

Effect of Polymer Additives and Process Temperature on the Physical Properties of Bitumen-Based Composites

Mehmet Doğan,¹ Erdal Bayramlı²

¹Department of Polymer Science and Technology, Middle East Technical University, Ankara 06531, Turkey

²Department of Chemistry, Middle East Technical University, Ankara 06531, Turkey

Received 9 September 2008; accepted 18 February 2009

DOI 10.1002/app.30280

Published online 27 April 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polymer modified bitumen (PMB) is a binder obtained by the incorporation of polymer into the bitumen by mechanical mixing or chemical reaction. This study deals with the modification of bitumen with three types of polymers (LDPE, EVA, and SBS) in the presence of filler (CaCO₃). The morphological, mechanical, rheological properties, and thermal conductivity of the PMBs have been analyzed by scanning electron microscopy, tensile testing, melt flow index (MFI) measurements and hot wire method, respectively. The results indicate that the above-mentioned properties of PMBs are influenced by polymer

and bitumen nature and its composition. The mechanical properties of composites prepared at different temperatures exhibit small differences. In general, the inclusion of polymer increases tensile strength and Young's modulus and reduces percentage strain and MFI values, also, polymer inclusion reduces the thermal conductivity values of the composites. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2331–2338, 2009

Key words: bitumen; composites; mixing; reinforcement; thermal conductivity

INTRODUCTION

Bitumen, which is a byproduct in vacuum distillation of crude oil, is a complex mixture of hydrocarbons, varying both chemically and in molecular size. These hydrocarbon components change from the nonpolar aliphatic wax compounds to highly polar condensed aromatics. The rest of the bitumen consists of heteroatoms such as nitrogen, oxygen, and sulfur.^{1–3} Bitumen binder is readily adhesive, highly waterproof, and durable making it a valuable engineering material. Bitumen has uses that range from the construction of the pavements of roads with an aggregate to waterproofing membrane in roofing and structural applications.^{4,5}

Several additives are being used to increase the performance of bitumen binders. Polymers are most widely used additives in bitumen modification. Mixing polymers into bitumen has important consequences on the engineering properties of bituminous materials. The extent of modification and the improvements in the performance characteristics will depend on bitumen nature, polymer chemical nature, its dosage and chemical compatibility, molecular weight, particle size, as well as blending process conditions such as type of mixing/dispersing device, time and temperature play important role in determining the

modified asphalt properties.⁶ Bitumen modification by polymers improves its mechanical properties, increases the viscosity, and allows an expansion of temperature range of service and the improvement of the deformational stability and durability.^{7,8}

The morphology of PMB is the result of the mutual effect of polymer and bitumen, consequently is influenced by bitumen composition, polymer nature and ratio.^{9,10} Most polymers are insoluble to some degree in the bitumen matrix, resulting eventually in gross separation of both phases. These phases may become a continuous phase or a dispersed one depending on polymer nature, concentration and its ability to swell with maltene molecules.^{6–8} Polymer is swelled by the maltenes which is low molecular weight portion of bitumen so that the remaining bitumen phase is artificially enriched in asphaltenes which is high molecular weight portion of bitumen. This is the case observed when elastomers and thermoplastics such as ethylene vinyl acetate (EVA), styrene butadiene styrene (SBS), low density polyethylene (LDPE), etc. are mixed with bitumen.^{6–10}

Polyolefins are produced from olefinic monomers; the resulting homopolymers have nonpolar, nonaromatic nature. The typical range for their solubility parameter is 15.6–17.4 MPa^{1/2}. This low solubility parameter reflects its incompatibility in an asphalt dispersion medium which is polar and aromatic. Polyolefins can also be copolymerized as either block or random copolymers such as SBS, EVA. The solubility parameter can be modified by the addition of

Correspondence to: E. Bayramlı (bayramli@metu.edu.tr).

TABLE I
Physical Properties of Bitumens

Binder	Penetration at 25°C, 100 g, 5 s (× 0.1 mm)	Softening point (ring ball method) (°C)
Bitumen A	20/30	57–67
Bitumen B	50/70	46–54

a more polar comonomer yielding a more compatible system.^{5,11,12} High-molecular weight polymers have profound effects on the properties of bitumen. As the molecular weight of polymers increases, their compatibility with bitumen sharply decreases.¹³

Thermal conductivity, k , is defined as the rate at which heat is transferred by conduction through a unit cross-sectional area of material when temperature gradient exists perpendicular to the area. In dielectric solids and liquids, which include most polymers, heat is conducted by the interactions of thermal vibrations of molecules and their component atoms.^{14,15} Most polymeric materials have k values between 10^{-1} and 10^0 W/m K. In comparison with the amorphous polymers, crystalline polymers are characterized by a more ordered, denser structure which yields a higher thermal conductivity. Thermal conductivity of polymers depends on a lot of parameter such as temperature, molecular weight, and orientation. When a polymer is oriented by stretching or by cold drawing the anisotropy of structure is reflected in a corresponding anisotropy in properties. Polymers show an increase in conductivity parallel to stretching with a decrease normal to the stretch direction.¹⁶

In this study, bituminous composites are prepared that can be used in automatic dish washers and refrigerators as insulating material. 50% volume fraction of CaCO_3 is used in composites in order to hinder the yielding of bituminous composites due to the gravity and the heat generated in whitewares. The main objective of this study is to determine the effects of polymer type and concentration on mechanical, thermal conductivity, rheological, and morphological properties of bitumen-based composites. Also, the effect of process temperature on mechanical and thermal properties of bituminous composites is investigated.

MATERIALS AND EXPERIMENTAL

Materials

Two different penetration grade bitumens were used in this study. Both of them were purchased from Tupras A.S (Turkey). Properties of the bitumens are shown in Table I. Thermoplastic polymers used in this study are LDPE (G03-5, Petkim, Turkey), styrene-butadiene-styrene block copolymer (SBS, Elastron D[®], Turkey), EVA (Alcudia[®] PA-461). The melt flow rate measured at 2.16 kg, 190°C and density of

LDPE are 0.2–0.4 g/10 min and 0.919–0.923 g/cm³, respectively. Density of SBS is 1.03 ± 0.02 g/cm³. The EVA copolymer contains 33% vinyl acetate and its density and melt flow rate (2.16 kg, 190°C) are 0.956 g/cm³, 45 g/10 min, respectively. CaCO_3 used in this study was supplied by OMYA Madencilik A.S. (Turkey) with trade name Omyacarb 3 Extra-GZ. The chemical composition of this product is 98.5% CaCO_3 , 1.5% MgCO_3 , 0.05% Fe_2O_3 . The average particle size is 5 μm with density 2.7 g/cm³.

Preparation of polymer-modified bitumens

Polymer, bitumen, CaCO_3 containing composites were prepared by using Brabender Plastic Coder, PLV 151. Owing to the high volume fraction of the inorganic filler, the shear rates generated are large and good mixing is achieved in 20 min. Mixing was achieved at 150°C, 60 rpm in 20 min. To investigate the effect of process temperature, some of the samples are also processed at 180°C. If not specified, the process temperature should be taken as 150°C. First bitumen and polymer are added and they were mixed for 5 min then a preweighed amount of CaCO_3 was added. The compositions were adjusted to have polymer volumes equal to 5%, 10%, 20%, and 50% of bitumen volume. All compositions with regard to polymer type and ratio are given in volume fraction and shown in Table II.

Tensile tests

Tensile tests were performed according to ASTM D 638-M 91a by using a Lloyd LS computer controlled tensile testing machine. All tensile tests were carried out at room temperature. The crosshead speed was 10 cm/min. Five samples were tested and average results with standard deviations were reported for each composition. Tensile tests were performed on dog bone shaped molded samples.

TABLE II
Compositions of Composites by Volume Fraction

Sample no.	Bitumen 20/30	Bitumen 50/70	CaCO_3	LDPE	EVA	SBS
NP	24.3	24.3	51.4	–	–	–
PE-5	23.23	23.23	51.22	2.31	–	–
PE-10	22.20	22.20	51.13	4.46	–	–
PE-20	20.43	20.43	50.98	8.17	–	–
PE-50	16.45	16.45	50.64	16.47	–	–
SBS-5	23.23	23.23	51.20	–	–	2.35
SBS-10	22.23	22.23	51.09	–	–	4.45
SBS-20	20.46	20.46	50.90	–	–	8.18
SBS-50	16.48	16.48	50.47	–	–	16.57
EVA-5	23.19	23.19	51.24	–	2.39	–
EVA-10	22.13	22.13	51.18	–	4.47	–
EVA-20	20.40	20.40	51.07	–	8.13	–
EVA-50	16.37	16.37	50.81	–	16.45	–

MFI measurements

The measurements were done according to ASTM D 1238 by using Coesfield Material Test, Meltfixer LT. The measurements were carried out at two different temperatures 150°C and 180°C with a load of 2.16 kg. The weight of sample passing through the die in 10 min, defined as melt index, was determined for all compositions. The results were recorded as gr/10 min.

Thermal conductivity

Thermal conductivity tests were performed according to hot wire test method (ASTM C 177, TS 4360-1, EN 993-14). Results were recorded as W/mK. Thermal conductivity tests are carried out on hot pressed composite rectangular specimens that have dimensions of 15 cm×7 cm×1 cm.

Scanning electron microscopy (SEM) analysis

A low-voltage SEM (JEOL JSM-6400) was used to analyze the tensile fracture surfaces of the composites to observe the effects of polymer type and concentration on the morphologies of the composites.

Fractured surfaces were coated with gold to provide conductive surfaces.

RESULTS AND DISCUSSION

Morphological analysis

SEM analyses have been performed in order to characterize the morphology of tensile fractured surfaces of bituminous composites. SEM images of these samples are presented at magnification of 2500×.

SEM micrographs of bituminous composites containing LDPE are given in Figure 1. No significant morphological difference is observed between the composite which does not contain polymer and the composite which contains 5% LDPE (Table II). The small polymer spheres swollen by compatible bitumen fractions are spread homogeneously in a continuous bitumen phase at low polymer content.^{17,18} The morphology of the tensile fractured surfaces changes when the polymer percentage reaches the 20% of the bitumen volume. As the polymer ratio increases, large polymer domains are formed. Plastic deformation of LDPE at the fracture

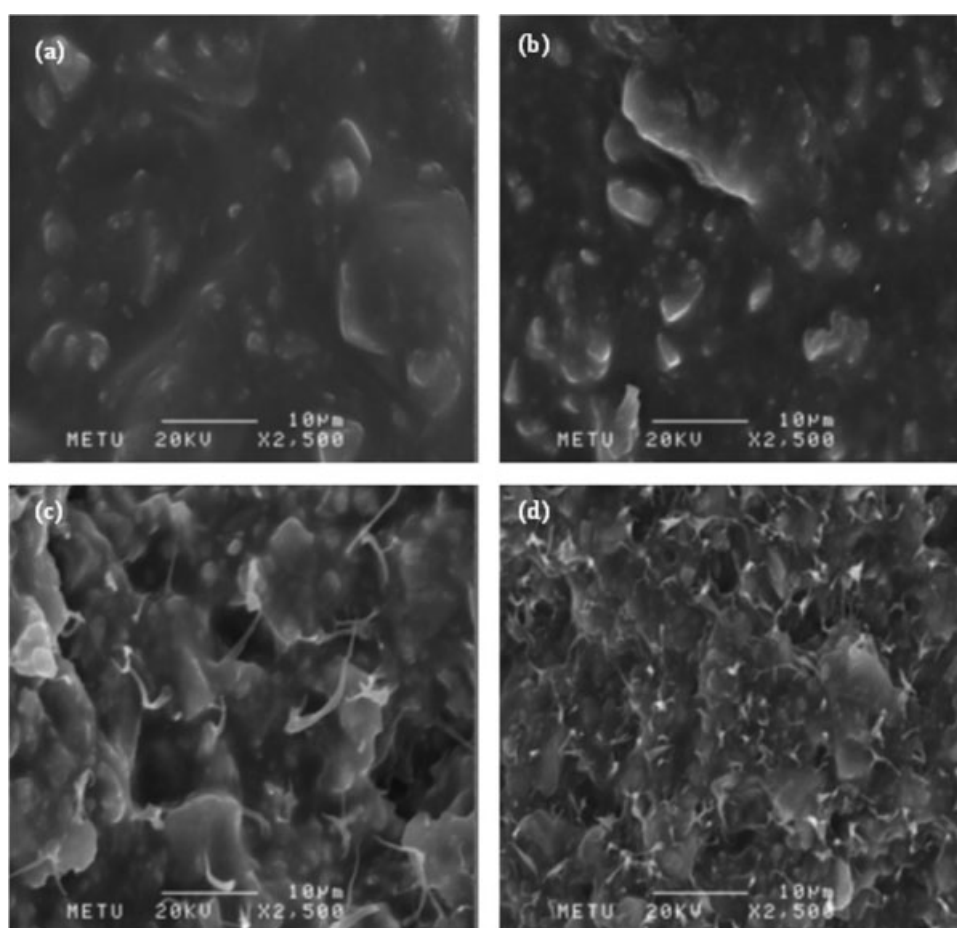


Figure 1 SEM micrographs of bituminous composites containing (a) no polymer (b) 5% LDPE (c) 20% LDPE (d) 50% LDPE at magnification of ×2500.

surfaces can also be observed as a result of ductile failure of LDPE, especially at 50% LDPE (PE-50).

SEM micrographs of bituminous composites containing SBS are given in Figure 2. When the amount of SBS increases, the filler (CaCO_3) becomes more visible with respect to composite containing no polymer. This may be due to swelling of SBS with maltene portions of bitumen. The butadiene phase of the polymer absorbs the lighter ends of the asphalt and swells as much as nine times its original volume.^{19–21} This may weaken the interaction between filler and bitumen.

SEM micrographs of bituminous composites containing EVA are given in Figure 3. When the ratio of EVA reaches 50%, plastic deformation is observed as a result of ductile behavior of ethylene part of EVA. EVA has affinity to CaCO_3 as seen SEM micrograph of 50% EVA containing bituminous composite. The reason of this affinity is the polar nature of EVA. EVA adheres to the polar surface of CaCO_3 .

Mechanical properties

The stress and strain behavior of bituminous composite shows rubbery characteristics. The composites

are well above their T_g and can undergo very large extensions without forming a neck and the cross-sectional area drops uniformly along the gauge length as extension increases.

Figures 4 and 5 represent the effect of polymer type and amount on tensile strength and percentage strain at break values of PMBs. As seen in the figures, the addition of polymer increases the tensile strength and reduces the percentage strain regardless of polymer type. There is a slight increase at the tensile strength of SBS when the polymer concentration increases but the increase in tensile strength is higher for EVA and much higher in LDPE for 50% polymer inclusion. According to SEM analysis, plastic deformation occurs during the tensile test for LDPE and EVA containing bituminous composites. The 8-fold increase in the maximum tensile strength with respect to composite with no polymer is interesting. This may be due to the formation of bi-continuous bitumen and LDPE phases which then can make use of the superior mechanical properties of LDPE. There is 4-fold increase in tensile strength of 50% LDPE compared to polymers at low concentrations (5 and 10%). The other two polymers SBS and

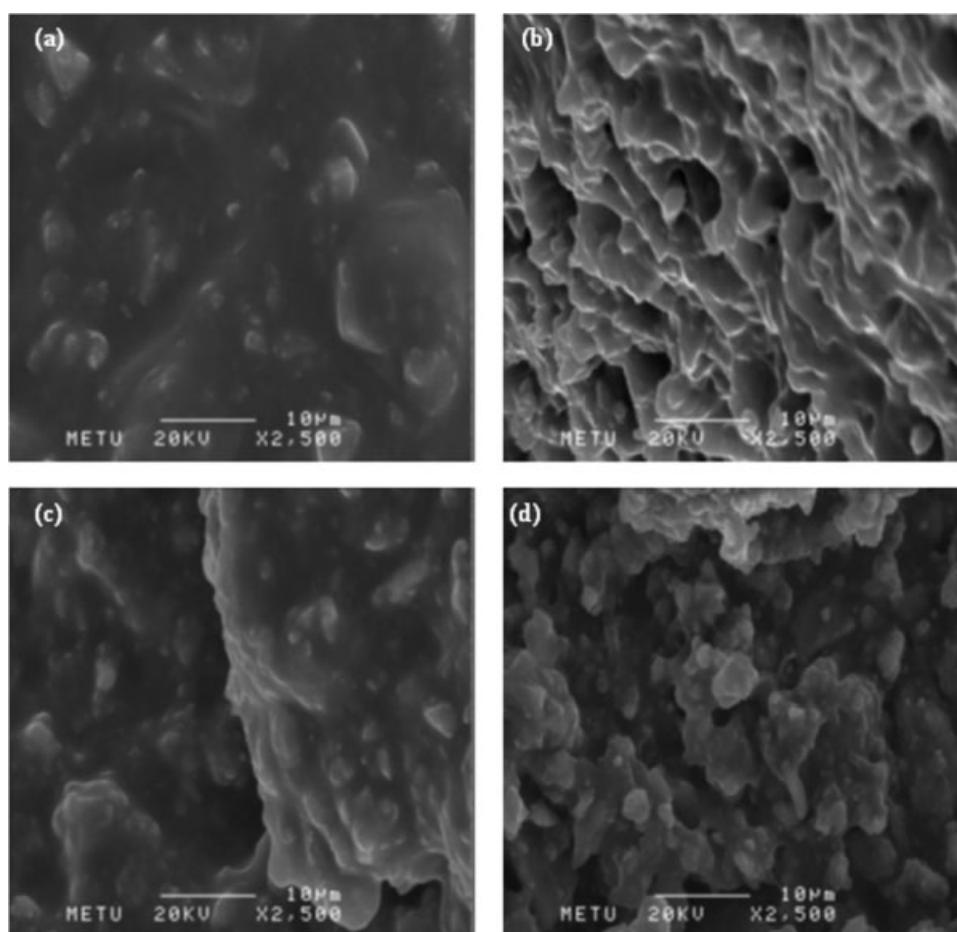


Figure 2 SEM micrographs of bituminous composites containing (a) no polymer (b) 5% SBS (c) 20% SBS (d) 50% SBS at magnification of $\times 2500$.

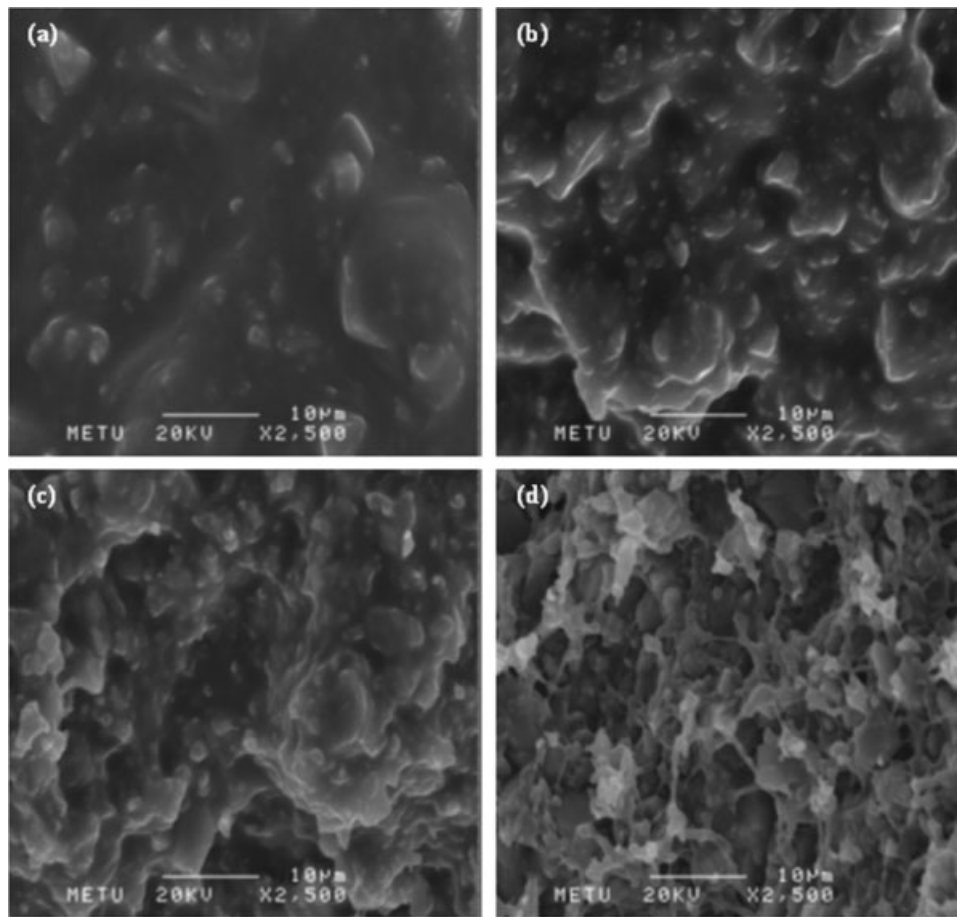


Figure 3 SEM micrographs of bituminous composites containing (a) no polymer (b) 5% EVA (c) 20% EVA (d) 50% EVA at magnification of $\times 2500$.

EVA exhibit a gradual increase in tensile strength as polymer volume fraction increases. At low polymer volume fraction (5%), EVA has about 30% higher tensile strength than the other polymers. This again can be due to the polar nature of EVA and CaCO_3 surface. This finding is also significant, because, polymers are mostly used at low volume fractions in applications of bituminous compounds.

Figure 6 represents the effect of polymer type and amount on Young's modulus values of bituminous composites. Young's modulus of bituminous composites increases as the polymer concentration increases. EVA has the highest Young's modulus value for low (5%, 10%) volume percentages of the polymer. The SEM micrographs show that there is good adhesion between EVA and the filler which also correspond to improved mechanical properties.

Process temperature has clearly some effect on the tensile strength and percentage strain at break values. Figures 7 and 8 show the effect of process temperature on tensile strength, percentage strain at break values of bituminous composites up to 20% polymer inclusion. There is no general trend for the

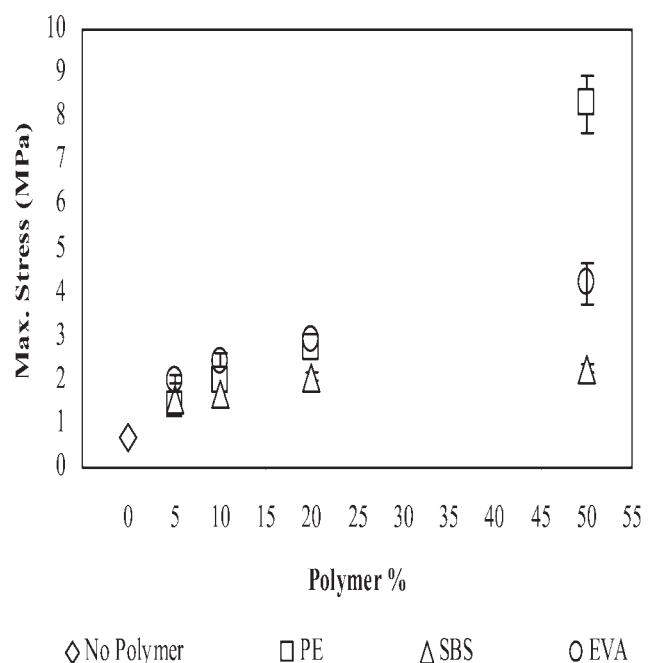


Figure 4 Effect of polymer type and amount on tensile strength of bituminous composites.

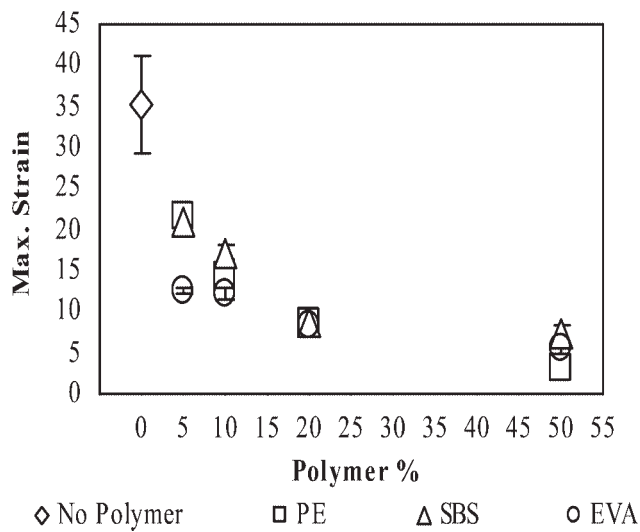


Figure 5 Effect of polymer type and amount on percentage strain at break values of bituminous composites.

three types of polymers investigated. For LDPE, maximum stress measured at room temperature decreases for polymers processed at higher temperature whereas it increases for EVA. For SBS, there is a fluctuating trend as polymer content at the composite increases. For the case of bitumen and CaCO_3 alone, a decrease in maximum stress is observed.

At the two temperatures investigated, mixing parameters can significantly change due to changes in viscosity ratios and shear rates generated inside the

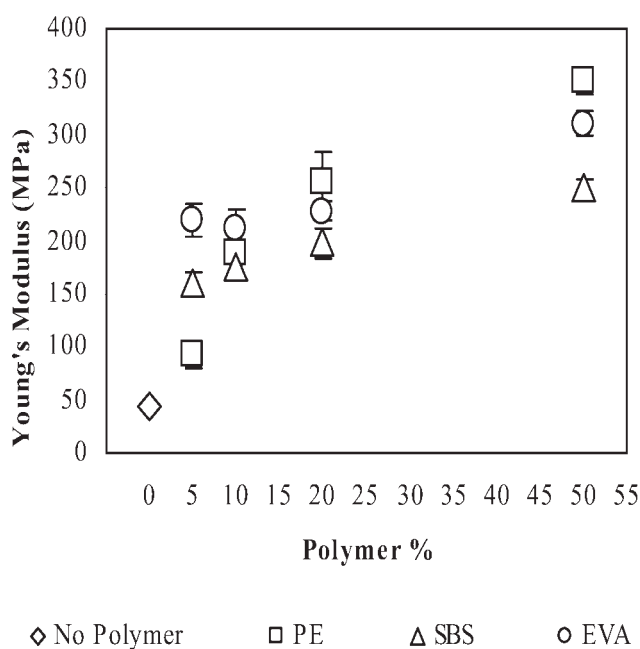


Figure 6 Effect of polymer type and amount on Young's modulus values of bituminous composites.

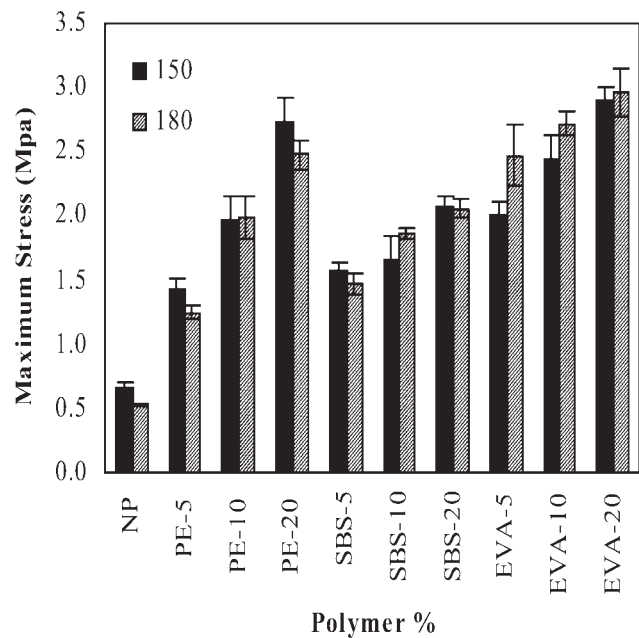


Figure 7 Effect of process temperature on tensile strength of bituminous composites which are prepared at two different temperatures.

mixing chamber. The goodness of mixing can, therefore, also change with the processing temperature. As a result of changes in polymer-bitumen interfacial areas, the adhesional interaction can also change. Considering all the complex factors that can have an effect on mechanical properties, it will be outside the scope of this study to derive definitive conclusions on the effect of processing temperature.

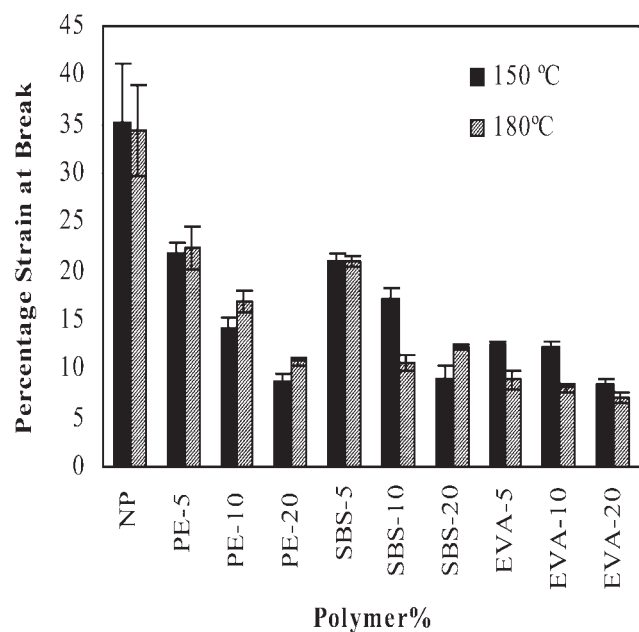


Figure 8 Effect of process temperature on percentage strain at break of bituminous composites which are prepared at two different temperatures.

In Figure 8, it is observed that the percentage strain values of LDPE increases at higher processing temperature. A fluctuating trend is also observed for SBS. Strain at break values decrease with increase in processing temperature for EVA.

Figure 9 gives the Young's modulus values for the specimen at two different processing temperatures. There is a decrease for LDPE and an increase is observed for SBS. A decrease at 5% EVA and then an increase at higher EVA percentages is found at the processing temperatures investigated. Thus, it is not possible to observe a trend for the mechanical behavior of the three types of polymers employed in the formation of bitumen composites at the two process temperatures given.

Flow characteristics

Figure 10 shows the effect of polymer type and amount on melt flow index (MFI) values of bituminous composites performed at 150°C and 180°C. Note that these temperatures are not the process temperature which is kept constant at 150°C. Increasing the polymer percentage reduces the MFI value of bituminous composite. Polymers with higher melt viscosity than bitumen as expected decrease the MFI values of the composite. Among the three polymers investigated, EVA gives a gradual and slow decrease in MFI values. The most probable reason is the polar nature of EVA which tends to have a stronger interaction with the filler CaCO_3 . The EVA-filler interaction may have stabilizing effect in terms of viscosity changes.

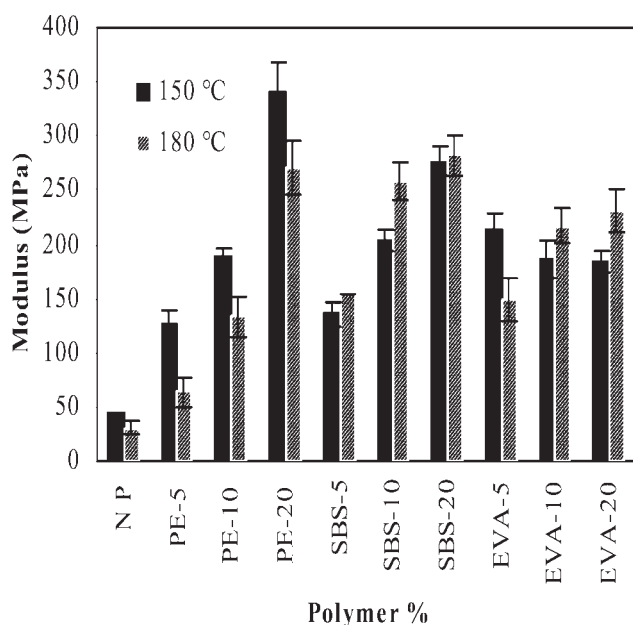


Figure 9 Effect of process temperature on Young's modulus values of bituminous composites which are prepared at two different temperatures.

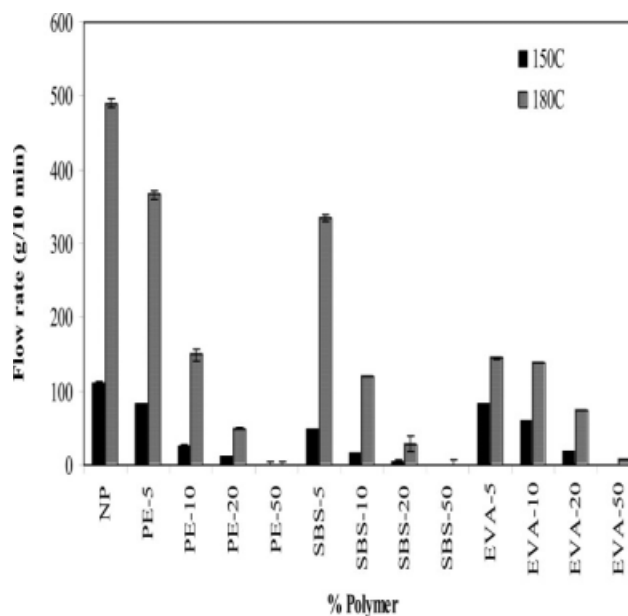


Figure 10 Effect of polymer type and amount on MFI values of bituminous composites.

Thermal conductivity

The ambient thermal conductivity values of the specimens are given in Table III. The addition of polymers in general reduces the thermal conductivities. It should be noticed that as polymer volume fraction increases there is a corresponding decrease in the volume fraction of bitumen. Overall heat conduction values of composites are less than that of CaCO_3 , but, larger than the conductivities of bitumen and the polymers. The thermal conductivities of bitumen, CaCO_3 , EVA, LDPE, and SBS are 0.17, 3.89, 0.26, 0.28, and 0.21 W/mK at 273 K, respectively.

The filler CaCO_3 occupies about half of the composite volume, so it has an important effect in the measured thermal conductivity values. It is interesting to observe a decreasing tendency in conductivity

TABLE III
Thermal Conductivities of the Bituminous Composites Prepared at Two Different Temperatures

Sample	Thermal conductivity (processed at 150°C) (W/m K)	Thermal conductivity (processed at 180°C) (W/m K)
NP	1.02	1.04
PE-5	0.89	1.00
PE-10	0.81	0.85
PE-20	0.81	0.79
SBS-5	0.80	0.88
SBS-10	0.74	0.82
SBS-20	0.81	0.76
EVA-5	0.77	0.80
EVA-10	0.76	0.77
EVA-20	0.76	0.79

as polymer volume fraction increases in spite of polymers which have higher conductivity values than the bitumen itself. One possible explanation is that at the volume fractions used the polymer phase is discontinuous and forms a non-connected dispersed phase. Their contribution to conductivity is therefore reduced. CaCO₃ on the other hand is over 50 volume percentage and might be forming a continuous path through aggregation of CaCO₃ powder. As polymer amount increases, volume fraction of bitumen is reduced. At the same time, as a consequence of reduced volume fraction cross-section areas of neat bitumen phase in the sample is also reduced. So, heat is forced to flow through a reduced cross-sectional area which can result in low thermal conductivities. The explanation given above is highly simplified but captures the main features of the heat flux data observed in Table III.

CONCLUSIONS

The addition of polymer of all types investigated increases the tensile strength and reduces percentage strain at break values of the samples. There is a small increase in tensile strength of the composites which contains SBS when the polymer percentage increases but there are higher increases at tensile strengths for EVA (at low EVA content) and much higher for LDPE (at 50% polymer content). The very high tensile strength value of LDPE at 50% volume percentage is thought to result from the formation of bicontinuous morphology. MFI decreases as polymer amount increases as expected. Interaction between CaCO₃ and EVA gives rise to a more gradual change in MFI values at both temperatures. No general trend is observed in the mechanical properties for the polymers processed at two different temperatures. The tensile strengths and the strain values measured and the initial modulus values showed fluctuations as polymer fraction increased in the composites. This is thought to occur due to the interplay of various factors as the processing temperature is changed.

From the SEM micrographs, as the polymer ratio increases for composites which contain LDPE or EVA, large polymer domains are formed. Plastic deformation and ductile failure of LDPE and EVA is observed. EVA has affinity to CaCO₃ as seen in the

SEM micrograph of 50% EVA containing bitumen composites. There is no plastic deformation of polymer observed for the composites which contain SBS.

The thermal conductivities decrease as the polymer content of the composite increases. This effect is basically due to the formation of dispersed polymer phase which reduces the cross-sectional area of the bitumen phase. Among the polymers, EVA has the lowest thermal conductivity due to its polar nature and its insulating capacity of the CaCO₃ powder.

References

- Herman, F. M.; Gaylord, N. G. *Encyclopedia of Polymer Science and Technology*; John Wiley & Sons, Inc.: New York, 1965.
- Illston, J. M.; Domone, P. L. *J. Construction Materials: Their Nature and Behavior*; Spon Press: London and New York, 2001.
- Abraham, H. *Asphalts and Allied Substances*; Van Nostrand: New York, 1945.
- Gerhartz, W. *Ullmann's Encyclopedia of Industrial Chemistry*; VCH Press: Germany, 1985.
- Wardlaw, K. R.; Shuler, S. *Polymer Modified Asphalt Binders*; ASTM: Philadelphia, 1992.
- Perez-Lepe, A.; Martinez-Boza, F. J.; Gallegosa, C.; Gonzalez, O.; Munoz, M. E.; Santamaria, A. *Fuel* 2003, 82, 1339.
- Selvavathi, V.; Sekar, V. A.; Sriram, V.; Sriram, B. *Pet Sci Technol* 2002, 20, 535.
- Garcia-Morales, M.; Partal, P.; Navarro, F. J.; Martı́nez-Boza, F.; Gallegos, C.; González, N.; González, O.; Munoz, M. E. *Fuel* 2003, 83, 31.
- Garcia-Morales, M.; Partal, P.; Navarro, F. J.; Gallegos, C. *Fuel* 2006, 85, 936.
- Lu, X.; Isacsson, U. *Polym Test* 2001, 20, 77.
- Rozeveld, S. J.; Shin, E. E.; Bhurke, A.; France, L.; Drzal, T. L. *Microsc Res Tech* 1997, 38, 529.
- Rubin, I. I. *Handbook of Plastic Materials and Technology*; John Wiley & Sons, Inc.: New York, 1990.
- Salamone, J. C. *Polymer Materials Encyclopedia*; CRC Press: New York, 1996.
- Yousefi, A. A.; Ait-Kadi, A.; Roy, C. *J Mater Civil Eng* 2000, 12, 113.
- Shah, V. *Handbook of Plastics Testing Technology*; John Wiley & Sons, Inc.: New York, 1998.
- Herman, F. M.; Gaylord, N. G. *Encyclopedia of Polymer Science and Technology*; John Wiley & Sons, Inc.: New York, 1970.
- Yousefi, A. A. *J Appl Polym Sci* 2003, 90, 3183.
- Fawcett, A. H.; McNally, T.; McNally, G. M.; Andrews, F.; Clarke, J. *Polymer* 1999, 40, 6337.
- Zubeck, H.; Raad, L.; Saboundjian, S.; Minassian, G.; Ryer, J. *J Cold Regions Eng* 2002, 16, 170.
- Lu, X.; Isacsson, U. *Fuel* 1997, 76, 1353.
- Lu, X.; Isacsson, U. *Construction Building Mater* 1997, 11, 23.