Swelling and Diffusion Characteristics of Polar and Nonpolar Polymers in Asphalt

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ABSTRACT: The swelling and diffusion characteristics of a polar polymer [ethylene vinyl acetate (EVA)] and a nonpolar polymer [low-density polyethylene (LDPE)] were studied with swelling experiments of the polymers in asphalt at different temperatures. The study showed that the diffusion mechanisms for LDPE and EVA were different and temperature-dependent. In the case of LDPE, the observed diffusion was anomalous at both swelling temperatures (70 and 90°C). LDPE at 90°C showed sigmoidal solvent-uptake behavior during the initial period of swelling and a sorption overshoot in a later period. EVA showed Fickian transport at 60°C and anomalous diffusion at a higher swelling temperature (70°C) with sigmoidal uptake behavior. An analysis of the diffusion coefficients and the Fourier transform infrared results showed that the diffusing molecules were different in the case of LDPE and EVA, and there were possible polymer–asphalt interactions. Differential scanning calorimetry and swelling studies showed that penetrant-induced crystallization affected the diffusion process in the case of LDPE. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 135–143, 2008

Key words: diffusion; polyethylene (PE); swelling

INTRODUCTION

Asphalt, which is a complex, heterogeneous mixture of various hydrocarbons, is used for a wide variety of applications, one of the important applications being paving. Asphalt is used largely as a binder for aggregate materials in the construction of highways and roads. The exact composition of asphalt is difficult to determine, and structure-based flow modeling is difficult, because these can vary with the crude oil source. However, the four major components of asphalt are classified as asphaltenes, polar aromatics, naphthene aromatics, and saturates.[1] The rheological behavior[2] and aging characteristics of asphalt are complex because of its colloidal nature and the change in the stability of the colloidal structure with temperature. To improve the performance of pavements and roads and to achieve certain desired properties, small amounts of polymers are added to asphalt (<6 wt %) to obtain polymer-modified asphalts (PMAs). Polymer modification of asphalt is expected to change the mechanical and aging behavior of the pavements. Polymers such as the styrene–butadiene–styrene block copolymer, styrene–butadiene rubber, low-density polyethylene (LDPE), ethylene vinyl acetate (EVA), and crumb rubber are widely used and studied polymers in the modification of asphalt.[3–5] Increased stiffness, reduced deformation under traffic loads, increased fatigue life, increased resistance to rutting and cracking, and improved resistance to low-temperature cracking are expected to be achieved by the addition of polymers to asphalt.[6–8] However, the physical and chemical interactions between polymers and asphalt are not understood clearly.

Polymers are known to swell during contact with certain fluids because of the diffusion and sorption of the fluid. The amount of substrate permeating the solid polymer depends on the nature of the fluid, the type of polymer, the temperature, and the total time of exposure. Earlier studies of PMA showed that when polymers are used for the modification of asphalt, this may result in the migration of certain components of asphalt into the polymer phase.[9,10] According to the type of component diffusing into the polymer, the colloidal nature of asphalt can become unstable, and this can result in a performance different than the expected one. However, it needs to be studied in detail whether asphalt diffusion into the polymer phase is dependent on factors such as the type of polymer and asphalt used and the temperature of processing and service conditions of PMA. Hence, in the case of PMA, it is important to understand the mechanism of diffusion of various components from the asphalt phase into the polymer during various stages such as the mixing of the polymer with the asphalt, the storage of the PMA, and the service life.

There have been numerous studies on the diffusion characteristics of various small molecules into

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various polymers.[11–14] However, there are no reported studies on the swelling and diffusion of asphalt components into polymers. In this work, semicrystalline polymers such as EVA (polar) and LDPE (nonpolar) were allowed to swell in asphalt at different temperatures. The main objective of the study was to determine the extent of swelling and nature of the diffusion of different components from the asphalt into the polymer and whether the diffusion process is affected by the polar/nonpolar nature of the polymer and the diffusing species. Swelling studies were carried out in two different grades of asphalt to determine the effect of the asphalt structure on diffusion. Fourier transform infrared (FTIR) studies and differential scanning calorimetry (DSC) analysis were carried out to characterize the chemical nature of the penetrant molecules and the physical changes in the polymer after swelling, respectively.

EXPERIMENTAL

Materials

The polymers used in the study were LDPE and EVA. EVA (vinyl acetate content = 18%) was procured from Hyundai Petrochemicals Co., Ltd. (Seosan Choongnam-Do, Korea). LDPE (grade Shriplas 2000; mp = 108°C, melt flow index at 190°C/2.16 kg = 40, density = 0.918 g/cc) was supplied by Shri Swasan Chemicals (M) Pvt., Ltd. (Chennai, India). The steady shear viscosity at 120°C for LDPE was 1300 cP, and for EVA, it was 7000 cP (measured with a rheometer from Anton Parr, GmBH, Germany). WAXD studies on the polymers before swelling showed that EVA had 28% crystallinity and LDPE had 40% crystallinity. The glass-transition temperatures of LDPE and EVA were −70 and −20°C, respectively (from dynamic mechanical analysis). Two grades of asphalt with different asphaltene contents were used in this study (grade 1, penetration index = 60/80; grade 2, penetration index = 80/100). The asphalt samples were supplied by Chennai Petroleum Corp., Ltd. (Chennai, India). The nomenclature for the samples used in the study is given in Table I.

Swelling and diffusion studies

Thin sheets of EVA and LDPE were compression-molded with a hydraulic press at 100 and 120°C, respectively, at a pressure of 50 bar. From these sheets, circular discs 2.5 cm in diameter and 1–2 mm thick were punched out for the swelling studies. Swelling experiments were carried out by the immersion of these polymer samples in asphalt under atmospheric pressure and at temperatures of 60 and 70°C for EVA and 70 and 90°C for LDPE. Isothermal experimental conditions were maintained by the asphalt being kept in an air oven that had an accuracy of ±1°C. Proper care was taken to check any evaporation loss and oxidation of asphalt by excessive exposure to atmospheric air. The swelling temperatures were selected to maintain the asphalt in the molten, liquid state and also to ensure that the polymer samples were not above their melting temperatures (T_ms). The polymer samples after immersion in asphalt were taken out at specific intervals of time and weighed. Samples removed from the asphalt medium were blotted with tissue paper. Small amounts of kerosene were used to remove the asphalt from the surface of the polymer samples. This was followed by cleaning with *n*-hexane. Cleaning was carried out carefully and quickly so that no kerosene or *n*-hexane residue was left on the samples during the weighing. Tests were conducted on duplicate samples simultaneously to ensure reproducibility of the measurements of sorption and swelling.

TABLE I
Nomenclature Used in the Study

Sample name	System
LDPE	LDPE without swelling
LDPE-H	LDPE kept at 70°C for 24 h
EVA	EVA without swelling
EVA-H	EVA kept at 70°C for 24 h
A-1	Asphalt grade 1
A-2	Asphalt grade 2
L/A-1	LDPE swollen in asphalt grade 1
L/A-2	LDPE swollen in asphalt grade 2
E/A-1	EVA swollen in asphalt grade 1
E/A-2	EVA swollen in asphalt grade 2

DSC studies were carried out on asphalts and on LDPE and EVA before and after swelling. DSC experiments were carried out on a Netzsch DSC 204 calorimeter between −120 and +200°C at a heating rate of 10°C/min for LDPE samples. For the asphalt and EVA samples, the temperature range was −100 to +100°C, and the heating rate was 10°C/min. The FTIR spectra of all samples were recorded at 25°C with a PerkinElmer FTIR machine with a resolution of 1 cm^{-1}.

To determine the asphaltene content of the asphalt samples,[1] 1–2 g of asphalt was refluxed with *n*-pentane for 15 min with continuous stirring. It was than allowed to stand for 8 h. The mixture was filtered with Whatman 42 filter paper and weighed. The asphaltene contents were found to be 32 and 37 wt % for A-1 and A-2, respectively.

RESULTS AND DISCUSSION

Swelling and diffusion studies were carried out on LDPE and EVA in asphalt at two different

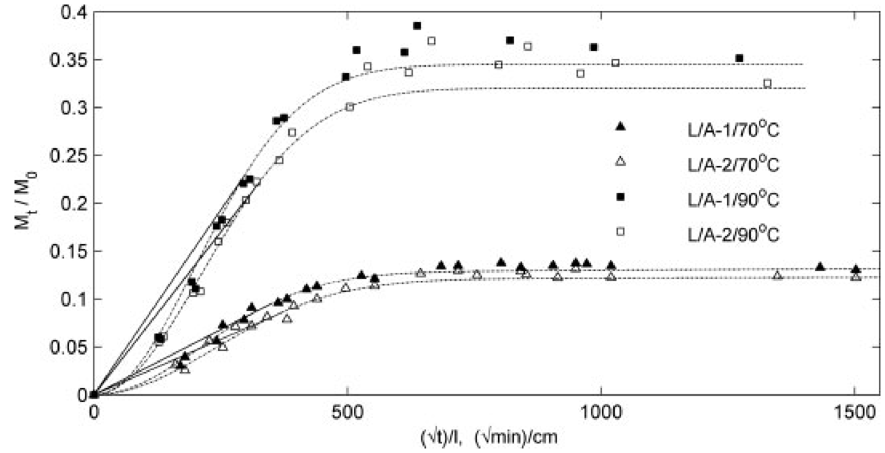

Figure 1 Relative weight uptake (M_t/M_0) versus $\sqrt{t}/l$ during asphalt sorption in LDPE at 70 and 90°C. The solid lines represent the Fickian model fit to the data, and the dotted lines represent the dual-sorption model fit. The Fickian model fit eventually merges with the dual-sorption model fit. Sigmoidal deviation and sorption overshoot (at 90°C) are evident.

temperatures and with two different grades of asphalt. The effects of the polarity of the polymers, asphaltene content of the asphalt, and swelling temperature on the diffusion characteristics of asphalt in the polymers are discussed in the following sections. Swelling experiments were carried out above the glass-transition temperatures of LDPE and EVA, which were semicrystalline in nature before swelling in asphalt.

Swelling and diffusion

The mechanism of transport of small molecules in polymers can be Fickian or non-Fickian, depending on various factors. In this work, gravimetric measurements were taken periodically on the polymer samples swollen in asphalt to study the swelling and diffusion characteristics.[15–17] In gravimetric studies, the amount of the organic solvent absorbed into the polymer with respect to time can be represented with the following relationship:

$$M_t = kt^n \qquad (1)$$

where M_t is the penetrant uptake at time t. The value of exponent n indicates the type of transport mechanism. When $n = 0.5$, the mechanism of transport is considered Fickian or case I transport. This occurs when the rate of diffusion of the penetrant is slower than the polymer segmental mobility. When the value of n deviates from 0.5, the mechanism of transport can be considered non-Fickian. In particular, when $n = 1$, the diffusion mechanism is called case II transport. It is a special case in which the penetrant front moves with a constant velocity. When n is between 0.5 and 1, the mechanism of transport is considered anomalous. In the case of anomalous transport, the diffusion and molecular relaxation rates of the polymer molecules are comparable. k is a constant that depends both on the interaction between the diffusing species and the polymer and on the structure of the polymer. It can be related to the diffusion coefficient for Fickian transport and is proportional to the front velocity in the case of case II transport.[15,16] From curves of the mass uptake of the penetrant versus time (Figs. 1 and 2), the values of n for LDPE and EVA in asphalt were calculated, and the results are given in Table II. The values of n were determined from the linear region of the mass-uptake curves being taken into account. The estimated values of n indicate that the transport of asphalt components into EVA at 60°C can be considered Fickian. However, the mechanism of transport in EVA became anomalous when the temperature of swelling was raised to 70°C. In the case of LDPE, the diffusion mechanism was anomalous at 70 and 90°C. The details are in the following sections.

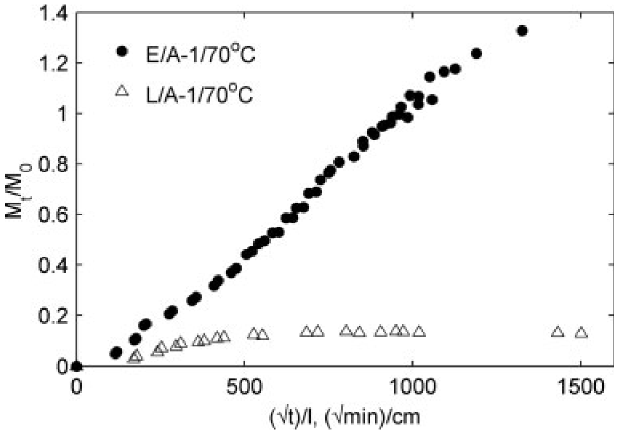

Figure 2 Comparison of asphalt uptake into EVA and LDPE at 70°C.

TABLE II
Values of *n*

Polymer and temperature	Asphalt	
	Grade 1	Grade 2
EVA at 60°C	0.54	0.53
EVA at 70°C	0.66	0.66
LDPE at 70°C	0.66	0.62
LDPE at 90°C	0.77	0.74

Diffusion mechanism

The swelling and diffusion studies were carried out with EVA and LDPE above their glass-transition temperatures, and both polymers were semicrystalline in nature. In the case of one-dimensional diffusion for a thin plane sheet of a polymer, with equal surface concentrations on either side of the sheet, the diffusivity can be determined with the following relationship:[18]

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}e^{-\frac{D\pi^2(2n+1)^2t}{l^2}} \qquad (2)$$

where D is the diffusion coefficient; M_t and M_∞ are the masses of solvent uptake at time t and at equilibrium, respectively; and l is the initial thickness of the polymer specimen. Equation (2) is applicable in the case of Fickian transport. However, for EVA swollen at 70°C and LDPE swollen at 70 and 90°C, the sorption-uptake curves show non-Fickian, anomalous behavior (refer to the *n* values from Table II and sigmoidal regions in Figs. 1 and 2). In the case of LDPE (at both swelling temperatures) and EVA at 70°C, the sorption-uptake curves are sigmoidal in shape during the initial period of swelling. Sigmoidal initial sorption describes polymer–penetrant systems that exhibit uptake curves with an inflection point when the mass uptake is plotted against the square root of time (Fig. 1). It is characterized by a lower diffusion coefficient in comparison with the Fickian diffusion. Anomalous, sigmoidal uptake behavior has been observed in many glassy and rubbery polymers, regardless of their amorphous or semicrystalline nature. The sigmoidal, anomalous penetrant uptake has been attributed to various factors such as stress effects, simple swelling, coupled diffusion and thermal effects, a surface layer with properties different than those of the interior, and solvent-induced plasticization of the polymer.[19] Many authors have tried to separate each of these effects with various experimental and theoretical approaches. In the case of LDPE and natural rubber, s-shaped, sigmoidal uptake trends were observed in the rubbery state when swelling studies were carried out in *n*-hexane and limonene.[19,20] Inclusion of a time-dependent surface concentration parameter was the only way to fit the observed s-shaped sorption curves. In this study, the mechanism of the sigmoidal uptake observed in the case of LDPE and EVA could not be elucidated because of the lack of enough experimental data (not included in the present scope of the study) and because of the complex nature of the system. Further studies are needed to establish the appropriate mechanism of diffusion in LDPE and EVA observed at higher temperatures, which could explain the sigmoidal uptake behavior. However, the models used to explain the sigmoidal uptake observed in glassy polymers and composites could be effectively used to fit the observed behavior, although they may be inadequate to explain the mechanism responsible for the sigmoidal uptake observed in rubbery polymers. The anomalous, sigmoidal penetrant uptake observed in glassy polymers is attributed to either polymer–penetrant interaction or coupled diffusion–relaxation mechanisms. There are several non-Fickian diffusion models available in the literature that explain the anomalous diffusion observed in glassy polymers and composites.[21] However, there are not many studies in which anomalous, sigmoidal uptake or sorption overshoot is observed in the case of rubbery polymers. At 90°C, LDPE shows a sigmoidal region in the initial stages of sorption uptake and a sorption overshoot at a later stage. Sorption-uptake curves for EVA at 60°C show Fickian diffusion, whereas EVA at 70°C shifts to anomalous transport with an initial sigmoidal uptake. No sorption overshoot was observed in the case of EVA at the experimental temperatures. The sigmoidal uptake observed in EVA at 70°C could be due to a polymer–penetrant interaction, which could be possible in the case of EVA because of its chemical structure. In the case of LDPE, the sigmoidal nature of the curve could be due to the coupled thermal and diffusion effects or polymer–penetrant interactions taking place at elevated temperatures or time-dependent surface concentration changes, which can result in a two-stage diffusion process. In the case of polymer–penetrant interaction as well as the coupled diffusion–relaxation mechanism observed in glassy polymers and composites, the equation for diffusion reduces to that of a dual-adsorption model used to explain the sigmoidal uptake observed in certain polymer composites.[21–23] In the dual-adsorption model, the penetrant molecules can get bound to microvoids that have a large enough volume to accommodate many molecules at a time by an adsorption process. Essentially, the model explains the slowing of uptake of penetrants when penetrants interact with the polymer. Bond and Smith[21] reasoned that in the case of moisture absorbed into an epoxy polymer, the amount of moisture absorbed by dissolution becomes related to the extent to which the interaction occurs and the effect of the interaction on the polymer network. They have suggested that as the penetrant molecule is polar and capable of interrupting the polymer network, it can possibly become chemically bound to sites within the network. Because there is a possibility of polymer–penetrant binding, the absorption mechanism can be called a dual-mode sorption, in which some penetrant molecules are diffused normally within the polymer, whereas others are partially immobilized by interaction with polymer molecules. At higher temperatures, asphalt and polymers such as LDPE and EVA could exhibit such diffusion processes. Hence, the dual-sorption model is used in this study to explain the sigmoidal uptake observed. In the dual-absorption model, for an initially dry sample, if P_D is the probability that the bound molecules will become free and P_L is the probability that the free molecules will become bound, when P_D and P_L are much smaller than $\frac{\pi^2 D}{l^2}$, the penetrant uptake can be expressed as follows:[24]

$$\frac{M_t}{M_\infty} = 1 - \frac{P_L e^{-P_D t}}{P_L + P_D} - \frac{8P_D}{\pi^2(P_L + P_D)} \times \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{-\frac{D\pi^2(2r+1)^2 t}{l^2}} \quad (3)$$

Because equilibrium swelling could not be observed in the case of EVA, the sorption coefficient (S), defined as the ratio of the mass of asphalt diffused at equilibrium (M_∞) to that of the initial mass of the dry polymer (M_0), could be used to eliminate M_∞ from eqs. (2) and (3).

Hence, with $\frac{M_\infty}{M_0} = S$, we get

$$\frac{M_t}{M_0} = S\left[1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{-\frac{D\pi^2(2n+1)^2 t}{l^2}}\right] \quad (4)$$

$$\frac{M_t}{M_0} = S\left[1 - \frac{P_L e^{-P_D t}}{P_L + P_D} - \frac{8P_D}{\pi^2(P_L + P_D)} \times \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{-\frac{D\pi^2(2r+1)^2 t}{l^2}}\right] \quad (5)$$

Equation (4), the expression for Fickian diffusion, was used for analyzing the swelling of EVA at 60°C because it follows a Fickian mode of transport. Equation (5), which is used in the case of the dual-sorption model, is applied in the case of LDPE and EVA swollen at 70°C to fit the experimental data, and diffusion coefficients were determined.[25] The diffusion coefficients obtained thus for LDPE and EVA in asphalt are given in Table III. In the case of solid polymers, the diffusion coefficient is known to increase as the molecular size of the diffusant decreases. Diffusion coefficients are found to be higher in the case of LDPE, and this indicates that smaller molecules could be penetrating LDPE in comparison with EVA.

TABLE III
Diffusion Coefficients of Asphalt in LDPE and EVA

Polymer and temperature	Diffusion coefficient × 10^8 (cm^2/min)	
	Asphalt 1	Asphalt 2
EVA at 60°C	9.1	9.1
EVA at 70°C	5.8	5.8
LDPE at 70°C	77	65
LDPE at 90°C	84	74

Effect of the polymer type

The solvent-uptake curves for EVA and LDPE in asphalt at 70°C are shown in Figure 2. During the initial period of swelling, both polymers show a sigmoidal uptake with a low rate of diffusion. The uptake of asphalt into the polymer reached equilibrium in the case of LDPE after 20 h at 70°C, whereas the uptake of asphalt contents into EVA kept increasing with time (120% weight change after 18 days of exposure to asphalt). The EVA samples became soft and rubbery after prolonged exposure to asphalt. In the case of LDPE samples, the mass uptake reached equilibrium and remained constant for long periods, indicating no further diffusion of asphalt components into LDPE. It is important to note that asphalt is also a complex colloidal mixture of various components such as saturates, asphaltenes, and aromatics with different degrees of polarity. Hence, it is probable that one or more components could migrate into the polymer, depending on the polarity of the polymer. The diffusion coefficients are also different for the two polymers, indicating differences in the size of the diffusing molecule. This indicates that there is a preferential diffusion mechanism depending on the type of polymer used. To verify this, IR studies were carried out on the swollen polymer samples, which showed that the diffusing components are different in the case of LDPE and EVA. Details of the chemical nature of the diffusant are discussed in the Effect of Polymer Crystallization section.

Effect of temperature

Sorption-uptake curves at 70 and 90°C for LDPE and at 60 and 70°C for EVA are shown in Figures 1 and 3. The shape of the sorption-uptake curve is sigmoidal in the case of EVA swollen at 70°C, whereas it is close to Fickian behavior at 60°C. Because of the sigmoidal uptake at 70°C, the diffusivity decreases slightly at that temperature. This could be due to the

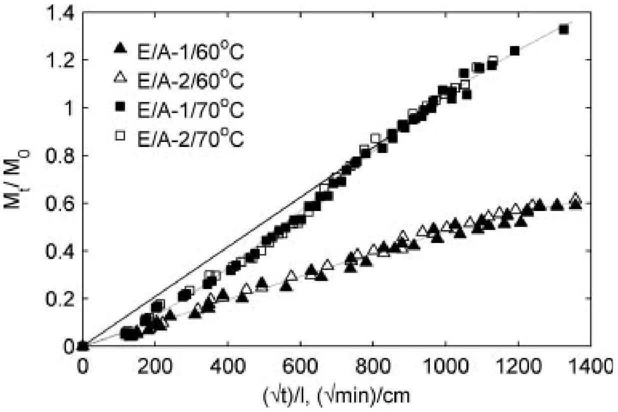

Figure 3 Relative weight uptake (M_t/M_0) versus $\sqrt{t}/l$ during asphalt sorption in EVA at 60 and 70°C. The Fickian model fit to the data is shown in the case of EVA at 60°C. For EVA at 70°C, the solid lines represent the Fickian model fit to the data, and the dotted lines represent the dual-sorption model fit. The Fickian model fit eventually merges with the dual-sorption model fit. Sigmoidal deviation for EVA swollen at 70°C is evident.

possible polymer–penetrant interaction found at the higher temperature in the case of EVA. In the case of LDPE, there is a significant difference in the shapes of the sorption-uptake curves at 70 and 90°C. For LDPE, a sorption overshoot appears at 90°C, which is characterized by a sorption-uptake curve with an absorbed penetrant content higher than the final equilibrium content.[21] Similarly, the values of n deviate from close to Fickian transport to close to anomalous transport at the higher temperature. The overshoot in sorption-uptake curves is considered to be due to the ongoing crystallization process in the case of semicrystalline polymers.[26–28] In the case of LDPE, the crystallization process undergoes changes due to the temperature and the presence of the penetrant molecules. The crystallization started around 80°C when LDPE was swollen in asphalt at 90°C, whereas the crystallization started only at 89°C when the experimental temperature was 70°C. Hence, when swelling is carried out at 90°C, the crystallization of the ordered regions of the polymer starts at lower temperatures, and the available volume for penetrant molecules decreases. This results in the ejection of penetrant molecules from LDPE. The overshoot was not observed in EVA and LDPE at 70°C because of the higher crystallization temperatures compared to the swelling temperature. Detailed discussion on the effects of swelling on the crystallization of the polymers is given in the Effect of Polymer Crystallization section.

Effect of the asphalt type

The asphaltene content, which mainly differentiates the two grades of asphalt, does not seem to affect the diffusion and swelling in EVA (Fig. 3). However, in the case of LDPE, the diffusion coefficients are slightly lower in the case of A-2, which has a slightly higher asphaltene content (Fig. 1). The asphaltenes and aromatics are more polar and have higher molecular weights than the saturates found in asphalt. Polarity can play two roles in this case. The polar–polar interaction can result in a decrease in the diffusivity and also can affect the selectivity of a particular component from the asphalt to diffuse into the polymer. This indicates that the diffusant species in EVA could be asphaltene or the polar aromatics. Diffusion coefficients are also lower in the case of EVA, indicating larger molecules diffusing from asphalt into EVA compared to LDPE.

Polymer–asphalt interactions

FTIR absorption peaks corresponding to asphaltene (a polar, aromatic component of asphalt) were compared with asphalt-swollen samples of LDPE and EVA to study the chemical nature of the penetrants diffusing into the polymers (Table IV). Many of the characteristic absorption peaks observed in asphalt are common to both LDPE and EVA too (Figs. 4 and 5). This makes the identification of the diffusing groups difficult. The nonpolar and less polar saturates and waxes found in asphalts have characteristic IR absorption peaks similar to those of LDPE and

TABLE IV
Characteristic FTIR Spectral Bands of Asphaltenes and Asphalt-Swollen EVA and LDPE

Band (cm^{-1}) in asphaltene	Structural feature	EVA/asphalt (60°C)	EVA/asphalt (70°C)	LDPE/asphalt (70°C)	LDPE/asphalt (90°C)
3433	—OH stretch	3456[a]	3455[a]	Absent	Absent
3052	Aromatic C—H stretching	Broad peak[a]	Broad peak[a]	Broad peak[a]	Broad peak[a]
2930–2700	Aliphatic C—H stretching	Absent	2777[a]	2865[a]	2951, 2835[a]
1600	Aromatic C=C stretching	1604	1600	1599	1601
1464, 1378	Aliphatic C—H bending	Broad peak[a]	Broad peak[a]	1452,[a] 1375[a]	1464,[a] 1364[a]
1031	S=O stretching	Broad peak[a]	Broad peak[a]	Absent	1033
869, 806, 746	Aromatic C—H bending	748	Absent	808	867, 811

[a] Peak common to the polymer and asphalt.

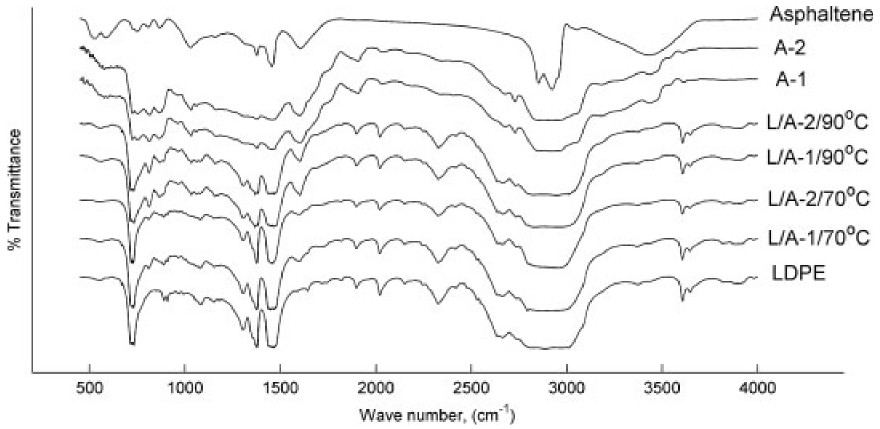

Figure 4 FTIR spectra of A-1, A-2, asphaltene, and LDPE before and after swelling.

EVA. However, an earlier work on asphalt structure[22] suggested that the more polar asphaltenes have OH groups and pyridine-like structures with absorptions at 3400 and 1600–1430 cm^{-1}, respectively. These groups are found only in the asphaltene part and could be used as markers for identifying the penetrant molecules in the polymer. Using the aforementioned groups, we have tried to analyze whether the asphaltenes are predominantly moving into one of the polymers on the basis of polar–polar interactions. The observations show that the IR peaks corresponding to the OH and pyridine groups are present in asphalt-swollen EVA, indicating that asphaltenes may be diffusing into the polar EVA. The diffusion coefficients also indicate that larger molecules such as asphaltenes may be penetrating EVA, resulting in the lower diffusivity compared to that of LDPE. The other characteristic peaks of asphaltenes are the C=C stretching at 1600 cm^{-1} and the S=O stretching at 1031 cm^{-1}. These could be observed in asphalt-swollen LDPE and EVA. The intensity of the C=C peaks increased when swelling was carried out at a higher temperature for both polymers, indicating higher amounts of asphalt diffusing into the polymers. In the case of EVA, when the temperature was increased from 60 to 70°C, the spread of the C=C peak increased, and this indicated possible chemical interactions. This could also explain the lower diffusivity values for EVA at 70°C and the sigmoidal uptake curve. The S=O stretching band at 1031 cm^{-1} was present at a lower intensity when swelling of LDPE was carried out at 90°C and was absent at 70°C. This could be due to mild aging of the asphalt at that swelling temperature. The S=O stretching band could not be identified in the case of EVA because there was a broad peak between 1500 and 700 cm^{-1}. Aromatic C—H bending was observed in the case of LDPE but was not prominent in the case of EVA. However, aromatic C—H stretching was observed in the case of asphalt/EVA at 70°C. Aliphatic C—H stretching was observed for the swollen LDPE at both temperatures, indicating the migration of characteristic aliphatic groups to LDPE. From this discussion, it may be

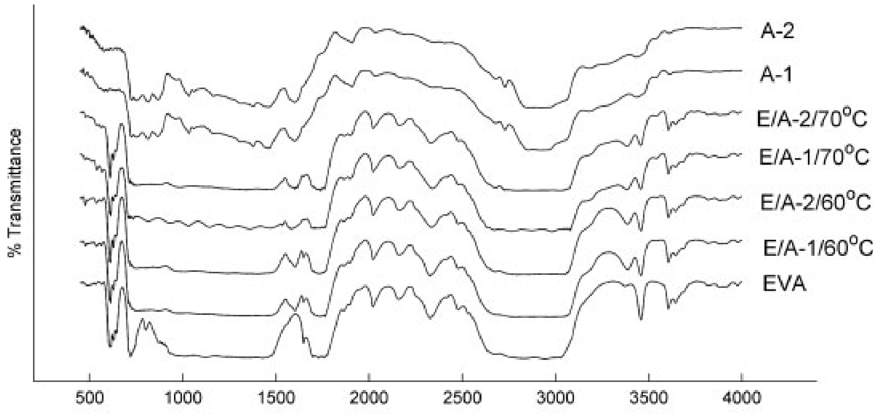

Figure 5 FTIR spectra of A-1, A-2, and EVA before and after swelling.

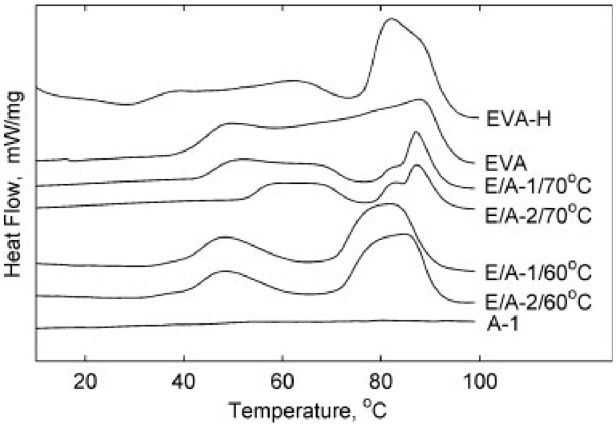

Figure 6 DSC scans of EVA before and after swelling, EVA after heating at 70°C for 24 h, and asphalt grades 1 and 2.

concluded that the species migrating into LDPE is not asphaltene.

In the case of EVA, the characteristic IR peak corresponding to 1700 cm^{-1} indicates the presence of carbonyl groups (Fig. 5). After swelling in A-1 and A-2 at 60 and 70°C, the intensity of the carbonyl group decreases, especially at the higher temperature, and this indicates probable chemical reactions involving this functional group.

Effect of polymer crystallization

Solvent-induced crystallization is a known phenomenon in many polymers below their glass-transition temperature[28] and in a few polymers above the glass-transition temperature, including LDPE.[26,27,29] Pure EVA shows a broad melting peak (T_m) around 87.6°C with a hump at 49.8°C (Fig. 6). The asphalt-swollen samples of EVA (swelling temperature = 60°C) show two clear crystalline melting peaks. The second melting peak shifts to a lower temperature compared to that of pure EVA. This is more prominent in the case of A-1 swollen samples compared to A-2 swollen samples. The crystalline regions of EVA undergo various changes during swelling, as can be observed in Table V and Figure 6. The crystalline regions corresponding to the melting peak of unswollen EVA (87.6°C) decrease in area, and a second broad melting peak appears at a lower temperature. When swelling is carried out at 70°C, there may be more crystallites melting, and this results in a reduction of the width of the second T_m peak. It is clear from the DSC studies of swollen and unswollen EVA that the crystallization and melting of crystallites are affected by the penetrant molecules. Penetrant-uptake curves did not show any sorption overshoot in the case of EVA, which is characteristic of penetrant-induced crystallization. Hence, it may be concluded that the penetrants diffusing into EVA may be plasticizing the rubbery regions.

TABLE V
Crystalline Melting Characteristics of Asphalt-Swollen EVA and LDPE in Comparison with LDPE, EVA, and Asphalt

	T_{m1} (°C)	T_{m2} (°C)
Asphalt 1	—	—
Asphalt 2	—	—
Pure EVA	50	88
EVA-H	61	82
E/A-1/60°C	50	82
E/A-2/60°C	48	85
E/A-1/70°C	52	87
E/A-2/70°C	62	87
Pure LDPE	—	113
LDPE-H	82	108
L/A-1/70°C	89	109
L/A-2/70°C	91	110
L/A-1/90°C	83	109
L/A-2/90°C	85	109

EVA-H and LDPE-H represent DSC of EVA and LDPE, respectively, after heat aging of the polymers at 70°C for 24 h.

The T_m values of swollen and unswollen samples of LDPE are given in Table V. The melting peak of unswollen LDPE, which is around 112°C, is split into two clear peaks with another melting peak around 89–91°C for LDPE swollen in asphalt at 70°C, and the second peak shifts further to 82–85°C when it is swollen at 90°C.

To verify whether crystallization in LDPE and EVA was due to aging, the unswollen polymer samples were subjected to aging at 70°C for 24 h, and DSC scans were carried out (EVA-H and LDPE-H in Figs. 6 and 7, respectively). The results show that exposure to a high temperature for a prolonged time can help the ongoing crystallization and melting processes in LDPE and EVA. The melting peaks

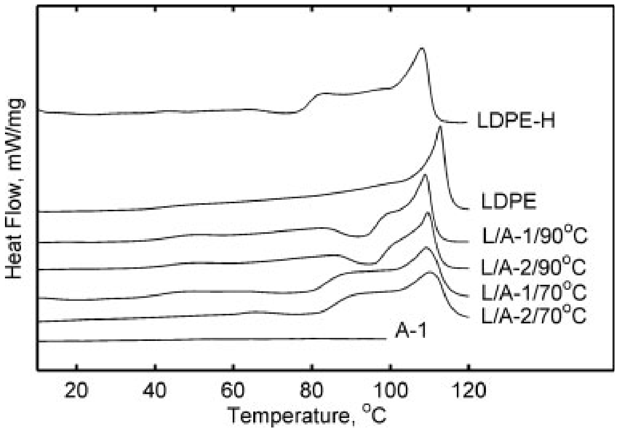

Figure 7 DSC scans of LDPE before and after swelling, LDPE after heating at 70°C for 24 h, and asphalt grades 1 and 2.

change in their width as well as position (Figs. 6 and 7 and Table V). If we compare the asphalt-swollen LDPE samples with aged samples (all at 70°C), it can be observed that the presence of penetrants from asphalt affects T_{m2} significantly, which is the main melting peak. In the case of aged polymers, T_{m2} decreases by 5–6°C, whereas in the case of asphalt-swollen samples, the effect is less pronounced (1–3°C). This could be due to the penetrant-induced crystallization overlapping with the melting process. T_{m1} shows behavior different from that of T_{m2} for LDPE and EVA. In the case of LDPE, T_{m1} appears on heat aging at 82°C, and it is at 89–91°C when LDPE is swollen in asphalt at 70°C. For EVA, T_{m1} shifts from 50 to 61°C on heat aging and is not affected by the presence of asphalt in A-2. However, T_{m1} is at 52°C when swelling is conducted in A-1. This indicates that in LDPE and EVA, the crystallization and melting are affected by the presence of asphalt.

CONCLUSIONS

Asphalt components were found to migrate to polar EVA and nonpolar LDPE upon swelling in asphalt. The total amount that diffused into EVA was an order of magnitude higher than that for LDPE. The diffusion of asphalt components into the polymer was found to be affected by the type of polymer, the swelling temperature, and the asphaltene content. The diffused molecules had a significant effect on the crystallization behavior of the polymers. The chemical nature of the penetrating molecules was different in EVA and LDPE, and the diffusion mechanisms were mostly anomalous because of polymer–penetrant interactions and the penetrant-induced crystallization in the case of LDPE. The study indicates that during processing as well as storage and service, it is possible for the asphalt components to migrate to the polymer. This could result in an unsteady colloidal state of the asphalt and softening of the polymer. This study indicates that the selection of a polymer for modifying the asphalt, optimization of the processing and storing conditions of the PMA, and long-term performance of the PMA will depend on the migration of the asphalt components into the polymer.

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