

# Preparation and Characterization of Asphalt-Modified Polyethylene Blends

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Eight asphalt samples from four manufacturers with grades from AC-10 to AC-30 were characterized by  $^{13}\text{C}$  nuclear magnetic resonance, dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). Glass transition temperatures ( $T_g$ s) and activation energies for the relaxation process of the asphalt were determined with DMA experiments. Polyethylene, a recyclable waste that is abundantly available either as virgin material not included in specifications or from solid waste classification processes, was slightly chlorinated to improve its compatibility with asphalt. High-density polyethylene (HDPE), chlorinated polyethylene (CPE), and maleated polyethylene (MGPA)-modified asphalts were studied with DMA in both bending and shear modes. DSC, fluorescence reflection microscopy, and Fourier transform infrared were also employed to characterize the polymer-modified asphalts. Creep resistance and low-temperature crack resistance of the asphalt and the polymer-modified asphalts were evaluated. The results confirm that CPEs with low chlorine contents (< 15 weight percent) are more compatible with asphalt than is HDPE. Marked improvements in blend properties are also observed with MGPA, provided that the degree of maleation does not exceed 3 percent.

Blends of polymeric materials with asphalt are complex and characteristically unique paving material systems. For any specific asphalt cement (AC), the physical properties of the asphalt-polymer blend are affected by the amount of polymeric material added, its composition, its molecular weight, and so on, but the most important variable may be the compatibility of the AC with the admixed polymer. The ability to enhance polymer-asphalt compatibility is complicated further by the variations in asphalt compositions within a given grade (1). Our research efforts are directed toward developing a simple method to estimate the compatibility of polymer additives with asphalt, to assess the phase structure of the asphalt-additive mixture, and to compare blended polymer-asphalt performances with those of the pure asphalt matrix. Chemical modification of polymers facilitates the preparation of polymer additives with varying degrees of crystallinity and polarity, factors that influence the compatibility of polymers in a matrix. Using dynamic testing techniques, we have assessed the performance of ACs modified with polyethylene that have been subjected to various degrees of chlorination and maleation.

Polymer additives should reduce the temperature sensitivity of ACs by increasing the high-temperature viscosity. Ideally, the resultant binder should have a very low thermal sensitivity throughout the range of use, but a low viscosity at mixing

temperatures (2). Resistance to permanent deformation as well as tensile and fatigue strength should be enhanced relative to the properties of the unmodified asphalt. However, the binder must maintain good adhesive properties and exhibit high aging resistance. A suitably modified binder should exhibit reduced plastic deformation at high temperatures, better low temperature resiliency, and better performance in service under heavy oscillatory loads.

The most important parameter governing the success of a polymer modifier in asphalts is its compatibility. The asphaltene are suspended in the oils by the resins, making asphalt a colloidal system. The introduction of any incompatible polymer under agitation into such a system at high temperature generally results in asphaltene flocculation and oil bleeding, leading to a binder having no cohesion (2). Polymers must improve not only AC properties, but the performance of binder-aggregate combination as well (3).

Plastics give strength to the asphalt, but the ability to recover from extension is lost (4). Thermoplastics that are partially crystalline, such as polyethylene (PE) and polypropylene (PP), have attracted increasing attention because this class of polymer combines the advantages of rubber and fibers. The crystalline segments of polyolefins serve as high-strength fillers in the asphalt-polymer blend and improve the blend properties over all service conditions. However, the polyolefins are only slightly compatible with asphalt; thus, the blends tend to separate at high temperatures. Ethylene-vinyl acetate copolymers (EVA) are more compatible and improve resistance to permanent deformation and increase modulus (3). The presence of vinyl acetate comonomers decreases the crystallinity of the PE blocks, leading to increased flexibility and toughness. In one study on surface dressings, the EVA-modified asphalt ranked among the best of the asphalts tested in the areas of fatigue resistance and field performance (5).

PE is a potentially useful modifier for increasing the low-temperature fracture toughness of asphalt concrete (6), and it may confer additional pavement stability at elevated temperatures, which would minimize rutting and distortion caused by creep. Further, because polyolefins make up approximately 60 percent of plastic solid wastes, a reliable source of PE, either from virgin material or from recycled waste, is assured. HDPE is highly crystalline, but the amorphous domain exhibits a low glass transition temperature. This allows PE to contribute additional toughness and ductility at low temperatures to PE-asphalt blends, particularly those prepared from soft asphalts. However, it is known that asphalt-PE mixtures have a tendency toward gross phase separation (i.e., gross incompatibility) when standing at an elevated tem-

perature for long periods (7). Therefore, modification of PE is needed to enhance its compatibility with asphalt. Chlorination of PE is a simple technique to change the polarity, reduce the crystallinity, and increase the density of the polymer to match the density of asphalt. If the density of the polymeric additive is comparable with that of the asphalt matrix, the driving force for gross phase separation is minimized. Partially chlorinated polyolefin waxes are known to improve stability of asphalt-polymer blends (8,9), so we elected to prepare and characterize PEs with various degrees of chlorination to improve the polymer interaction with polar components of asphalt. The extent of chlorination can be used to vary the crystallinity of the polymer additive.

## EXPERIMENTAL WORK

### Nuclear Magnetic Resonance and Fourier Transform Infrared Characterization of Asphalt

The application of nuclear magnetic resonance (NMR) to the analysis of asphalt samples is well established (10-12). Samples were dissolved in deuterated chloroform at a concentration of 10 percent [weight/volume (w/v)]; spectra were measured using Bruker 200 MHz Fourier transform nuclear magnetic resonance. A relaxation agent, Cr(acac)<sub>3</sub>, 12 mg/ml, was added to the <sup>13</sup>C NMR samples. Using an interpulse time of 6 sec and more than 8,000 scans, reliable quantitative spectra can be obtained (13). The observations on eight samples of Louisiana asphalts are summarized in Table 1. Asphalt samples, 5 percent (w/v) chloroform solution in a 1-mm cell were examined by quantitative Fourier transform infrared

(FTIR) using a Perkin Elmer 1700 FTIR. The overlapped peaks in 1550-1800 cm<sup>-1</sup> were resolved by a curve fitting program based on the work of Petersen and his colleagues (14). The results (Table 1) show significant differences in composition among asphalt samples of the same grade.

### Crystallinity of Asphalt

Linear paraffins present in asphalt readily crystallize. The relative crystallinity of a given asphalt can be measured by DSC (15,16). A Seiko DSC 220C calibrated for temperature and enthalpy with indium was employed to estimate the relative volume of the crystalline phase in each of the asphalt samples. The DSC was conducted on  $\approx$  10 mg samples sealed in an aluminum sample pan using an empty aluminum sample pan with cap as a reference. Initially each sample was cooled at 3°C/min to -45°C and then heated at 3°C/min. The heats of fusion ( $\Delta H_f$ ) observed are listed in Table 1. The percent crystallinity was estimated from this data by assuming that completely crystallized hydrocarbons in an asphalt matrix exhibit an average enthalpy of 200 Joules/gram (J/g).

### Chlorination of Polyethylene

HDPE was supplied by Paxon Polymer Co. The polymer had weight and number average molecular weights of  $8.5 \times 10^4$  and  $1.9 \times 10^4$ , respectively; M.I. = 25, m.p. 131°C,  $\Delta H_f$ , 343 J/g. Solution chlorination was performed in 1,1,2,2-tetrachloroethane (TCE); the polymer was dissolved at 130°C to a concentration of 7 percent (w/v) under nitrogen flow. The

TABLE 1 NMR and DSC characterization of asphalt composition

Sample	ACA	ACB	ACC	ACD	ACE	ACF	ACG	ACH
Grade	AC-10	AC-20	AC-10	AC-20	AC-10	AC-20	AC-20	AC-30
Arom H%	5.5	6.1	6.9	6.0	6.3	6.8	7.1	5.7
Arom C%	28.2	30.4	37.3	34.1	33.4	33.7	34.0	24.5
Linear Aliph%	41.8	41.6	22.5	21.8	19.5	21.2	22.3	23.2
Phenolics <sup>a</sup>	0.0086	0.0058	0.0069	0.003	0.012	0.0093	0.0036	0.004
Pyrrolics <sup>a</sup>	0.0142	0.0112	0.0225	0.0135	0.0137	0.014	0.0145	0.0137
Carboxylic Acid <sup>a</sup>	0.109	0.0828	0.0318	0.021	0.0220	0.0311	0.0242	0.0324
Ketone <sup>a</sup>	0.133	0.13	0.0275	0.0195	0.0796	0.043	0.027	0.0362
Quinolone <sup>a</sup>	0.0412	0.0298	0.0269	0.027	0.023	0.0238	0.0175	0.0109
Sulfoxide <sup>a</sup>	0.0022	0.001	0.0014	0.0036	0.0043	0.004	0.0008	0.0015
$\Delta H_f$ (J/g)	7.7	7.8	8.5	9.2	5.8	8.6	11.3	9.6
% cryst. <sup>b</sup>	3.9	3.9	4.3	4.6	2.9	4.3	5.7	4.8
Cracking Temp T <sub>c</sub> (°C)	-12	-9	-3	-5	-20	-10	0	-3

<sup>a</sup> in mmol/g asphalt.

<sup>b</sup> Average entropy for 100% crystallinity = 200 J/g [14]

solution was then maintained at 110°C under a constant flow of chlorine gas, and the reaction was initiated with 2,2-azobis(2-methylpropionitrile) (AIBN), 0.02 g/l g of HDPE. After the desired reaction time, the reaction mixture was quenched in a large volume of methanol. The product was separated by filtration, washed several times with methanol, and vacuum dried at 55°C for a week. The properties of the CPEs prepared for this study are as follows: CPEA, 2.7 weight percent Cl, mp 125°C,  $\Delta H_f$ , 301 J/g; CPEB, 8.9 weight percent Cl, mp 114°C,  $\Delta H_f$ , 206 J/g; CPEC, 15.2 weight percent Cl, mp 106°C,  $\Delta H_f$ , 99 J/g; and CPE D, 2.7 weight percent Cl, amorphous. The microstructure and morphology of chlorinated PEs have been reported (17,18), and the factors controlling these parameters are documented. Asphalt polymer blends (APBs) were prepared by melting the desired quantity of polymer (PE or CPE) in asphalt at 150°C while stirring at a rate of 200–500 rpm for 2 hr under N<sub>2</sub> atmosphere. All APBs contain 5 percent by weight of polymer unless otherwise mentioned.

### Preparation of Maleated PE

The maleation was conducted using conditions described by Gaylord (19). Low-density polyethylene (LDPE), 20 g, MI = 0.22, was dissolved in 150 ml dichlorobenzene (DCB) at 130°C, and a mixture of 4 g of maleic anhydride (MAH) and 0.68 g triethyl phosphate (TEPA) was added. After raising the reaction temperature to 150°C, the maleation was initiated by adding 1 ml dicumyl peroxide (DCP) solution (0.5 g DCP in 15 ml DCB); further 1 ml aliquots of DCP solution were injected every 15 min. The MAH content was controlled by reaction time. The polymer used in this study was allowed to react for 1 hr; the resultant maleic anhydride content was 2.8 weight percent. At the end of the reaction, the solution was allowed to cool to room temperature and poured into 750–1000 ml methanol; the precipitate was washed several times with methanol and dried in vacuo at room temperature for more than 72 hr.

The maleated polymers were mixed with asphalts at 180°C under N<sub>2</sub> for 4 hr. The polymer contents are 5 weight percent unless otherwise mentioned.

### DMA Bending Mode Measurements

In a typical DMA experiment, an asphalt sample was heated to 150°C in a sand bath. The asphalt sample was then poured into a brass mold and kept at room temperature for at least an hour. The sample size was 50 mm long, 10 mm wide and 1.68 mm thick. The sample was run in bending mode at cooling rate of 1°C/min using 0.1 percent strain at the desired frequency. The  $T_g$  was identified as the temperature corresponding to the maxima of loss modular  $E''$  at each frequency. Imposition of a larger strain (1 percent) on the asphalt samples at 50 Hz in DMA experiments will induce cracking at a specific temperature during the cooling. The temperature, called cracking temperature ( $T_c$ ), can be used to estimate the low-temperature cracking resistance of asphalt or asphalt/polymer blends.

### DMA Shearing Mode Measurements

The shearing mode measurements were conducted at temperatures well above the glass transition temperature of asphalts and polymers employed. The samples were "sandwiched" between two parallel plates with a size of 10 × 10 mm. Sample thickness was held to about 1.5 mm, measured with a deviation of ±0.05 mm. Master curves were used with reference frequency of 20 Hz.

## DISCUSSION OF RESULTS

### Compatibility Analysis by Differential Scanning Calorimetry

The thermal behavior of asphalts is complex, and depends on their sources, methods by which they are manufactured, and thermal history. In a typical asphalt there are three transition temperatures ( $T_r$ ) at -42°C ( $T_{r1}$ ), -10°C ( $T_{r2}$ ) and 43°C ( $T_{r3}$ ), and one melting peak at 28°C. A thermogram of a chlorinated PE containing 15.2 percent chlorine (CPEC) exhibits two transition temperatures at -15°C and 80°C, Figure 1, curve E. Because of the high-scale expansion required to illustrate the low temperature transition, the melting peak at 106°C is completely off scale.

The DSC curves of AC10-CPEC blends of various concentrations are compiled in Figure 1. In Curve C, obtained with a blend of CPEC with AC10 (20/80, w/w), the following changes are observed: a new  $T_r$  is observed at -13°C instead of  $T_{r2}$ s at -10°C and -15°C for AC10 and CPEC respectively, the melting peak for AC10 and  $T_r$  at 80°C of CPEC disappear, leaving an intermediate  $T_r$  of 42°C, and the melting peak for CPEC is lowered to 95°C. The melting peak of AC10 cannot be seen in all blends, but the  $T_{r3}$  transition becomes stronger when polymer concentration is increased. The melting peak of CPEC was shifted downward a maximum of 12° at a CPEC concentration of 10 weight percent. Figure 2 is a compilation of thermograms of AC10-HDPE blends at various concentrations. Note that  $T_{r1}$  broadens as the concentration of HDPE is increased,  $T_{r2}$  disappears at 30 percent HDPE, and the melting peak of AC10 disappears in all blends.

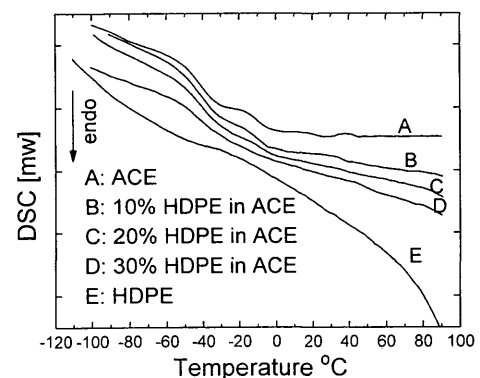
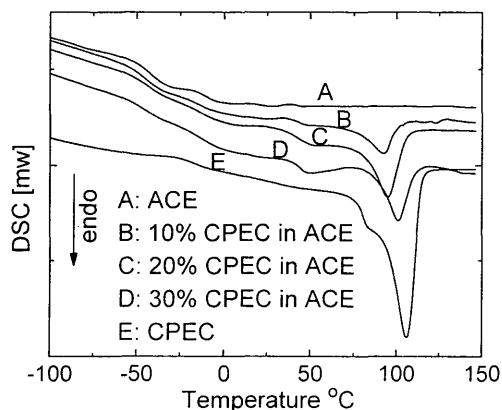


FIGURE 1 DSC thermogram of AC10/CPEC blends at various weight ratios.



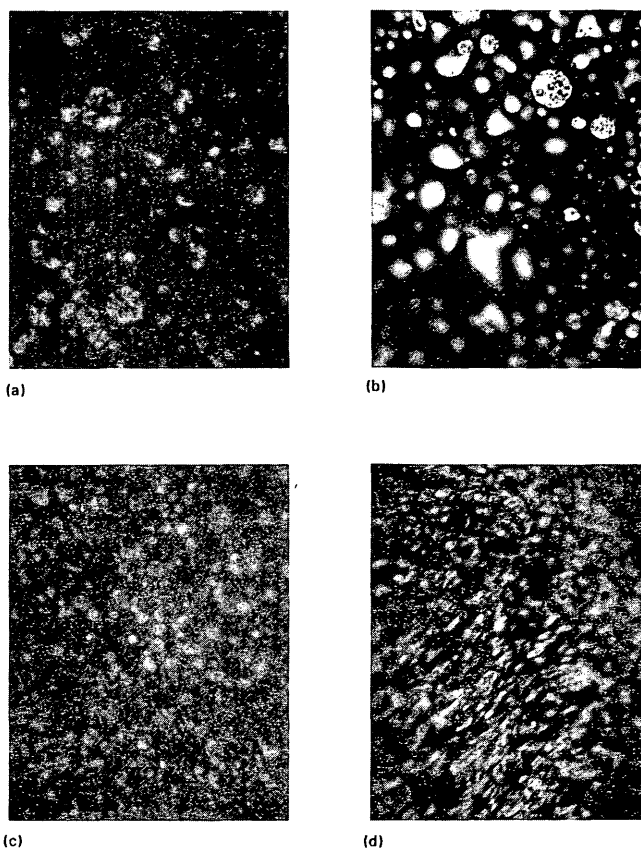
**FIGURE 2** Partial DSC thermogram of AC10/HDPE blends at various weight ratios.

The multiple transitions observed in DSC thermogram of AC10 (Figure 1) shows that AC10, like most asphalts, is a heterogeneous rather than a homogeneous system. It has been found that saturates and aromatics make the main contributions to thermal effects observed in DSC thermogram of asphalts (16). After the maltenes were removed from AC10 by solvent extraction, all three of transition temperatures decreased, and no crystalline fraction was detected. The transitions of AC10 become broad or weak as the concentration of HDPE increases, and no asphalt melting point is observed. Clearly, HDPE interacts with the saturates fraction and extracts them from the asphalt. In contrast, the transitions of AC10 become stronger when concentration of CPEC increases; blends of CPEA and CPEB exhibit intermediate properties. Apparently, introduction of chlorine atoms onto the polymer chain adjusts the interaction parameters to reduce single component extraction.

All melting peaks from polymers move toward low temperatures as polymer concentration decreases. The magnitude of the melting point depression indicates the extent of the interactions between the polymers and AC10. There are sufficient quantities of saturates in AC-10 to plasticize low concentrations of polymer; however, as the concentration of polymer is increased beyond 10 percent, the saturates are completely extracted and the relative concentration of the plasticizer decreases. Thus, the reduction in the melting point depression as the polymer concentration increases confirms the complete extraction of asphalt components into the polymer phase. These results suggest that high concentrations of any polymer additive will disrupt the compatibility of the asphalt mixture.

### Fluorescence Reflection Microscopy

The macrostructure of the asphalt polymer mixtures was examined using fluorescence reflection microscopy (FRM). Our observations (Figure 3) confirm previous reports (2,20) that there are basically two phases existent in asphalt-polymer blends, a continuous asphalt-rich phase and a polymer-rich phase. The dispersed polymer-rich phases are expected to improve the toughness of brittle asphalt at low temperature and reinforce asphalt at high temperatures (21,22). The CPE-rich phase is larger than the HDPE-rich phase in asphalt



**FIGURE 3** Fluorescence reflection microscopy images: (a) 5 percent HDPE in AC-10, (b) 5 percent CPEC in AC-10, (c) 10 percent HDPE in AC-10, and (d) 10 percent CPEC in AC-10.

blends prepared under comparable conditions, indicating that a higher percentage of the asphalt components have been absorbed in the polymer phase. Samples containing 10 weight percent CPEC exhibit bicontinuous phase morphology; the phase transformation is accompanied by a marked increase in viscosity. Blends with 10 weight percent HDPE retain the polymer droplets in an asphalt-continuous phase.

The enhanced compatibility of CPE in asphalt can be attributed to a change in the polymer polarity as well as to changes in morphology stemming from the reduced crystallinity. In crystalline polymers like HDPE, interaction with solvents and reagents is limited to the readily accessible amorphous regions. Selective extraction of the saturates from the asphalt matrix by HDPE would be expected; this process would disrupt the balance of components in asphalt mixtures and promote phase separation. Although chlorination of HDPE was conducted in solution, analysis of the chlorine distribution in the chains indicates that chlorination is not perfectly random. Runs of unreacted methylene groups that can crystallize remain. Chlorinated methylene groups do not enter the crystallites, so the amorphous region contains a higher chlorine content than that measured in bulk samples. Thus the amorphous regions are substantially more polar, and the presence of chlorine atoms on the polyolefin chain will improve the compatibility of the polymer with aromatic components and functional groups containing heteroatoms, such as, *N*, *S*, *O*, in asphalt. The polar components of asphalt would have a

greater affinity for the amorphous regions of CPE and a corresponding increase in the compatibility of these polymers with asphalt would be expected. Introduction of chlorine adjusts the interaction parameters to reduce single component extraction; thus the delicate equilibrium among the asphalt components is maintained.

### Low-Temperature Cracking

The low-temperature cracking test is quite sensitive to polymer-asphalt interactions. Because asphalt is a rather low molecular weight material compared with the polymer additives, it becomes quite brittle at temperatures below its glass transition. The amorphous regions of the polymer additives remain flexible at low temperatures, whereas the crystalline phases provide tie points to limit chain reptation. Thus these polymers should be effective impact modifiers. However, the extent of polymer contribution to blend properties depends on the degree of compatibility with the asphalt matrix.

As can be seen in Table 2, the blends do indeed exhibit  $T_c$ s below the  $T_g$  of pure asphalt measured at the same frequency. We have shown that the  $T_c$  of pure asphalt falls above the corresponding  $T_g$  (Table 1), so the polymer component has improved the low temperature properties of the blends. Furthermore, CPE-modified asphalts have lower  $T_c$ s than HDPE-modified asphalts, as might be expected from a more amorphous polymer with a higher degree of interaction with asphalt.

### Dynamic Rheology

Rheological measurements under oscillating conditions yield the dynamic mechanical properties of polymers (i.e., the storage modulus,  $G'$ , the loss modulus,  $G''$ , and a mechanical damping or internal friction,  $\tan \delta$ ). In studies of the response of a material to vibrational forces, stress, strain, frequency, and temperature are the key variables. When a material is subjected to cyclical stress under conditions analogous to those encountered in the intended applications, the data reflect both short- and long-term responses to the stress conditions. If time-temperature superposition can be applied, dynamic data

obtained at short-time intervals at high temperature can be transformed to yield long loading time data relevant to thermal cracking (23).

On a molecular basis, the magnitude of  $G'$  depends on the nature of the conformation rearrangements that can take place within the period of the deformation (24). Examination of plots of  $\log G'$  versus either temperature or frequency (Figure 4) reveals that the slope of the curve for ACE-HDPE is close to that for ACE. In other words, adding HDPE to ACE simply induces a parallel shift of the  $\log G'$  curves toward high temperature or low frequency. The presence of HDPE particles results in the development of partially separated regions in the asphalt matrix, which are characterized by a higher rigidity than in the bulk asphalt. A contributing factor to both the parallel shift and the slight difference between slopes of the two curves is the selective adsorption of asphalt components by HDPE. Adsorption of the saturates by HDPE enriches the asphalt phase with aromatics resins and asphaltenes and creates a more rigid continuous phase. The dynamic mechanical response of ACE-HDPE is mainly from the continuous asphalt phase that is indirectly affected by the presence of HDPE.

Compared with that of ACE-HDPE, slopes of  $\log G'$  curves of ACE-CPE blends decrease and become more linear (Figure 5). Asphalt is much more temperature sensitive or frequency sensitive than the polymer additives employed. The decrease in temperature sensitivity exhibited by the blends may imply that the polymer rich phase is increasingly directly involved in responding to the dynamic mechanical load. The effect is particularly pronounced in the higher temperature regimes. Introduction of chlorine atoms enhances compatibility among the polymer additives and asphalt; thus the volume of the polymer-rich phase will be increased because of the improved "solubility" in the asphalt.

### Creep Testing

A constant stress creep test was run at 5, 15, 25, and 35°C, respectively, with a Bohlin CS rheometer using a cone and plate mode; the stress applied was 590 Pa. The tests (Figures 6,7) illustrate a pronounced difference among HDPE and CPE blends. Two different asphalt samples, AC-10 and AC-

TABLE 2 Glass transition temperature ( $T_g$ ) from  $E''$  and cracking temperature ( $T_c$ ) of concerned asphalts, polymers, and asphalt-polymer blends

Sample	$T_g$ (°C)			$T_c$ (°C)
	1 Hz	10 Hz	50 Hz	
ACE	-32.2	-26.6	-22.5	-20
ACD	-14.9	-9.9	-4.1	-5
CPEB	-12.7	-7.9	-5.7	-- <sup>a</sup>
CPEC	-15.2	-12.4	-9.4	-- <sup>a</sup>
ACE-HDPE	-30.3	-25.0	-20.5	-23
ACE-CPEB	-31.9	-26.3	-21.6	-28
ACE-CPEC	-31.8	-25.7	-21.4	-31
ACD-HDPE	-14.3	-8.5	-3.7	-7
ACD-CPEB	-16.9	-10.8	-6.0	-8
ACD-CPEC	-16.6	-10.4	-6.7	-10

<sup>a</sup> the test was not conducted.

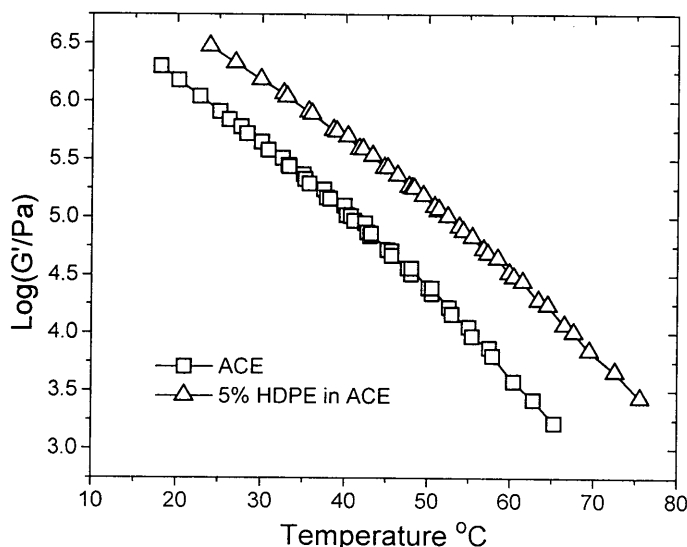


FIGURE 4 Plot of  $\log G'$  versus temperature for Curve A, AC-10 (ACE), and Curve B, 5 percent HDPE in ACE.

20, were blended with HDPE, semicrystalline CPEB (8.9 weight percent Cl) and amorphous CPEC (15.2 weight percent Cl). With the exception of the AC-10 blend at 15°C, the presence of HDPE did not change the creep behavior significantly. The compliance curves observed for the HDPE blends parallel those obtained with pure asphalt. However a significant difference in the compliance of CPE blends was observed; further it is possible to distinguish among the degrees of chlorination in the two CPE samples.

#### Creep Recovery

The resiliency of the asphalt blends was evaluated with the constant stress rheometer by imposing a stress for a given

period of time, then releasing the stress and allowing the sample to relax to an equilibrium deformation. This test is intended to be analogous to the Resiliency Test (ASTM D3883), but it can be run on relatively small samples without requiring special sample preparation. The samples were examined under two conditions: long-term (1,000-sec strain imposition) and short-term (10-sec strain imposition). The results are summarized in Table 3. The creep gives an indication of the resistance of the binder to deformation and the recovery percentage gives an indication of the elastic resiliency of the binder. The short-term tests probe the sample response under conditions of elastic strain; higher recovery values indicate a more durable binder. The long-term tests examine the resistance of the samples to creep and the interaction of the polymer matrix

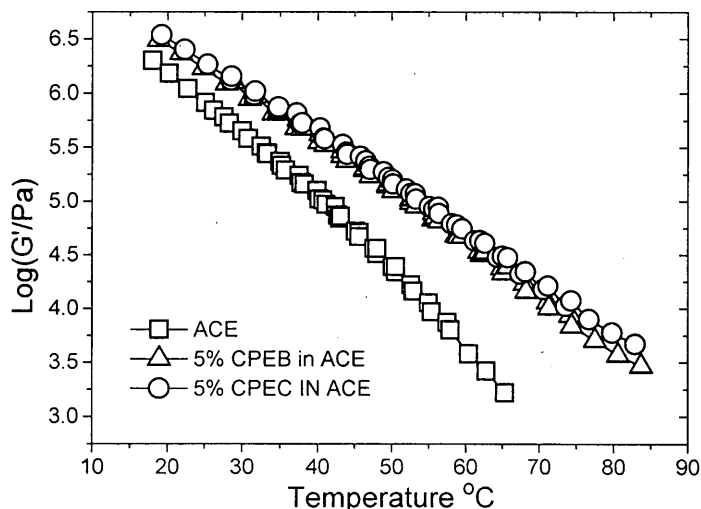


FIGURE 5 Plot of  $\log G'$  versus temperature for Curve A, ACE-10 (ACE); Curve B, 5 percent CPEB in ACE; and Curve C, 5 percent CPEC in ACE.

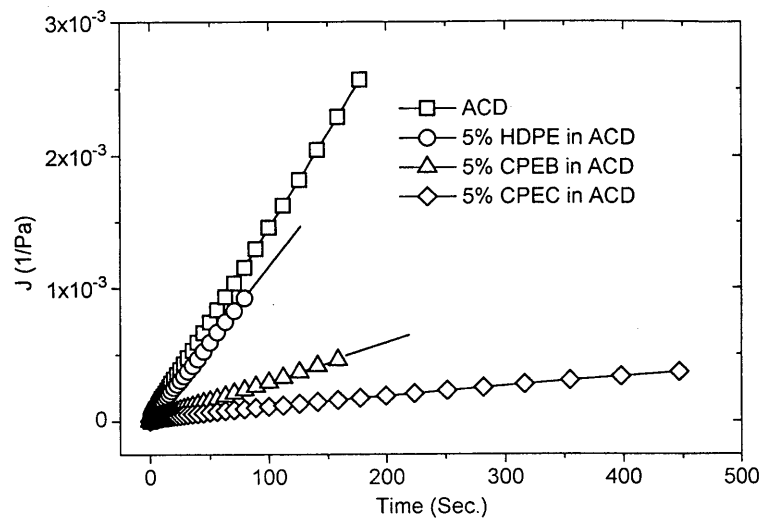


FIGURE 6 Constant stress creep curves at 35°C. Curve A, AC-20 (ACD); Curve B, 5 percent HDPE in ACD; Curve C, 5 percent CPEB in ACD; and Curve D, 5 percent CPEC in ACD.

with the asphalt; pure asphalt samples do not exhibit any recovery under these conditions.

Typical plots for long-term recovery of polymer asphalt blends are shown in Figure 8. Note that high-density PE exhibits very low resistance to creep and very little recovery; thus the interaction between HDPE and the asphalt matrix is limited. Modification of the PE by either chlorination or maleation reduces the extent of creep significantly and a notable recovery is observed.

Typical results of short-term tests are shown in Figure 9. The elastic recovery of modified PE blends is quantitative; pure PE blends develop a permanent set.

## CONCLUSIONS

1. Low-level chlorination of PE can be controlled to produce semicrystalline polymeric additives. Chlorinated PEs containing less than 15 weight percent chlorine interact more extensively with an asphalt matrix than with PE. The interaction is substantiated by changes in the DSC, creep resistance, and blend rheology.

2. Maleation of PE must be controlled to low levels (< 4 percent) to maintain compatibility of the asphalt blends. However, the interaction of slightly modified samples is clearly improved.

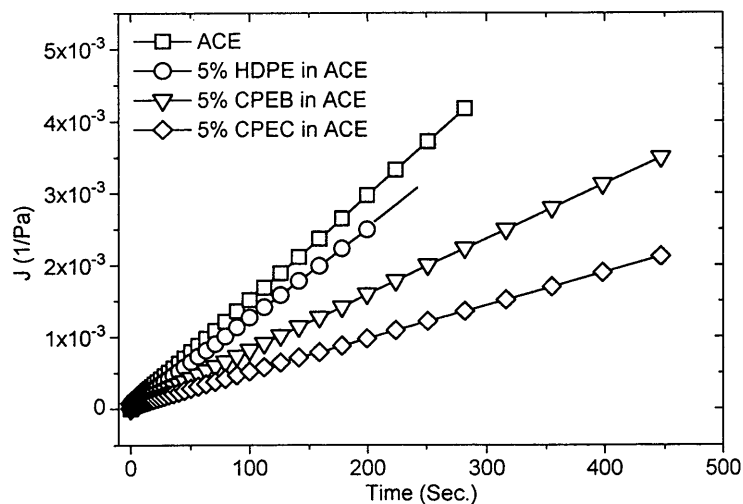
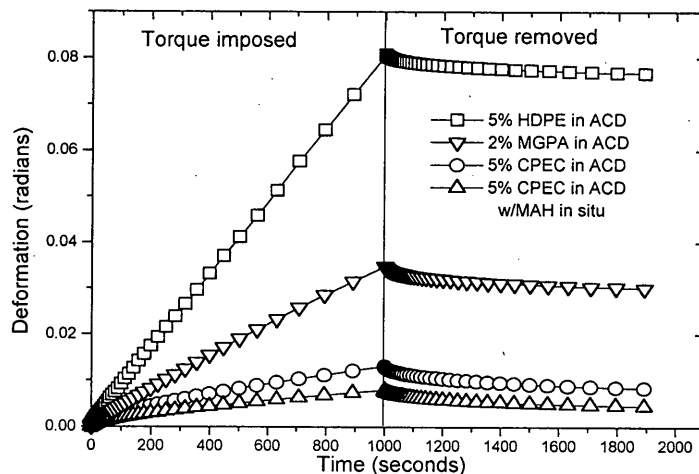
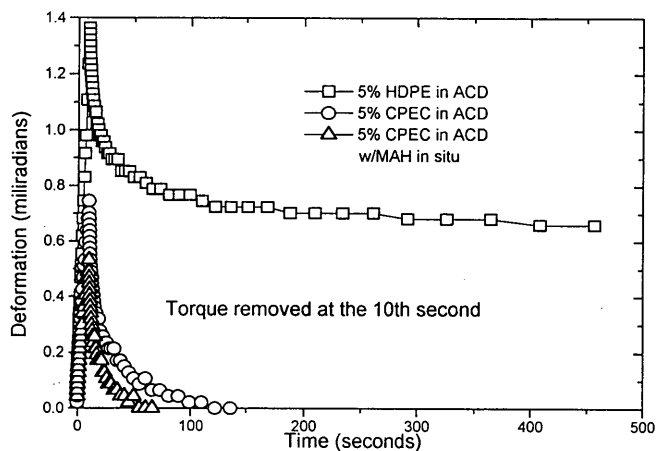


FIGURE 7 Constant stress creep curves at 35°C. Curve A, AC-10 (ACE); Curve B, 5 percent HDPE in ACE; Curve C, 5 percent CPEB in ACE, and Curve D, 5 percent CPEC in ACE.

**TABLE 3** Summary of creep-recovery tests on polymer-modified asphalts at 35°C

Sample	Creep @ 10 sec. (milliradians)	Recovery (%)	Creep @ 1000 sec. (milliradians)	Recovery (%) @ 1000 sec.
ACB	13	25 @ 500 sec.	119	0
ACD	21	13 @ 500 sec.	207	0
5% LDPE in ACB	6.9	71 @ 500 sec.	481.0	2
5% CPEC in ACB	2.7	100 @ 112 sec.	45.9	48
5% MGPA in ACB	0.4	100 @ 28 sec.	5.4	44
5% HDPE in ACD	1.4	51 @ 500 sec.	80.7	5
5% CPEC in ACD	0.7	100 @ 112 sec.	13.7	34
5% CPEC in ACD w/MAH in situ	0.53	100 @ 45 sec.	7.9	43
5% LDPE in ACD	0.92	74 @ 500 sec.	47.3	8
2% MGPA in ACD	0.90	83 @ 500 sec.	26.0	16

**FIGURE 8** Long-term creep recovery at 35°C for polymer-asphalt blends.**FIGURE 9** Short-term creep recovery of polymer-asphalt blends at 35°C.

3. DSC can be used to ascertain the asphalt crystallinity and the distribution of asphalt components among phases in asphalt-polymer blends.

4. The low-temperature cracking properties of asphalts closely parallel the  $T_g$ s measured at 50 Hz (Table 2). Both the  $T_g$  and low-temperature cracking temperatures increase when the crystalline asphalt component increases.

5. Asphalt-PE blends are more rigid than asphalt but the temperature sensitivities are parallel (Figure 5). Asphalt-CPE blends are less temperature sensitive and the temperature sensitivity varies inversely with the CPE chlorine content (Figure 6). The decrease in temperature sensitivity observed implies that the polymer-rich phase is responding more directly in CPE blends.

6. Constant stress creep tests and creep recovery tests are very sensitive methods for detecting asphalt-polymer interaction.



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