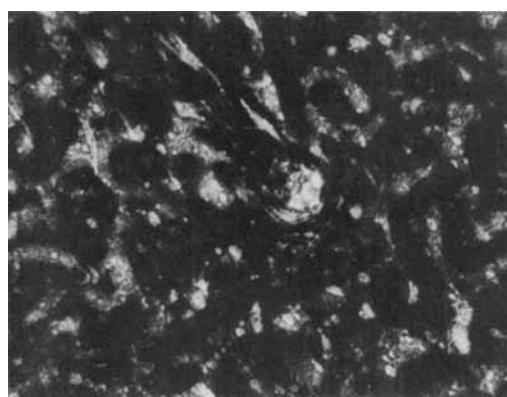


4c

Figure 4 B80/100-TR1101 blends—batch-to-batch reproducibility: (a), morphology at 60°C; (b), after 1.25 h at 100°C; (c), after 3.25 h at 115°C.



5a



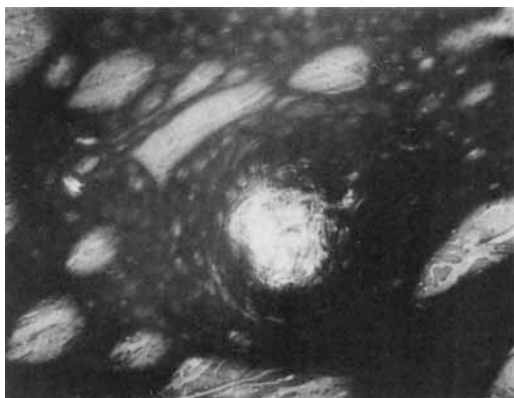
5b



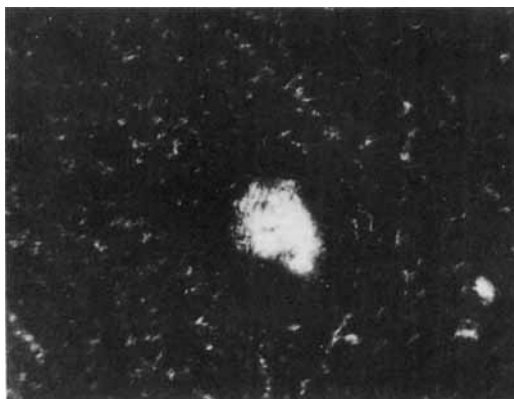
5c

Figure 5 Morphology of an ionomeric B80/100-TR1101 blend (sample A): (a), at 120°C; (b), after 35 min at 135°C; (c), after 45 min at 165°C.

impossible an evaluation of the degree of dispersion of the polymer within the ionomeric blends. These domains become increasingly visible with incipient



6a



6b

Figure 6 Ionomeric blends (sample A)—batch-to-batch reproducibility: (a), morphology at 120°C; (b), morphology after 35 min at 165°C.

macroscopic demixing [Fig. 5(b)] and diminishing thickness of the preparation [Fig. 8(b)].

Evidence for Ionomer Formation

Upon addition of ZAD to a blend of maleated B80/100 and TR1101, the formation of acetic vapors is observed immediately. This phenomenon, still perceptible after a reaction time of 3.5 h, suggests that the neutralization step is slow.

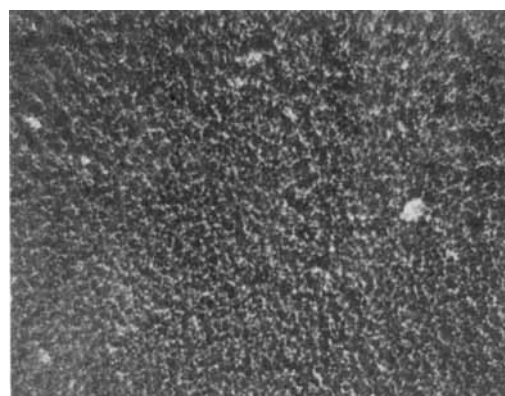
The reaction products have a higher viscosity than either B80/100 or blends of initial bitumen and SBS with the same polymer content. Samples D (Table III) do not creep fast enough to be poured into molds, even at temperatures as high as 190°C. Moreover, microscopic preparations of these samples are not observable under 185°C, whereas cor-

responding temperatures for regular blends lie between 60–70°C.

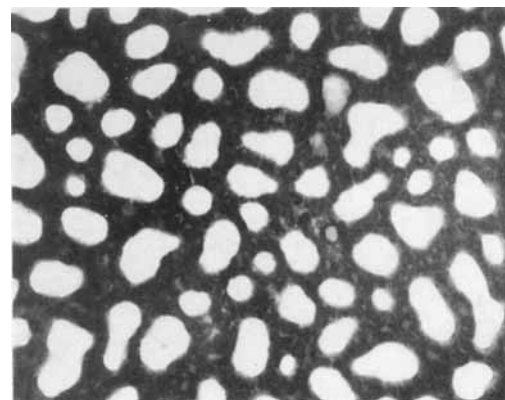
Solubility tests reveal no gel of macroscopic size,



7a

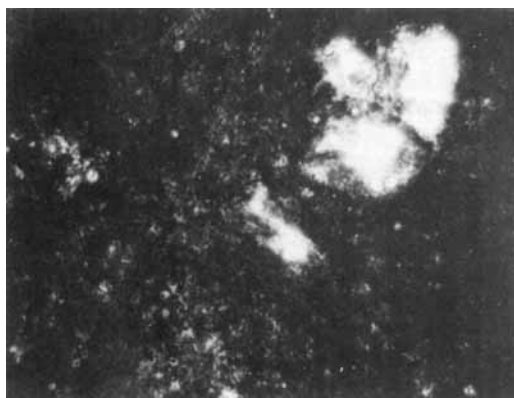


7b

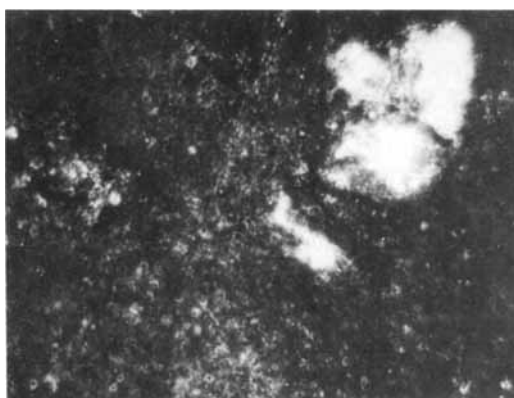


7c

Figure 7 Morphology of maleated B80/100–TR1101 blends: (a), at 100°C; (b), after 1.25 h at 100°C; (c), at 170°C.



8a



8b



8c

Figure 8 Morphology of an ionomeric B80/100-TR1101 blend (sample D): (a), at 185°C; (b), after 45 min at 185°C; (c), after 1 h at 195°C.

but attempts to analyse reaction products with GPC fail: Clogging of the precolumn filters (porosity: 500 nm) occurs, which may be due to the presence of

small-sized gel particles. This provides an additional evidence in favor of the formation of ionomers.

Comparison of the Hot-Storage Stabilities of Regular Blends, Blends of Maleated B80/100 and TR1101, and Ionomeric Blends

Hot-stage optical microscopy had been used previously to measure phase-separation temperatures of blends comprising bitumen and either SBS¹ or atactic polypropylene.²⁹ We chose this technique to study the morphological evolution of the various blends when these materials underwent a heat treatment.

Figures 7(b) and 7(c) show changes in the morphology of a blend of maleated B80/100 and maleated TR1101 during thermal treatment on the hot stage. An evolution, albeit slow, is perceptible at a temperature comprised between 110–115°C, after an annealing time of 1.25 h, the size of the polymer-rich domains has increased to an extent such that these domains become observable [Fig. 7(b)]. When the temperature is raised to 170°C, the growth of the polymer-rich phase is so quick that droplets with a mean size of about 30 μm form within minutes.

Blends of starting materials evolve still faster [Figs. 3(a)–(d) and 4(a)–(c)]: An increase in the mean size of polymer-rich domains can be observed after 1.15 h annealing at 100°C [Figs. 3(c) and 4(b)], and droplets (average size 50 μm) can be seen to form within 1.25 h at 115°C [Fig. 3(d)]. The faster evolution of regular blends with respect to blends of maleated materials mainly results from differences in mixing conditions, which themselves have an influence on the degree of dispersion of the polymer: A comparison of either Figure 3(a) or 4(a) with Figure 7(a) shows that both homogenization and distributive mixing were less efficient for regular blends than for blends of maleated materials.

In contrast to the above-mentioned blends, the morphology of ionomeric blends evolves more slowly, as can be seen for both samples A [Figs. 5(a)–(c)] and D [Figs. 6(a)–(c)]. In the first case, Figure 5(b) shows an increase in the size of the polymer-rich domains after 35 min of annealing at 135°C, and droplets grow to a mean size of 100 μm within 35 min at 165°C. However, the polymer-rich domains of ionomeric blends appear darker [Figs. 5(c) and 6(b)] than those of the other blends: This may mean that these domains contain a higher proportion of bituminous material. Figures 8(b) and 8(c) show the morphology of an ionomeric blend (sample D) after an annealing time of, respectively, 1 h at

185°C and 3 h at 195°C. The observed evolution cannot be ascribed with certainty to an increase in the size of polymer-rich domains: It might result from an overall decrease in the thickness of the preparation.

In any case, observations made with the hot-stage optical microscope show that the thermal stability of the blends increases on neutralizing the carboxylic moieties grafted on both B80/100 and TR1101. Moreover, the higher the degree of neutralization, the higher the increase in stability. These observations speak in favor of the formation of ionomers.

CONCLUSIONS

Synthesis of ionomeric bitumen-SBS blends is, as far as we know, a new approach for the improvement of the stability of bitumen-polymer blends. It proved successful in preventing the macroscopic phase separation of the latter. This solution should be applicable to a wide variety of bitumens and polymers.

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REFERENCES

1. E. J. Van Beem and P. Brasser, *J. Inst. Petr.*, **59**(566), 91 (1973).
2. G. Kraus and K. W. Rollmann, *Kautschuk Gummi, Kunststoffe*, **34**(8), 645 (1981).
3. G. Zenke, *Asphaltstr.—stationäre Mischwerk*, **19**(1), 5–16 (1985); *ibidem*, **19**(4), 170–182 (1985); *ibidem*, **19**(6), (1985).
4. M. Epinat, PhD Thesis, Université de Bordeaux I (1975).
5. H. E. Hoppel and H. Teichmann, German Patent 2,255,173 (1972).
6. Shell Co., French Patent 2,115,900 (1972).
7. P. Jew, J. A. Shinizu, M. Svazic, and R. T. Woodhams, *J. Appl. Polym. Sci.*, **31**(8), 2685 (1986).
8. C. G. Bazuin and A. Eisenberg, *Ind. Eng. Chem. Prod. Res. Dev.*, **20**, 271 (1981).
9. W. J. Macknight and R. D. Lundberg, *Rubber Chem. Techn.*, **57**(3), 652 (1984).
10. A. D. Wilson and H. J. Prosser, *Developments in Ionic Polymers*, Applied Science Publishers, London, 1983, Chap. 1, p. 1.
11. L. Ciplijauskas, M. R. Piggott, and R. T. Woodhams, in *Ions in Polymers*, Adv. Chem. Ser., Am. Chem. Soc., **187**, 174 (1980).
12. K. L. Smith, A. E. Winslow, and D. E. Petersen, *Ind. Eng. Chem.*, **51**, 1361 (1959).
13. E. P. Otocka and F. R. Eirich, *J. Polym. Sci. (A-2)*, **6**(5), 921 (1968).
14. T. Sulzberg and R. J. Cotter, *J. Polym. Sci. (A-1)*, **8**(10), 2747 (1970).
15. A. Eisenberg, P. Smith, and Z. L. Zhou, *Polym. Eng. Sci.*, **22**(17), 1117 (1982).
16. M. Hara and A. Eisenberg, *Macromolecules*, **17**, 1335 (1984).
17. A. Eisenberg, *Polym. Mat. Sci.*, **58**, 978 (1988).
18. J. Le Bras, C. Pinazzi, and G. Milbert, *C. R. Acad. Sci.*, **246**, 1214 (1958).
19. C. Pinazzi, J. C. Danjard, and R. Pautrat, *Bull. Soc. Chim. Fr.*, 2433 (1961).
20. N. K. Baramboim and V. I. Popov, *Nauchn. Trudy Mosk. Tekhnol. Inst. Legkoi Prom.*, **19**, 54 (1961).
21. G. Meyer, J. M. Widmaier, and J. M. Toussaint, *Bull. Soc. Chim. Fr.*, 286 (1975).
22. S. Tazuke and H. Kimura, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 2707 (1977).
23. J. Grosmanin, A. Verschave, and J. Marvillet, French Patent 2,201,336 (1972).
24. R. C. Duty and Hsing Fong Liu, *Fuel*, **59**, 546 (1980).
25. S. E. B. Petrie, *J. Polym. Sci. (A2)*, **10**, 1255 (1972).
26. M. J. Richardson, *Polym. Test.*, **4**, 101 (1984).
27. N. B. Colthup, L. H. Daly, and S. E. Wiberley, *Introduction to Infra-Red and Raman Spectroscopy*, Academic Press, New York, 1964.
28. G. Socrates, *Infra-Red Characteristic Frequencies*, Wiley, New York, 1980.
29. F. Kuegler, *Modifizierung von Bitumen mit Hochpolymeren*, Vortrag 4, Gemeinschaftstagung des Österreichischen Gesellschaft für Mineralölwissenschaft/DGMK, Salzburg, 1976.

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