Synthesis of asphalt binders from renewable resources and their rheological properties

M.H Mohammed, G. Airey, A. Collop & T. Parry
Nottingham Transportation Engineering Centre, School of Civil Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, UK

C. Hayes
School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, UK

ABSTRACT: At present, most adhesives and binders are mainly produced from petrochemicals and the fact that petroleum reserves are a finite resource means that in the future it may become necessary to produce these materials from renewable sources. Suitable resources may include polysaccharides, plant oils and proteins. This paper deals with the synthesis of polymer binders from monomers that could be produced from renewable resources. The aim has been to investigate if these synthetic binders show similar properties to bitumen so that future binders could be synthesised from renewable sources. Samples of poly(ethyl acrylate) (PEA) of different molecular weight, poly(methyl acrylate) (PMA) and poly(butyl acrylate) (PBA) were synthesised from ethyl acrylate, methyl acrylate and butyl acrylate, respectively, by atom transfer radical polymerization (ATRP). The fundamental rheological properties of these binders were tested by using a dynamic shear rheometer (DSR). The results indicate that PEA has rheological properties similar to that of 100/150 penetration grade bitumen, although 100/150 penetration grade bitumen is stiffer at ambient temperatures than PEA binder. At low temperatures, PEAs are softer than 100/150 penetration grade bitumen but have a greater elastic response compared to the more viscous response of the 100/150 penetration grade bitumen. High molecular weight PEA binders show better rheological properties than the low molecular weight PEA binders. However, PBA being highly viscous at room temperature cannot be used by itself as an asphalt binder but may be used to modify stiffer grade bitumen. PMA, on the other hand has similar rheological properties to that of 15 penetration grade bitumen at ambient temperatures but tends to be stiffer than the hard bitumen at temperatures greater than 60°C.

1 INTRODUCTION

Most adhesives and binders, including bituminous materials that are used for road building, are derived mainly from fossil fuels. However, petroleum reserves are becoming depleted and the need to reduce fossil fuel usage is driving the development of adhesives and binders from alternative sources, especially from renewable sources.

Adhesives based on soy protein, starch, cellulose and other polysaccharides have been used over the years for a wide range of adherents such as wood, paper, plastic, metal, leather, and glass (Shields 1976). Renewable natural resources including sugars, triglyceride oils and proteins have been tested as alternative sources for producing adhesives and binders (Ahmad 2004, Chakrapani et al. 2003, Kaplan 1998, Emengo et al. 2002, Shields 1976, Tsujimoto et al. 2004, Uyama et al. 2003). Large quantities of renewable sources such as triglyceride oils, proteins, starch and other carbohydrates are available from various botanical sources, photosynthetic micro-organisms and algae and there are good technical and economic prospects in utilizing them from these sources. A range of different vegetable oils have been developed in recent years with the knowledge of their physical and chemical properties obtained through the application of scientific research and development (Kaplan 1998, Tan et al. 2002).

The present investigation is an initial study of the synthesis of polymer binders from monomers

that could be produced from triglyceride oils and carbohydrates. The objective of the project is to investigate if these polymers show rheological properties similar to bitumen and if they can replace bituminous materials or could be used to improve their properties. Synthetic polymeric materials such as ethylene vinyl acetate (EVA) have been used in road construction for more than 20 years in order to improve both the workability of the asphalt during construction and its deformation resistance in service (Airey 2002, Cavaliere et al.1993, Goos et al. 1996, Loeber et al. 1996).

Samples of poly(butyl acrylate) (PBA), poly(ethyl acrylate) (PEA) and poly(methyl acrylate) (PMA) were synthesised from butyl acrylate, ethyl acrylate and methyl acrylate respectively, by atom transfer radical polymerization (ATRP).

The ATRP technique involves the abstraction of a halogen from an alkyl halide (Methyl-2-bromopropionate (MBP)) by a transition metal compound such as copper bromide (CuBr) and a ligand $N,N,N^{'},N^{'},N^{''}$-pentamethyl diethylenetri-amine (PMDETA) in a redox process. This produces an alkyl radical that undergoes propagation as in conventional free radical polymerization. However, the free radicals are also able to abstract the halogen back from the metal, reproducing the dormant species. These processes are rapid, and the dynamic equilibrium that is established favours the dormant species. The concentration of the active radicals is therefore very low, limiting radical–radical coupling/ disproportionation reactions as the principal mode of termination.

2 EXPERIMENTAL

2.1 Materials

Butyl acrylate (BA), ethyl acrylate (EA) and methyl acrylate (MA) (all from Aldrich, 99.9%) were distilled at atmospheric pressure over calcium hydride (CaH_2). MBP (Aldrich, 99.9%) and PMDETA (Aldrich, 99.9%) were used as received. CuBr (Aldrich, 98%) was also directly used as received without any further treatment in order to avoid an oxidation of the Cu(I) compound in the open air.

2.2 Atom transfer radical polymerization

A required amount of CuBr was introduced to a three-necked round bottom flask containing a magnetic stirrer and connected with a three-way stopcock and a condenser. The flask was then sealed with a rubber septum and was cycled five times between vacuum and nitrogen, using a high purity nitrogen gas. The mixture containing required amounts of monomer, initiator and ligand was degassed by nitrogen purging for 30 minutes before it was injected to the reaction flask using a syringe. The reaction flask was then placed in a preheated oil bath at a desired temperature. After a given time, the reaction was stopped by quenching and the reaction mixture was dissolved in tetrahydrofuran (THF). The reaction conditions are given in Table 1. The dissolved polymer solution was passed through a neutral alumina column to remove copper bromide catalyst. The polymer solution was precipitated into a large amount of methanol and water (1:3) mixture. The precipitated polymer was then dried and was characterized by dynamic mechanical analysis (DMA) (Airey 2002).

2.3. Rheological Experiments

Rheological measurements of the polymer binders were performed using dynamic mechanical methods consisting of frequency sweeps in an oscillatory-type testing mode performed within the region of linear viscoelastic (LVE) response. The oscillatory tests were conducted by using a dynamic shear rheometer (DSR). Oscillating shear stresses and strains were applied to samples of binder sandwiched between parallel plates at different loading frequencies and temperatures as shown in Figure 1.

DSR provides the viscoelastic parameters such as complex shear modulus (G*) and the phase angle (δ). G* is defined as the ratio of maximum shear stress to maximum strain and provides a measure of the total resistance to deformation when the binder is subjected to shear loading. It contains elastic and viscous components which are known as the shear storage modulus (G') and shear loss modulus (G''), respectively. These two components are related to the complex shear modulus and to each other through the phase angle (δ) which is the phase, or time, lag between the applied shear stress and shear strain responses during a test (Airey 2004).

Comment [T4]: Please bring the table closer to this paragraph.

Comment [T5]: Supply a reference.

Table 1. Condition of polymerisation, percentage yield and molecular weight of the polymerized butyl acrylate, ethyl acrylate and methyl acrylate.

Polymer Sample	Condition [M]:[MBP]:[CuBr]:[PMDEAT]	Temperature (°C)	Time (h)	Yield (%)	M_{th} (g/mol)
PEA 1	400:1:1:1	100	4	87	34967
PEA 2	1000:1:1:1	100	6	89	89167
PEA 3	600:1:1:1	100	4	82	49367
PEA 4	600:1:1:1	100	5	84	50567
PBA	400:1:1:1	100	4	76	39079
PMA	1000:1:1:1	100	6	90	77567

Notes: M (monomer) = ethyl acrylate or butyl acrylate or methyl acrylate.

Initiator (I) = methyl-2-bromopropionate (MBP).

Theoretical molecular weight (M_{th}) = Formula weight of MBP + ($[M]_0/[MBP]_0$) x formula weight of monomer x conversion or % yield = 167 + ($[M]_0/[MBP]_0$) x formula weight of monomer x conversion or % yield.

$[]_0$ = initial concentration; $[M]_0/[I]_0$=400/1 for PEA1.

The phase angle, defined as the phase difference between stress and strain in an oscillatory test, is a measure of the viscoelastic balance of a material's behaviour. If δ equals 90° then the material can be considered to be purely viscous in nature, whereas δ of 0° corresponds to purely elastic behaviour. Between these two extremes the material behaviour can be considered to be viscoelastic in nature with a combination of viscous and elastic responses.

Various geometries, such as cone and plate, parallel plates, and cup and plate, can be used in dynamic mechanical testing. For many materials cone and plate geometry is preferred as shear stress and shear rate are constant over the entire area of the plate, thereby simplifying calculations and giving accurate fundamental rheological properties. However, in the present tests parallel plate geometry was used to avoid the very small gap present at the centre of the cone and plate geometry.

Two testing plate geometries were used, namely a 8 mm diameter spindle with a 2 mm testing gap and a 25 mm diameter spindle with 1 mm testing gap. The selection of the testing geometry is based on the operational conditions with the 8 mm plate geometry generally being used at low temperatures (-5°C to 35°C) and the 25 mm geometry at intermediate to high temperatures (25°C to 80°C). The DSR tests reported in this paper were performed under the following test conditions:

● Mode of loading: Controlled-strain.

● Temperatures: 5, 10, 15, 20, 25, 35, 40, 45, 50, 55, 60, 65, 70 and 75°C.

● Frequencies (Hz): 0.1000, 0.1585, 0.2512, 0.3981, 0.6310, 1.0000, 1.5849, 2.5119, 3.9811, 6.3096, and 10.0000

● Spindle geometries: 8 mm diameter with 2 mm gap (5–35°C); 25 mm diameter with 1 mm gap (25–75°C).

● Strain amplitude: Within linear viscoelastic (LVE) response (0.5–10%) depending on G^*.

For each test, samples were prepared by heating the binder at 150°C and then pouring the hot binder into 8 mm or 25 mm diameter silicon moulds as required. The gap between the upper and lower spindles of the DSR was set to a height of 25 μm plus the required testing gap at the mid-point of the testing temperature range.

Once the gap had been set, the molded binder was placed onto the bottom (lower) plate of the
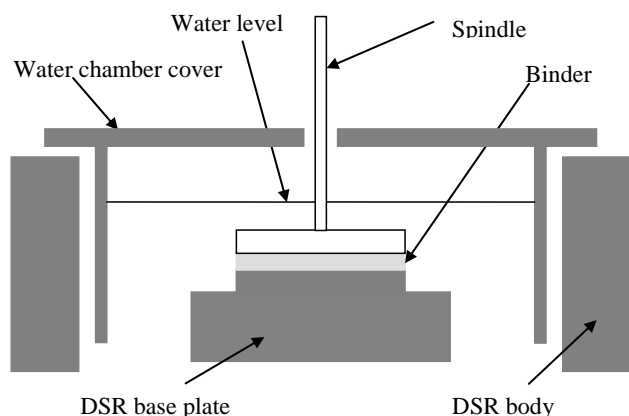
Figure 1. Dynamic shear rheometer testing configuration using a controlled stress rheometer.

DSR. The upper plate of the DSR was then gradually lowered to the required testing gap plus 25 μm. The binder that was squeezed out between the plates was then trimmed off from the edge of the plates using a hot blade. Finally, the gap was set as required for the test and the slightly squeezed binder was left around the circumference of the testing geometry (Airey 2003).

The rheological properties of the binders were measured in terms of their complex shear modulus (stiffness and overall resistance to deformation), G^*, and phase angle, δ, (viscoelastic balance of rheological behaviour).

3 RESULTS AND DISCUSSION

3.1. Polymerization

Table 1 shows the condition of polymerisation, percentage yield, molecular weight, reaction temperature and reaction time of the polymerized butyl acrylate, ethyl acrylate and methyl acrylate. At a reaction temperature of 50°C, only a trace amount of product yield was obtained. Therefore a higher reaction temperature was chosen as lower reaction temperatures produced less radical species, owing to a poor dissociation of C–X (X refers to an halogen atom such as Br, Cl, etc) bonds in the initiator and in the propagating chain ends. As a result, a few active species were produced and thus only a few monomers experienced a propagation step. This resulted in low percentage yield and molecular weight of the

product. On the other hand, bimolecular termination became more significant at higher reaction temperatures due to more propagating chains and a higher rate of termination.

3.2 Dynamic Viscoelastic Properties

Isochronal plots of complex modulus (G^*) and phase angle (δ) versus temperature at 1.0 Hz for the polymer binders and two control bitumens (a hard 15pen and soft 100/150pen) are shown in Figures 2 and 3, respectively. The complex modulus results in Figure 2 show that all the poly(ethyl acrylates) (PEAs) have lower G* values compared to the 100/150pen and 15pen bitumen in the temperature range 5-30°C. However, as the PEAs are less temperature susceptible compared to the conventional, petroleum derived bitumens, the G* values at temperatures greater than 30°C in the case of PEA2 and around 35°C in the case of other PEAs are higher than the G^* values of the softer 100-150pen bitumen. The rheological behaviour of PBA and PMA differs from that of the four PEAs with the softer PBA having consistently lower G^* values over the entire temperature domain compared to the 100/150pen bitumen, while PMA is more comparable to the 15pen bitumen. Once again due to the lower temperature susceptibility of the polymer binders, the G^* values of PMA are relatively lower than the hard 15pen bitumen at temperatures between 25°C and 55°C but higher at temperatures above 55°C. PMA therefore continues to be relatively stiff (high G* values) even at high temperatures (70°C to 80°C).
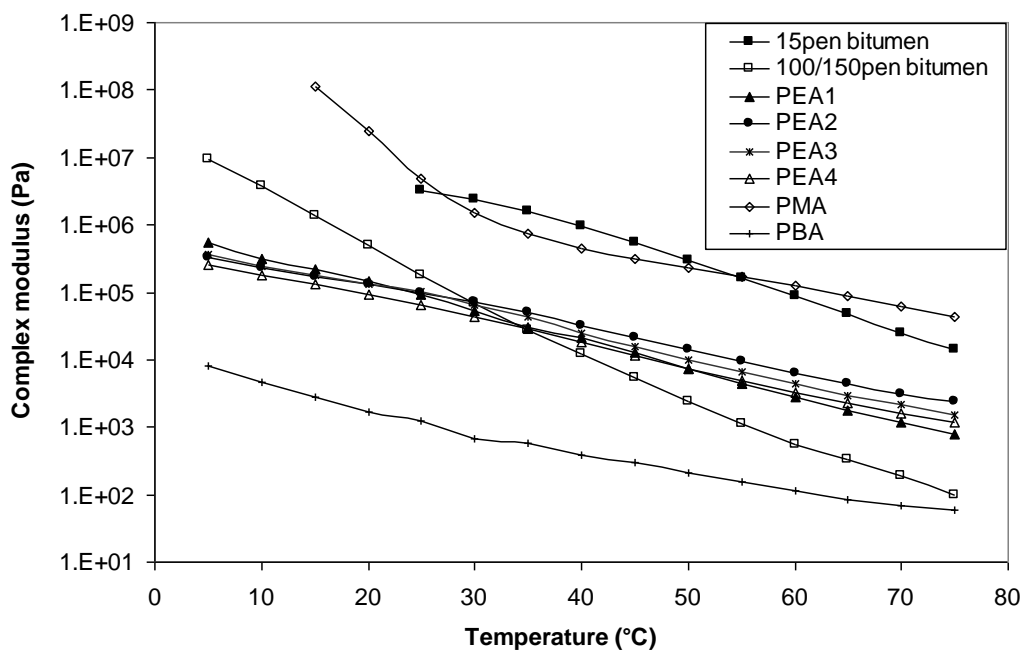
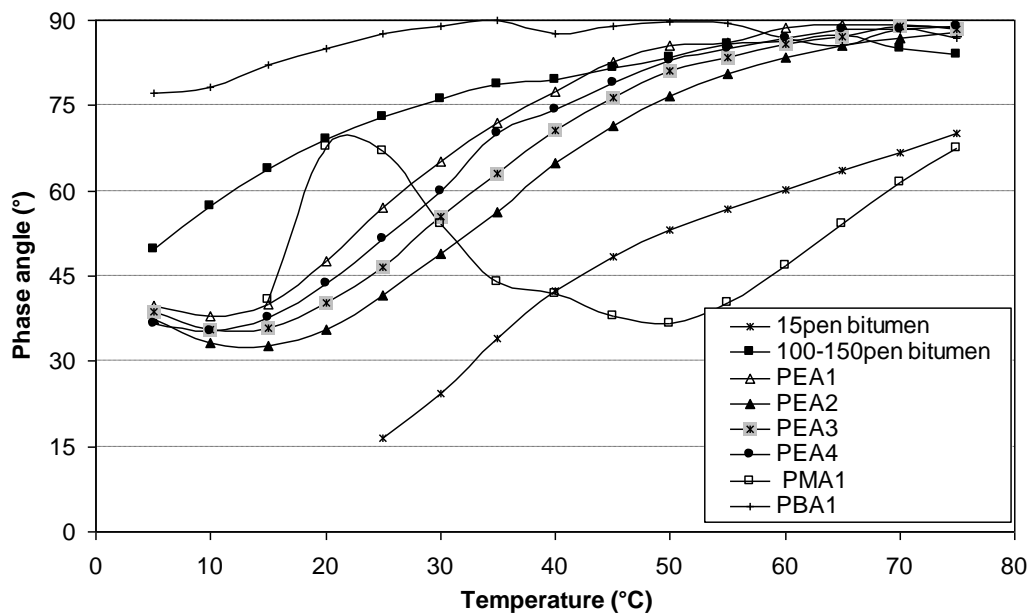Figure 2. Complex modulus of polyacrylates and bitumen materials at 1.0 Hz

Figure 3. Viscoelastic responses of polyacrylates and bitumens at 1.0 Hz

The above observations are also confirmed in terms of the viscoelastic nature of the polymer binders and control bitumens in Figure 3. The softer PBA shows a predominantly viscous response with phase angles between 80° and 90° in the temperature region 5°C to 75°C. The PEAs and PMA tend to show a more "bitumen-like" viscoelastic response with their phase angles increasing with temperature from a more elastic to increasingly viscous rheological response. Similar to the complex modulus parameter, the phase angles of the PEAs are more comparable to those of the softer 100-150pen bitumen, while the phase angles of PMA are closer to the harder 15pen bitumen. Similar to the observations of complex modulus for PMA in Figure 2, the phase angles of PMA do not change significantly as a function of temperature and remain within a range of 30° to 70° (balanced viscoelastic response) over the entire temperature domain. It is also obvious from Figures 2 and 3 that PEA2, which has higher molecular weight than the other PEAs, shows higher complex modulus and lower phase angles.

3.3 Rheological master curves and black diagram

The frequency dependency of complex modulus and phase angle in terms of rheological master curves and the rheological data in the form of a Black diagram for the PEAs and three control bitumens (15pen, 50pen and 100/150pen) are shown in Figures 4 to 6, respectively. The rheological master curves were produced at a reference temperature of 25°C using the time–temperature superposition principle (TTSP) (Ferry 1980) and shift factors determined for the G^* master curves. The complex modulus master curves in Figure 4 show that the complex moduli of PEA2 and 100/150pen bitumen are similar at lower frequencies while other PEAs show slightly lower complex moduli than PEA2 and 100/150pen bitumen. However, as the frequencies are increased the complex modulus of 100/150pen bitumen increases more than the complex moduli of the PEAs.

Comment [T7]: In the legends please refer to 15pen bitumen and 100/150pen bitumen, as in previous figures.
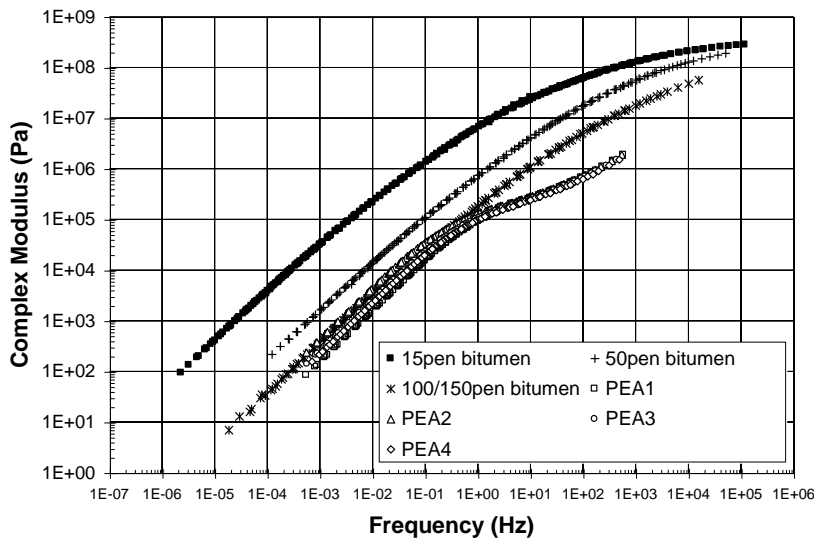

Figure 4. Master curves of complex modulus at 25 °C for PEAs and bitumens
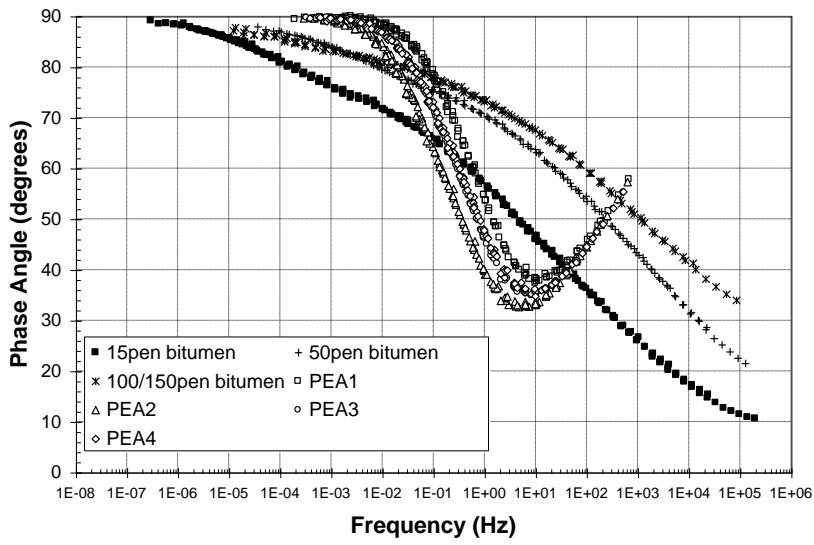
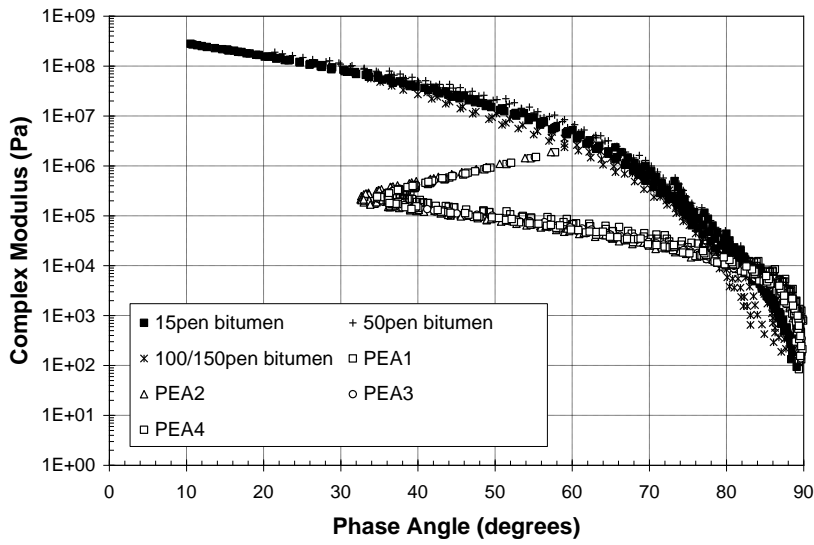Figure 5. Master curves of phase angle at 25 °C for PEAs and bitumens

Figure 6. Black diagrams for PEAs and bitumens.

Figure 5 shows that the phase angles of the PEAs and control bitumens decrease with increasing frequencies but the phase angle for the PEAs, unlike the bitumens, does not get lower than 32° and at this point the curves show a reversal towards higher phase angles. This trend is also observed in Figure 6 where the complex modulus increases with decreasing phase angle but the phase angle for PEAs unlike bitumen does not get lower than 32° and at this point again the curves show a reversal towards higher phase angles. This indicates that the PEAs have lower elastic dominated response at low temperatures and high frequencies compared to that found for petroleum derived bitumens.

4 CONCLUSIONS

The results indicate that PEA has rheological properties similar to that of a soft 100/150 penetration grade bitumen. However, 100/150 penetration grade bitumen is stiffer at ambient temperatures than PEA binder. At low temperatures, PEAs are softer than the 100/150 penetration grade bitumen, but also tend to be more elastic in terms of their rheological response. High molecular weight PEA binders show more bitumen-like rheological properties than the low molecular weight PEA binders. PBA is considerably softer and more viscous in nature at ambient temperatures compared to conventional bitumens and therefore cannot be used by itself as an asphalt binder but could be used to modify stiffer grade bitumen. PMA has complex modulus values similar to that of the hard 15 penetration grade bitumen at ambient temperatures but tends to be stiffer than 15pen bitumen and at higher temperatures greater than 60°C. The data shown in this paper indicate that synthetic polymer binders can be produced that partly replicate the rheological properties of conventional, fossil fuel based bitumens.

REFERENCES

Ahmad, S., Haque, M.M., Ashraf, S.M., & Ahmad, S. 2004. *Eur Polym J* 40: 2097–2104.

Airey, G.D. 2002. Rheological evaluation of ethylene vinyl acetate polymer modified bitumens *Construction and Building Materials* 16: 473–487.

Airey, G.D. & Hunter, A.E. 2003. Dynamic mechanical testing of bitumen – sample preparation methods. *ICE Transport*, 156 (TR2): 85-92.

Airey, G.D., & Rahimzadeh, B. 2004. Combined bituminous binder and mixture linear rheological properties. *Construction and Building Materials* 18: 535–548.

Cavaliere, M.G., Diani, E., & Vitalini Sacconi, L. 1993. Polymer modified bitumens for improved road application. *Proceedings of the 5th Eurobitume Congress, Stockholm* 1A (1.23): 138–142.

Chakrapani, H., Liu, C., & Widenhoefer, R.A. 2003. *Org. Lett.* 5: 157–159.

Emengo, F. N., Chukwu, S. E. R., & Mozie, J. 2002. *International Journal of Adhesion and Adhesives*, 22, (2): 93-100.

Ferry, J.D. 1980. *Viscoelastic properties of polymers*, New York:Wiley.

Goos, D., Carre, D. 1996. Rheological modelling of bituminous binders a global approach to road technologies. *Proceedings of the Eurasphalt & Eurobitume Congress, Session 5: Binders-Functional Properties and Performance Testing, E&E.5.111, Strasbourg.*

Kaplan, D.L. 1998. *Biopolymers from renewable resources*, Berlin: Springer.

Loeber, L., Durand, A., Muller, G., Morel, J., Sutton, O., Bargiacchi, M. 1996. New investigations on the mechanism of polymer-bitumen interaction and their practical application for binder formulation. *Proceedings of the Eurasphalt & Eurobitume Congress, Session 5: Binders-Functional Properties and Performance Testing, E&E.5.115, Strasbourg.*

Shields, J. 1976. *Adhesives handbook.* London: Butterworth.

Tan, C.P. & Che Man, Y.B. 2002. *Photochem. Anal.* 13: 129–141.

Tsujimoto, T., Uyama, H., & Kobayashi, S. 2004. *Macromolecules* 37: 1777–1782.

Uyama, H., Kuwabara, M., Tsujimoto, T., & Kobayashi, S. 2003. *Biomacromolecules* (4): 211–215.