Mathematical and Experimental Investigations of Modeling, Simulation and Experiment to Promote the Life-Cycle of Polymer Modified Asphalt

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16. Abstract
The formulation of constitutive equations for asphaltic pavement is based on rheological models which include the asphalt mixture, additives, and the bitumen. In terms of the asphalt, the rheology addresses the flow and permanent deformation in time, under different temperatures, and under different loading conditions. Currently, there are various laboratory methods used to determine the rheological parameters of the asphalt. Unfortunately, most of these test are conducted in the linear viscoelastic region, therefore the true picture of asphalt during in-service has not been fully investigated. Furthermore there are quite few polymer-modified asphalts that have been used. The mathematical models needed to formulate and model these materials are limited. This study attempt to develop a mathematical approach to modeling of polymer modified asphalt which is applicable in pavement design.

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DESCRIPTION OF THE PROBLEM

This work involves studies of the processing of materials involving viscoelastic (polymer) fluids with inclusions in a solvent, and the goal is to avoid demixing and phase separation processes in order to create a more tightly bonded surface on spreading and solidification. Table 1 gives the example of bitumen additives.

Polymer modification of asphalt in highway and airport pavements results in the modification of certain properties such as a) elasticity, b) tensile strength, c) high and low temperature susceptibilities, d) viscosity, and e) adhesion and cohesion. The polymer modified asphalts can:

- be more resistant to rutting and thermal cracking
- display a longer life-time as pavement
- display increased traffic induced resistance.

The proper modification of the asphalt can have a major of influence on the performance and the aging of the pavement. Various laboratory studies have demonstrated that the same asphalt with a different block polymer imbedded may have different properties. In the ideal case the polymers form a continuous (entangled) network, and in the less desirable cases discontinuity properties (phase separations) are exhibited between the asphalt and the polymer leading to poor physical properties. Asphalt modification currently is undergoing a major transformation. Polymers composed of functional groups compatible with asphalt have been formulated. Furthermore, the future application of polymers may entail matching polymer properties with anticipated in-service physical requirements (e.g., thin overlays, overlays on concrete, or full depth pavements) Issues such as: a) how does the aging of polymer modified asphalt affect the durability, b) what changes in chemical composition with aging cause reduction in pavement performance, are important.

APPROACH

Previous studies have shown that asphalt binders exhibit dramatic changes in elasticity with temperature and also exhibit dramatic changes in elasticity with aging (Glaser et al, 2011). Mathematical models of polymer modified binder are absent in the pavement literature. Various testing methods have been developed by pavement researchers to address the performance characteristics of the polymer modified asphalts.

Some Mathematical Models (Yusoff, 2012)

Jongepier and Kuilman's Model

Jongepier and Kuilman developed a mathematical model for describing the master curve of the (linear) complex modulus for bitumen. The model was based on the basic assumption that the

relaxation spectrum for bitumen is approximately log normal in shape. In general, this model is reasonably accurate when considering the viscoelastic properties of bitumens.

Dobson's Model

Dobson's Model for fitting the master curve expresses frequency in terms of the modulus. His result, a universal master curve was used as a basis for characterizing bitumen using a graphical comparison. In general, this method for describing temperature dependency appears to be reasonably accurate as well.

Dickinson and Witt's Model

Dickinson and Witt performed dynamic mechanical testing on 14 bitumens and developed analytical expressions based on their frequency dependencies. Dickinson and Witt disputed Jongepier and Kuilman's basic assumption of log Gaussian distribution of relaxation times.

Christensen and Anderson (CA) Model

Christensen and Anderson developed a mathematical model for describing the viscoelastic behavior of bitumen after performing mechanical analysis on Strategic Highway Research Program (SHRP) core bitumens. They noted four main parameters namely glassy modulus, steady state viscosity, crossover frequency and the rheological index for characterizing properties of bitumen.

Fractional Model

This model developed by Stastna et al was based on a generalization of the Maxwell Model. The Fractional Model has a relatively low number of parameters when compared to a superposition of Maxwell models to emulate the broad range of relaxation times. Details concerning the exact determination of parameters were not presented in their papers and as a result have led to criticisms of the model.

Christensen Anderson Marasteanu (CAM) Model

The CAM Model is a model developed to improve the descriptions of unmodified and modified bitumen by applying Havriliak and Nagami Model to the initial CA Model.

Bahia and Co-workers' Model

This model has the capability of modeling bitumen as a viscoelastic fluid and asphalt mixture as a viscoelastic solid in a universal form.

Al-Qadi and Co-workers' Model

Al-Qadi and co-workers also proposed a model for describing the rheological behavior of unmodified and modified bitumens in the LVE regions.

Currently in pavement engineering applications, most of the characterizations of polymer modified asphalt have been developed based on laboratory testing. What is missing is a theoretical understanding and modeling which is capable of addressing quantitatively the variables which affect the polymer in processing and ultimately in modified asphalt in-service pavements. This is very important since in pavement engineering, engineers and decision makers must rely heavily on prediction modeling to assess both the long term behavior and life cycle costing of the pavement. Therefore appropriate theoretical, experimental and field proven models are needed. This work proceeds in 3 stages a) development of mathematical models, b) laboratory studies and c) field studies (Currently (b) and (c) are ongoing). The mathematical/theoretical analysis identified variables and parameter groupings that influence pavements. Experimental protocol will be developed to verify both the magnitude, and the influence of important variables. Finally a field site will be selected. Successful completion of this project will have a major influence on infrastructure asset management.

METHODOLOGY

The mathematical/theoretical modeling and analysis was carried out on the composite mixture in its fluid state in bulk. The modeling is being developed for a polymer network formed by the entangled polymer molecules, a network which contains inclusions of variable size and distribution fine and coarse aggregates. The density of the network, the ability of the network to break (disentangle) and or possibly to reform (re-entangle) as well as the effect of the size of the inclusions relative to the effective network size is being examined. Predictions are for basic rheological flows of the mixtures for example simple shear, extension, and step strain. The spatio-temporal predictions of the model(s) in each situation (relaxation time, relaxation dynamics, homogeneity or inhomogeneity of flows, possible demixing processes) are analyzed through model simulations and are to be compared with those of the bulk fluids in experiment. Later refinements will include the processing (spreading and drying of the asphalt) and the wear properties of the result. It is assumed that a well-mixed tightly networked asphalt with appropriate mean size inclusions will generate the longest lifetime under wear.

Mathematical models of viscoelastic fluids range from purely phenomenological (e.g. the power-law model or the Cross model) to models which attempt to include the physical processes and kinetics involved. The `simplest' model which models the entanglement and disentanglement of long molecules, that is models the kinetics of polymer networks is the constitutive equation for the stress known as the Lodge (or equivalently the Maxwell) model which, in tensorial form, is a coupled system of quasilinear partial differential equations for the stress components. Some asphalt literature uses fits to a Maxwell model, those fits are generally to linearized versions of the model, a linearization which is realized in experiments in Small Amplitude Oscillatory Strain (SAOS). In these experiments a plate-plate, cone-plate, or a Couette rheometer are used under controlled strain or strain-rate such that one plate is held fixed, the other (or the cone) undergoes a displacement of the form $d=\gamma_o\sin(\omega t)$ for small strain γ_o over orders of magnitude of frequency.

The in phase and out of phase responses are measured. While useful for determining many properties, SAOS does not clarify the nonlinear response of the model and thus LAOS (Large Amplitude Oscillatory Shear) (Zhou et al 2010) experiments should be carried out as well as shear rate controlled, extensional, and step strain experiments. There are a number of nonlinear viscoelastic model constitutive equations in the rheology literature, all derived to include various mesoscale physical phenomena, for example the Giesekus model (DPL 1987), and more recently the two species VCM (Vasquez, McKinley, Cook) model. The Lodge and Giesekus models are single species models (the network strands are either connected to the network or not considered) and recently these have been examined with the addition of a Newtonian solvent so that the total stress is the polymer stress τ_p plus the solvent stress $\eta_s \gamma$. The Maxwell (Lodge) and Giesekus models are nonlinear version of the Lodge (upper convected Maxwell) single species models. The VCM model is a two species model which keeps track of attached and unattached polymer (broken from the network) strands. This two species model, with Newtonian solvent, was developed particularly for self-assembled surfactant structures but in appropriate limiting conditions is relevant to monodisperse polymer mixtures (long roughly similar length polymers in a sea of shorter inclusions).

These models are all (nonlinear) variants of a Maxwell model and hence exhibit exponential relaxation in time. The few results that do exist on experiments on (high temperature, fluid) asphalt mixtures with binders suggest that the relaxation is power-law, not exponential (Christensen et al). One model considered in the asphalt literature is a variant of the Maxwell model known as the fractional Maxwell model (Badami et al, 2011) corresponding to a spring and a dashpot connected in series with these elements being fractional (thus a hard or soft nonlinear spring or damper). Fractional models have been considered in a number of applications in the mathematical and physics literature (Hilfer, 2000) (Podlubny, 1999) among others. The linearized equation for the stress if the fractional elements are in series and/or in parallel (Kelvin elements) is:

$$\sigma + \frac{(G_1 \lambda_1)^{\alpha_1}}{(G_2 \lambda_2)^{\alpha_2}} D^{\alpha_1 - \alpha_2} \sigma = \lambda_1^{\alpha_1} G_1 D^{\alpha_1} \varepsilon$$

With $\alpha_1 = 1$ this is the fractional Maxwell model of order $1 - \alpha_2$. The response of this model to small amplitude oscillatory shear, $\gamma = \gamma_0 \omega \cos(\omega t)$ has the form:

$$\sigma = \gamma_0 (G'(\omega)\sin(\omega t) + G''(\omega) \cos(\omega t))$$

where for $\alpha_1=1$, $\alpha_2=0$, $G_2=1$, the Maxwell model, the in phase component, the storage modulus, is $G'=G_0((\omega^2\lambda^2)/(1+\omega^2\lambda^2))$ and the out of phase component, the loss modulus, is $G''=G_0((\omega\lambda)/(1+\omega^2\lambda^2))$

For the fractional Maxwell model the response can be determined asymptotically, that is if $\alpha_1=1$, the storage modulus $G' \sim \omega^{2-\alpha_2}$ as $\omega\sim0$, and $G' \sim \omega^{\alpha_2}$ for $\omega\sim\infty$; and the loss modulus $G''\sim\omega$ for $\omega\sim0$ and $G'' \sim \omega^{\alpha_2}$ for $\omega\sim\infty$. This in comparison to the results above for the straight Maxwell model in which the storage modulus behave like ω^2 for small frequencies, like 1 for large frequencies, and the loss modulus behaves like ω for small frequencies, and $1/\omega$ for large frequencies.

The fractional model can also be solved for its relaxation after a step strain. After a step strain the straight Maxwell model relaxes with an exponential relaxation $\sigma \sim e^{-t/\lambda}$ (here $\lambda=\lambda_1$ is the relaxation time). The solution for the power law case is found using Mittag-Leffler functions (Podlubny, 1999) and for the case $\alpha_1=1$, $\sigma \sim \dfrac{1}{\Gamma(1-\alpha_2)}\left(\dfrac{t}{\lambda}\right)^{\alpha_2-2}$. Note that the behavior for large time and short time, just as that for large frequency and small frequency, have a fixed relationship relative to the power in the equation. If the experimental results show a different power law relationship for large or small asymptotics, then this model is too simplistic.

For larger amplitudes the spatial nature of the convected derivative must be included making even the "linear" Maxwell model quasilinear. Understanding the correct formulation of a tensorial UCM fractional model requires some work. Unfortunately if the model is altered at all (for example the power of the fractional derivative changing in time indicating ageing of the material) understanding how this translates to that solution formalism is unclear and perhaps not even possible to formulate in simple terms.

The UCM model and the fractional variants are macro scale models which result from mesoscale modeling of the polymer coupled with a closure approximation to integrate the model to the macroscale. In order to circumvent the need for closure approximations and our inability to formulate a "correct" model on the macroscale, we may instead carry out simulations of the entangled network/suspension mixture at the mesoscale incorporating random size inclusions and random tangling/breaking of the network, then test the simulations against experiment.

In conclusion our goal is to work across disciplines, civil engineering and mathematics, to carry out experiments and couple those results with mathematical modeling to better understand the properties of polymer modified asphalts. In the process we will be cross training graduate students in understanding experimental responses of varied asphalt mixtures and in the mathematical modeling to better predict properties of polymer modified asphalt mixtures in understanding fluid/bulk (at high temperatures), eventually in application (cooling and thin films) and hardening.

FINDINGS

Under this grant one math graduate student was funded (Yun Zeng). Additionally the grant supported a research trip for that graduate student, and a co-PI (Cook), to Massachusetts Institute of Technology (MIT) to consult and work with Dr. Gareth McKinley in the Mechanical Engineering Department. The co-PIs also traveled to Dover for consultation with Karl Zipf at Delaware Department of Transportation (DelDot) and for a tour of his asphalt and of the concrete testing labs.

The present work is on modeling highly entangled fluids such as soft materials and gels using a network approach. These fluids relax more slowly than do those of "standard" visco-elastic fluids, namely the relaxation exhibits power-law behavior $\sigma(t) \sim t^{-\alpha}$, or a stretched exponential pattern $\sigma(t) \sim \exp(-t^{\alpha})$, as opposed to an exponential decay $\sigma(t) \sim \exp(-t)$. Relaxation tests on polymer and wax modified bitumen do show power law relaxation at certain temperatures [Celauro et. al. 2009]. Experiments on some polymer-modified-bitumen, and as well on surfactant solutions, show that as the temperature of the mixture decreases the relaxation time $\lambda \to \infty$. The storage modulus G' and loss modulus G'', under a Small Amplitude Oscillatory Shear (SAOS) experiment, transition from intersecting at a finite value of frequency $\omega = 1/\lambda$ (with λ being known as the relaxation time) to being almost parallel on a log-log plot, indicating a power law time decay. Understanding the properties of the polymer modified bitumen mixture as the temperature changes, both with and without additives, may lead to more refined testing procedures and more relevant capabilities of the rheometric (laboratory) tests in predicting the properties of modified asphalt on roadways.

To date models to capture power-law relaxation characteristics have been confined to explicit scalar ad hoc models (KWW, Nutting) and to macroscales scalar fractional differential equation models (Hilfer, 2000). As noted, these models suffer from not being directly derived from material properties and not having identifiable tuning parameters (e.g. for temperature dependence). Yang et. al. (Yang, 2010) formulated a tensorial version of the fractional Maxwell model, however this model does not relate directly to the (mesoscale) physics of the interactions. Fractional differential equations in scalar form have been extensively examined and directly related to a continuous time random walk (CTRW) process as opposed to a regular random walk (Brownian motion) at the mesoscopic level. A CTRW with a waiting time distribution with non-finite mean is typified by a Mittag-Leffler (as opposed to Poisson) distribution. Such a "slow" process (a fat tailed distribution in time) has been related to materials in which they are entrapments. Modified bitumen at certain temperatures does consist of highly entangled polymers, the entanglements confining each strands motion. This type of entrapment is related to reptation effects, namely the polymer strands are so entrapped that they are effectively confined within a tube, defined by their neighbors, hence their only allowed motion is snake-like (reptative) along their backbone out of the tube. Close to equilibrium stochastic modeling has been carried out for an almost equilibrium system by (Cates, 1987), who was able to show an evolution from stretched exponential relaxation (in the pure reputation case) through power-law relaxation (as the entanglements breaking times became smaller as anticipated with increased temperature) to exponential relaxation (when entanglement breaking time was short, thus breakage effects dominated over reputation). These simulations did not account for the effect of external forcing (e.g. shearing flow effects), moreover the predictions were confined to assuming

that the initial polymer length distribution was asymptotic.

The authors examined transient network models in which the entangled physical system is simplified as a network consisting of bead-spring dumbbells. The entanglements can break and reform continuously. The breakage and reformation processes are slowed down due to entanglements, therefore, the mechanisms are modeled using a continuous time random walk processor that the lifetimes of each dumbbell follow a Mittag-Leffler probability distribution instead of exponential distribution. The time evolution equation for the probability distribution function $\varphi(Q,t)$ to find a specific segment vector Q at time t is

$$\frac{\partial \varphi}{\partial t} = -\frac{\partial}{\partial Q} \cdot [\kappa \cdot Q]\varphi + \frac{\varphi_{eq}}{\lambda} - \frac{\varphi}{\lambda}$$

where $\varphi_{eq}(Q)$ is the equilibrium distribution of dumbbell configurations. The imposed flow field is described by $\kappa = \nabla v^t$, where v is the velocity. The last two terms of the above equation represent creation and loss of network segments. The breakage and reformation processes are now governed by a Mittag-Leffler distribution, where the cumulative distribution function of the waiting times follows a one-parameter Mittag-Leffler function $E_\alpha(-(t/\lambda)^\alpha)$. When $\alpha = 1$, the model reverts to the Lodge network model [Bird et. al. Dynamics of Polymeric Liquids] and the second moment gives us exactly the Upper Convected Maxwell (UCM) model (which predicts an exponential stress relaxation). For $0 < \alpha < 1$, the model predicts a much slower stress relaxation behavior. The model is solved under steady shear flow followed by cessation of the steady shear flow. Figure 1 shows that the stress growth is faster with a smaller parameter α and the stress relaxation is slower with a smaller α. This behavior is due to the fat-tailed Mittag-Leffler distribution for the waiting times of the attachment and detachment processes. The attachment/detachments happen less frequently with a smaller α, thus, the network strands tend to live longer and be stretched more by the flow. This behavior is confirmed by examining the length distributions of all dumbbells at time $t = 10$ for simulations under shear flow with different α. The cumulative distribution of all lengths is plotted in Figure 2, where we observe a broader distribution of lengths for smaller α.
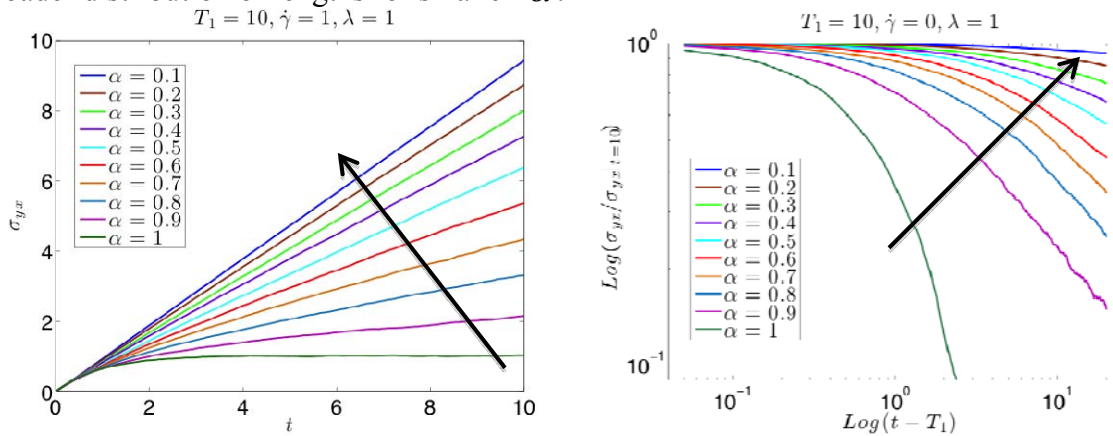

Figure 1 Shear Stress growth and Relaxation

Left: Shear stress growth under steady shear flow for $0 < t < 10$ with different α. Here the scaling is such that $\lambda = 1$ and we have chosen $\dot{\gamma} = 1$. Right: Shear stress relaxation after cessation

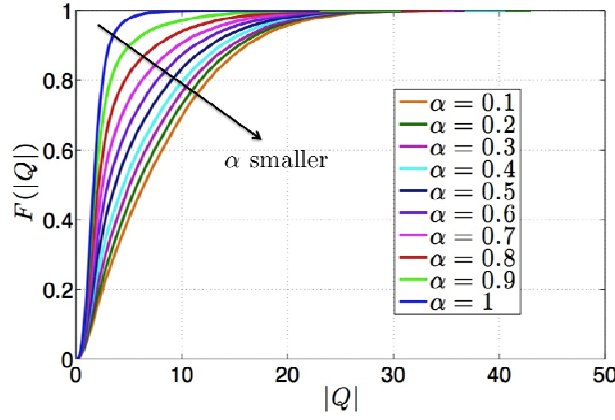of steady shear flow for $t > 10$ with varying α. The shear stress is normalized by its value at t=10.

Figure 2 Cumulative Distribution of all network strands lengths under steady shear flow at time t=10

The parameters are the same as those in Fig. 1.

For a step strain experiment, we use a ramp in strain rate with the velocity $v_x = \gamma_0 b^2 \exp(-bt)$, b large. Following a step strain we the stress relaxation data is well fit with a one-parameter Mittag-Leffler function $E_\alpha(-(t/\lambda)^\alpha)$. When $\alpha = 1$, the stress relaxation is purely exponential. When $0 < \alpha < 1$, the relaxation is much slower with an initial stretched exponential pattern followed by a power law behavior for large time.
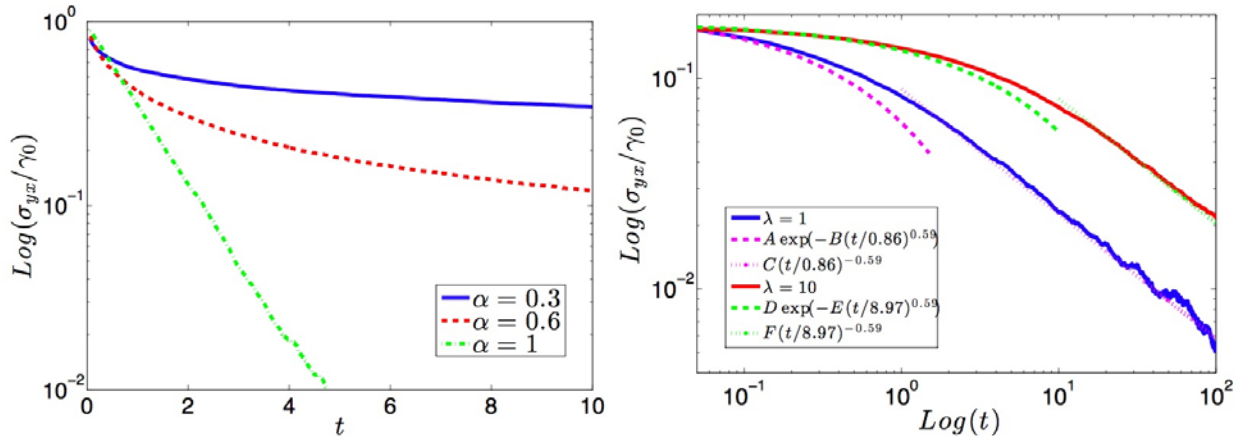

Figure 3 Shear stress relaxation following a step strain for parameters

Left: Shear stress relaxation following a step strain for parameters λ $\alpha = 0.3, 0.6, 1$ with $\lambda = 1$, $\gamma_0 = 10, b = 100$. Right: stress relaxation following a step strain for $\alpha = 0.6$ with $\lambda = 1$ and $\lambda = 10$ exhibit initial stretched exponential behaviors for $t \ll \lambda$ and then power law patterns for $t \gg \lambda$.
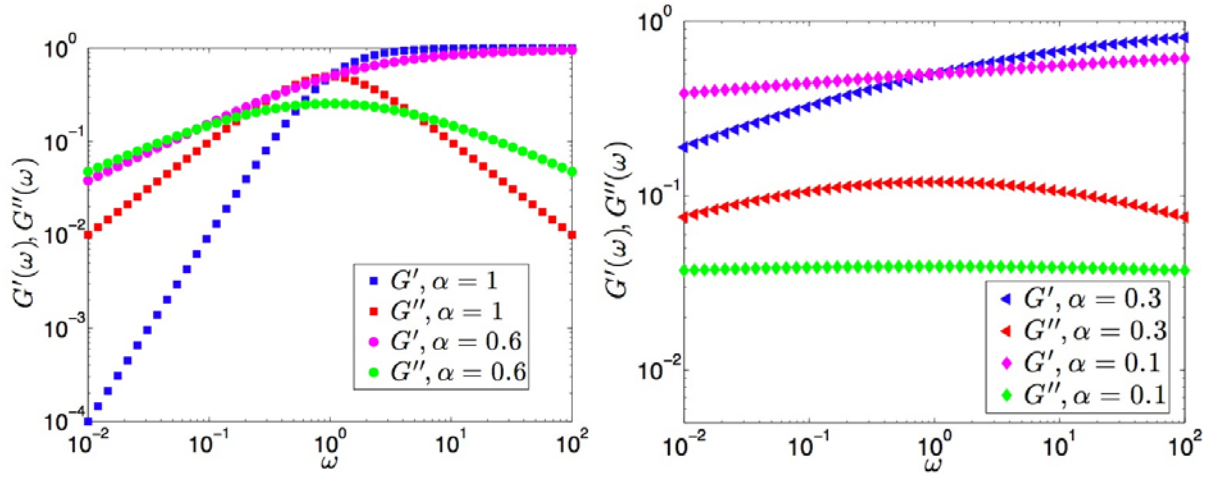
SAOS:

Figure 4 Storage modulus G' and loss modulus G"

Storage modulus G' and loss modulus G'' for $\alpha = $ 0.1, 0.3, 0.6 and 1. The relaxation time of the system(which is inverse to the intersection frequency of G', G'')is increasing with smaller α.

The results were generalized to modeling networks in which the network segments themselves are modeled as elastically active strands (that is the strands are modeled as elastic dumbbells with the end masses connected or disconnecting from the network), more specifically a Lodge-type model, with Mittag-Leffler distribution process for the breaking and reforming, but also explicit inclusion of a "reptative" effect. This work is being completed as a paper to be submitted.

The authors also examined network models in which the disconnected segments are tracked along with the connected network segments, thus two species models similar to the work of (Cifre et. al., 2007). In these models theyis also able to track the orientation effects of the strands that is the drag on the dumbbell is reduced if the dumbbell is oriented along the flow direction. This non-linear effect has been introduced in earlier deterministic models (Giesekus), and in a network model in which connection and disconnection processes are governed by a Poisson distribution (Sieminis et. al.,2002) but not in slow, power-law, relaxation situations not in simulations in which the stress of the two species (connected and disconnected strands) is tracked.

CONCLUSIONS
This latter work is ongoing and will be directly compared, in its predictions, with experiments. The next thrust for this work is to connect it directly to laboratory measurements, to the long time behavior of the modified bitumen roads, and to possible new testing procedures.

RECOMMENDATIONS

- The rheological models for polymer-modified asphalt must be verified with experimental data especially beyond the linear viscoelastic region.
- The new rheological models, after experimental verification, must be calibrated with field data.

REFERENCES

Airey, G.D. (2009), Chapter 23: Bitumen Properties and Test Methods. ICE Manual of Construction Materials, Institution of Civil Engineers, UK.

Badami, J.B., and M. L. Greenfield, Maxwell model analysis of Bitumen rheological data, J. of Materials in Civil Engineering, Oc.t 2011, pp. 1387-1389.

Bird, R. Byron, Cjares, Cirtoss. Robert C. Armstrong and Ole Hassager (1987). Dynamics of Polymeric Liquids: Volume 2: Kinetic Theory. " John Wiley & Sons, Inc.

Bird, R. Byron, Robert C. Armstrong and Ole Hassager (1987). "Dynamics of Polymeric Liquids: Volume 1." John Wiley & Sons, Inc.

Cates, M.E., Macromolecules, (1987), 20, pp. 2289-2296.

Celauro C., M. Di Paola, D. Lo Presti, F. Marino, A. Pirrotta, Modeling of the viscoelastic behavior of paving bitumen using fractional derivatives, Mecanica die Material e dell Strutture, 1 (2009) pp. 38-51

Celauro, DiPaola, Lo Presti, Marino, Pirrota, Modeling of the viscoelastic behavior of paving bitumen using fractional derivatives, Meccanicadei Materiali e delleStrutture 1., (2009) pp. 38-51.

Christensen, D.W. Jr., D. A. Anderson, "Interpretation of dynamic mechanical test data for paving grade asphalt cements", J. Assoc. Asphalt Paving Technol. 61, pp. 67-116

Cifre, J.G. Hernandez, R. Pamies, A.-L.Kjoniksen, K.D. Knudsen, B. Nyström, J. Garcia de la Torre, Brownian dynamics simulation of reversible polymer networks using a non-interacting bead-and-spring chain model, J. Non-Newt. Fluid Mech., 146, 2007, pp.3-10

Committee Report of the Committee on Characteristics of Bituminous Materials (2003).Transportation Research Board, Washington, DC.

Glaser, R., Farrar, M., Huang S. C., Schabron, J., Turner, F. (2011). Asphalt Aging and Fatigue. Western Research Institute.

Hilfer, R., Applications of Fractional Calculus in Physics, World Scientific Publishing Company, 2000

Larson, R., Constitutive equations for polymer melts and solutions, Butterworth's, Boston, 1998

M. Cromer, L. P. Cook and G. H. McKinley, Pressure driven flow of a model of entangled wormlike micellar solutions,

Marasteanu, M., T. Clyne, J. McGraw, X. Li, R. Velasquez, High-temperature rheological properties of asphalt binders, Transp. Res. Rec., 1901, pp. 52-59, 2005

N.M. Wasiuddin, R. Saha, W. King Jr., L.Mohammad, Effects of temperature and shear rate on viscosity of Sasobit-modified asphalt binders, J. Pavement Res. Technol. 5(6) 2, pp. 369-378

Pipe, C., N.J. Kim, G.H. McKinley, P. Vasquez, L.P.Cook, Wormlike micellar solutions II: comparison between experimental data and scission model predictions. ADD IN JOURNAL

Podlubny, I., Fractional Differential Equations Academic Press, 1999

Polacco, G. O.J. Vacin, D. Biondi, J. Statna, L. Zanzotto, Dynamic master curves of polymer modified asphalt from three different geometries, Applied Rheology, 13(3) 2003, pp. 118-124

Polacco, G. S. Filippi, M. Paci, F. Giuliani, F. Merusi, Structural and rheological characterization of wax modified bitumen, Fuel, 95, pp. 407-416, 2012

Rehage, H. and Hoffmann, H. (1991). Viscoelastic Surfactant Solutions - Model Systems for Rheological Research. Molecular Physics, 74(5), 933- 973.

Seimenis, M., L.E. Wedgewood, A network model with free-strand dynamics for polymer melts, Rheol. Acta, 41, pp. 93-102, 2002

Yang, P., Y.C. Lam, K-Q Zhu, Constitutive equation with fractional derivatives for the generalized UCM model, J. Non-Newtonian Fluid Mech., (2010), 165, pp. 88-97.

Yusoff, N.I. (2012). Modelling the linear Viscoelastic Rheological Properties of Bituminous Binders. Thesis submitted to the University of Nottingham

Zhou, L. , L. P. Cook, G.H. McKinley, Probing shear-banding transitions of entangled liquids using Large Amplitude Oscillatory Shearing (LAOS) deformation, J. Non-Newtonian Fluid Mech., 165, 2010

Table 1 General classification of bitumen additives and modifiers (Airey, 2009)

Type		Generic examples
1	Fillers	• Mineral fillers: Crusher fines • Lime • Portland cement • Fly ash • Carbon black
2	Extenders (chemical modifiers)	• Organo-metallic compounds • Sulphur • Lignin • Polymers

3	Rubbers
	(thermoplastic elastomers)
	  a. Natural latex
	  b. Synthetic latex
	  c. Block copolymer
	  d. Reclaimed rubber
		• Natural rubber
		• Styrene-butadiene-rubber (SBR)
		• Polychloroprene latex
		• Styrene-isoprene-styrene (SIS)
		• Crumb-rubber modifier

4	Plastic (thermoplastic polymers)	• Polyethylene (PE)/polypropylene (PP) • Ethylene acrylate copolymer • Ethylene vinyl acetate (EVA) • Polyvinyl chloride (PVC) • Ethylene propylene or EPDM • Polyolefins
5	Combinations	• Blends of polymers in 3 and 4
6	Fibres	• Rock wool • Man-made: polypropylene • Polyester • Glass-fibre • Mineral • Cellulose
7	Oxidants	• Manganese salts
8	Antioxidants	• Carbon • Calcium salts • Amines
9	Hydrocarbons	• Recycling and rejuvenating oils • Hard and natural asphalt (gilsonite, TLA)
10	Anti-stripping agents (adhesion improvers)	• Amines • Lime
11	Waste materials	• Roofing shingles • Recycled tyres • Glass
12	Miscellaneous	• Silicones • De-icing calcium chloride granules