

RHEOLOGICAL ANALYSIS AND REINFORCEMENT EFFECTS OF POLYMER MODIFIED ASPHALT

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Introduction

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, etc., but the most important variable may be the compatibility of the AC with the admixed polymer and the ability to enhance compatibility is critical to the commercial applications of reinforced ACs. 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 measure the blended polymer/asphalt performance relative to that of the pure asphalt matrix. Using dynamic testing techniques, we believe that a better assessment of asphalt cement performance can be obtained.

Polyethylene is a recyclable waste which is abundantly available either as virgin off spec material or from solid waste classification processes. Polyethylene is a useful asphalt modifier for increasing the low temperature fracture toughness of asphalt cements(1) and it may also confer additional pavement stability at elevated temperatures which would minimize rutting and distortion due to creep. Due to gross incompatibility, polyethylene/asphalt blends tend to separate when allowed to stand at elevated temperatures. We are exploring the potential for simple chemical modification of polyethylene to enhance its compatibility with asphalt. A low degree of chlorination may assure a favorable interaction with the polar components of asphalt. Further, the extent of chlorination can be utilized to vary the crystallinity of the polymer additive. The microstructure and morphology of chlorinated polyethylenes have been evaluated(2). In solution chlorination, attack occurs randomly along the chain and the resultant insertion of chlorine atoms destroys the crystallinity of the polymer.

Experimental

Materials used High density polyethylene (HDPE) was supplied by Allied Signal. A high melt index (MI = 25) sample with weight and number average molecular weights of 85,000 and 19,000 respectively was used as the substrate for chlorination as well as a standard for the polymer asphalt blends. Solution chlorination of HDPE was conducted in 1,1,2,2-tetrachloroethane (TCE) at 110° C(3); samples with 8.9 wt% and 15.2 wt% chlorine were used in this study. Asphalt samples from Southland, AC10, and Exxon, AC20, were used as the

continuous phase; detailed characterization of these samples is reported in the previous paper (4). The asphalt polymer blends were prepared by melting 5% polymer in asphalt at 150°C while stirring for 2 hours under N₂ atmosphere. The samples are identified as follows: ACD, Exxon Asphalt AC20; ACE, Southland Asphalt AC10; Asphalt blends: HDPE, High Density Polyethylene; CPEB, CPE with 8.9 wt% CI content; CPEC, CPE with 15.2 wt% CI content.

Fluorescence Reflection Microscopy The macrostructure of the asphalt polymer mixtures was examined using fluorescence reflection microscopy (FRM). The sample was fractured on dry ice and then the fracture surface was observed through a set of filtering lenses, where the asphalt phase appears dark yellow and the polymer phase bright. Figure 1 shows two FRM pictures of asphalt polymer blends. Clearly, the blends are two phase systems; the size of the CPE phase is larger than that of the HDPE phase for samples prepared under identical conditions.

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 at the desired frequency. The Tg was identified as the temperature corresponding to the maxima of loss modular E'' at each frequency.

Imposition of a larger strain (1 %) 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 size of 10 x 10 mm. Sample thickness was held to about 1.5mm, measured with a deviation of ±0.05mm. Master curves were used with reference frequency of 20 Hz.

Constant Stress Creep Test The test was run at 5, 15, 25, 35°C, respectively, with Bohlin CS rheometer using a cone and plate mode. The stress applied was 590 Pa.

Results and Discussion

Low temperature cracking. The low temperature cracking test is quite sensitive to polymer/asphalt interactions. Since asphalt is a rather low molecular weight material, it becomes quite brittle at temperatures below its glass transition. In contrast, the T_g's of HDPE and CPE are greater than 30°C below the cracking temperatures of the blends. The amorphous regions of these polymers remain flexible while 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 upon the degree of compatibility with the asphalt matrix.

As can be seen in Table 1, the blends do indeed exhibit Tcs below the Tg of pure asphalt measured at the same frequency. We have shown that the Tc of pure asphalt falls above the corresponding Tg () so the polymer component has improved the low temperature properties of the blends. Furthermore, CPE modified asphalts have lower Tcs than HDPE modified asphalts as might be expected from a more amorphous polymer with a higher degree of interaction with asphalt. Thus, our data indicate that CPE's are more compatible with asphalt than HDPE and are more effective in low temperature reinforcement.

Our fluorescence reflection microscopy observations confirm previous reports [5,6] that there are basically two phases existent in asphalt-polymer blends, an asphalt rich phase and a polymer rich phase. As fact of matter, the hetero-phased systems are advantageous from a practical point of view; the dispersed polymer rich phases are expected to improve the toughness of brittle asphalt at low temperature and reinforce asphalt at high temperatures [7-9]. Since the polymers are not completely miscible in the asphalt continuous phase, their presence does not increase the melt viscosity of the blends excessively; asphalt cements prepared from these blends should flow smoothly and coat the aggregate efficiently.

The enhanced compatibility of CPE in asphalt can be attributed to a change in the polymer polarity as well as 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. In HDPE, these regions are composed of $-CH_2-$ segments more compatible with the saturates in asphalt. One would expect selective extraction of the saturates from the asphalt matrix by HDPE; 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. It was reported [10-13] that the CH_2/COO ratio was an important factor controlling the miscibility of blends prepared from a series of aliphatic polyester with polyvinylchloride; polymers with a higher polarity were more miscible. The polar components of asphalt would have a greater affinity for the amorphous regions of CPE and one would expect a corresponding increase in the compatibility of these polymers with asphalt. Introduction of chlorine adjusts the interaction parameters to reduce single component extraction thus the delicate equilibrium among the asphalt components is maintained.

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, $\tan \delta$. The storage modulus reflects the internal stiffness of a material under dynamic loading conditions; the corresponding stress response is in phase with the applied strain. The loss modulus is the viscous, damped response of the material; the corresponding stress is out of phase with the applied strain. This phase lag results from the time necessary for molecular rearrangements and is associated with relaxation phenomena. 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-term 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. (14)

On a molecular basis, the magnitude of G' depends on the nature of the conformation rearrangements can take place within the period of the deformation [15]. Examination of plots of $\log G'$ versus either temperature or frequency (figure 2) reveals that the slope of the curve for ACE-HDPE is very close to that for ACE. In another 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 3). 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 more and more 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 between the polymer additives and asphalt, thus the volume of the polymer rich phase will be increased due to improved 'solubility' in the asphalt. A morphological conversion from a particle filled matrix (HDPE blend) to a three dimensional network may occur in CPE blends.

Creep. Creep tests (figures 4-7) illustrate a pronounced difference between HDPE and CPE blends. At 35°C the presence of HDPE did not change the creep behavior significantly. Further one can distinguish between the degrees

of chlorination in the two CPE samples; the more amorphous samples were more resistant to creep.

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References

1. P. Jew and R. T. Woodhams, *Asphalt Paving Technology*, **55**, 541 (1986).
2. B. H. Chang, R. Ziegler and A. Hiltner, *Polym. Eng. Sci.* **28**, 1167 (1988) and references cited therein.
3. Zhaoyao Qiu *Thesis* Louisiana State University, p50, 1991
4. W.H. Daly and Zhaoyao Qiu, Fuel Chemistry Division Preprints, 1992.
5. B. Brule; Y. Brion and A. Tanguy, *Asphalt Paving Technology*, **57**, 41-64, (1988).
6. C. Lenoble, *Prepr. - Am. Chem. Soc., Div. Pet. Chem.*, **35(3)**, 541-49, (1990).
7. C. B. Bucknall and W. W. Stevens, *J. Material. Sci.*, **15**, 2950, (1980).
8. C. B. Bucknall and C. J. Page, *J. Material. Sci.*, **17**, 808, (1982).
9. P. Juliano, *Polymer Eng. Sci.*, **24**, 1359, (1984).
10. M. Aubin and R. E. Prud'homme, *Macromolecules*, **13**, 365, (1980).
11. M. Aubin and R. E. Prud'homme, *Polym. Eng. Sci.* **24**, 350, (1984).
12. M. Aubin; Y. Bedard; M. F. Morrissette and R. E. Prud'homme, *J. Polym. Sci., Polym. Phys. Ed*, **21**, 233, (1983).
13. J. E. Harris; D. R. Paul and J. W. Balow, *Polym. Eng. Sci.*, **23**, 676, (1983).
14. H. S. Pink, R. E. Merz and D. S. Bosniack, *Asphalt Paving Tech.* **49**, 64 (1980).
15. R. B. Bird; R. C. Armstrong and O. Hassager, *Dynamics of polymeric liquids, Volume 1, Fluid Mechanics*, 2nd Edition, John Wiley & Sons, Inc., New York, 1987.

Table 1. Glass Transition Temperature (Tg) from E'' and Cracking Temperature (Tc) of Concerned Asphalts, Polymers and Asphalt-polymer Blends

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

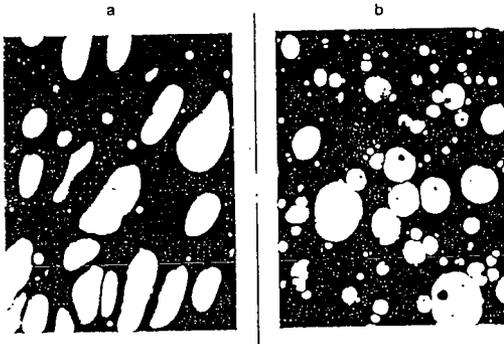


Figure 1 Pictures of fluorescence reflection microscopy. (a) 5% CPEC in ACD. (b) 5% HDPE in ACD.

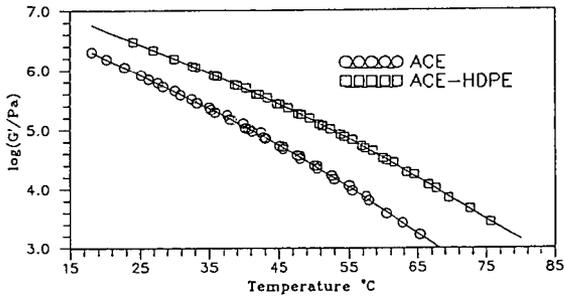


Figure 2 Plot of $\log G'$ versus temperature.

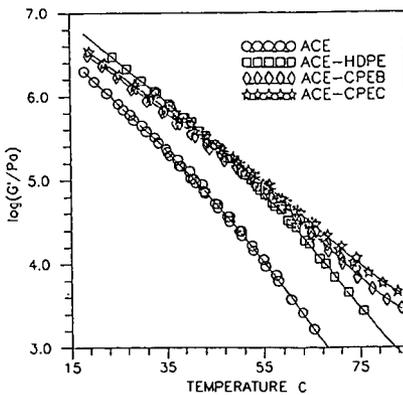


Figure 3 Plot of $\log G'$ versus temperature for ACE, ACE-HDPE, ACE-CPEB and ACE-CPEC.

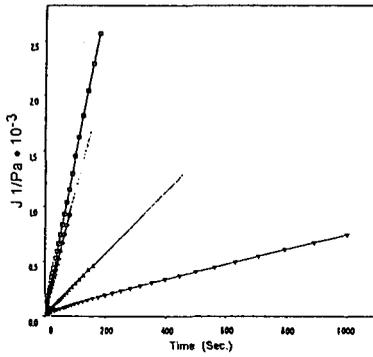


Figure 4 Constant stress creep curves at 35°C (from top to bottom: ACD, ACD-HDPE, ACD-CPEB, ACD-CPEC)

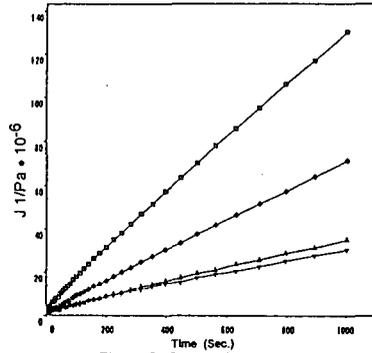


Figure 5 Constant stress creep curves at 15°C (from top to bottom: ACD, ACD-HDPE, ACD-CPEB, ACD-CPEC)

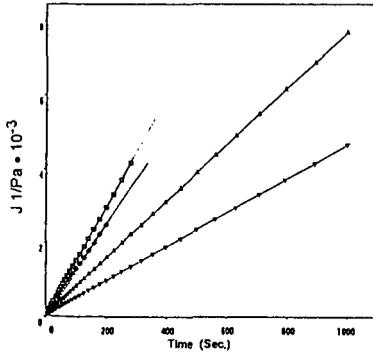


Figure 6 Constant stress creep curves at 35°C (from top to bottom: ACE, ACE-HDPE, ACE-CPEB, ACE-CPEC)

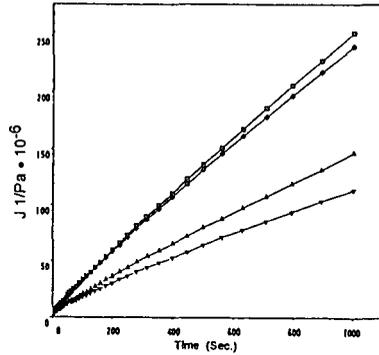


Figure 7 Constant stress creep curves at 15°C (from top to bottom: ACE, ACE-HDPE, ACE-CPEB, ACE-CPEC)