

RHEOLOGICAL PROPERTIES OF SOUTHERN PINE OLEORESINS

IMANE BELYAMANI¹, JOSHUA U. OTAIGBE^{1*}, C. DANA NELSON², BRIAN L. STROM³, JAMES H. ROBERDS²

¹School of Polymers and High Performance Materials, The University of Southern Mississippi,
118 College Drive #5050, Hattiesburg, MS 39406, USA

²USDA Forest Service, Southern Research Station, Southern Institute of Forest Genetics,
23332 Success Road, Saucier, MS 39574, USA

³USDA Forest Service, Southern Research Station, 2500 Shreveport Highway,
Pineville, LA 71360, USA

* Corresponding author: joshua.otaigbe@usm.edu

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ABSTRACT:

Despite the economic and ecologic importance of pine oleoresins, their rheology remains little explored. In this report we describe rheological properties of oleoresins produced by mature trees of four southern pines native to North America (loblolly, slash, longleaf, shortleaf). Results indicate that these oleoresins are structured fluids that exhibit viscoelastic behavior, but differ in flow behavior. Slash pine oleoresin exhibited Newtonian flow behavior while the oleoresin from the longleaf and shortleaf pines showed pseudoplastic behavior and the loblolly pine oleoresin showed Bingham fluid behavior with a yield stress of about 1.980 Pa. Temperature-dependent viscosities for the oleoresin samples studied were well described by the Arrhenius model, yielding flow activation energies ranging from 153.5 to 219.7 kJ/mol. The viscosity of the slash pine oleoresin sample was found to be less sensitive to temperature than that of the shortleaf or longleaf pine samples. The time-temperature superposition principle was successfully applied to pine oleoresins to show behavior over the temperature range of 25–65 °C typical for a thermorheologically simple system. Such behavior is consistent with the temperature dependent viscoelastic properties found for these complex fluids, and supports the effective use of rheological evaluations for describing physical properties of pine oleoresins.

KEY WORDS:

Southern pines, oleoresins viscoelasticity, crystallization, viscosity, Bingham fluid, time-temperature superposition

1 INTRODUCTION

Oleoresins produced by pine trees are complex and dynamic mixtures of phytochemicals [1]. These compounds have long been of commercial interest, having been relied on since the earliest of times to waterproof boat hulls and improve seaworthiness and durability of accessories such as ropes [2]. Commercial uses served as the genesis and namesake of the naval stores industry which, in the southeastern region of the USA, evolved to producing spirits of turpentine and raw chemicals and remained economically important for about 150 years [3]. Pine oleoresin remains the largest stock volume of essential oils in nature and continues to be a significant source for raw materials and products ranging from turpentine to fatty acids and biofuels among other diverse uses [1, 4, 5].

In addition to its direct commercial value, pine oleoresin is of interest to forest ecologists because of its

role in tree resistance to insects and diseases [6, 7]. It functions as a generalized defense against any wound agent that severs oleoresin ducts in the act of penetrating the outer bark of a pine tree. The oozing oleoresin that results from wounding provides both chemical and physical resistance properties [7–9]. Volatile components (mostly monoterpenes) of pine oleoresin have been extensively characterized and their role in tree resistance, as well as their use as semiochemicals by insects, is well documented [5, 7, 10, 11]. Nevertheless, characterization of the physical properties of pine oleoresins (such as viscosity) has been challenging, primarily because of the complex chemical nature of oleoresin and structural instabilities that often develop during handling and use. The most troublesome of these has been the rapid crystallization of the oleoresin of many species, which makes the use of established methods problematic for characterizing physical properties such as viscosity.

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Species	c_1	c_2	T (K)	E_a^* (kJ/mol)
Slash pine	187.2	450.61	298	706.39
			308	722.18
			318	737.47
			328	752.27
			338	766.60
Shortleaf pine	205.46	595.85	298	586.31
			308	605.81
			318	624.99
			328	643.84
			338	662.36
Loblolly pine	225.19	440.12	298	869.99
			308	888.52
			318	906.43
			328	923.75
			338	940.50
Longleaf pine	178.15	484.84	308	667.41
			318	682.99
			328	698.12
			338	712.82

Table 6: WLF model parameters estimated for the tested pine oleoresin samples.

over the experimental temperature range of the TTS experiment. The temperature dependence of the shift factors can also be studied using the WLF (Williams-Landel-Ferry) expression (Equation 7):

$$\log a_T = \frac{-c_1(T-T_o)}{c_2+(T-T_o)} \quad (7)$$

where c_1 and c_2 are the WLF parameters. Figure 15 shows the temperature dependence of shift factors as embodied in the WLF equation for the four pine oleoresin samples at the studied temperature range. It is evident from Figure 15 that the experimental data are very well described by the WLF equation as indicated by coefficients of determination ranging between 0.999 and 1 for the pine oleoresin samples studied. Based on the obtained values of c_1 and c_2 , shown in Table 6, apparent activation energy E_a can be determined according to the modified form of the WLF equation [28]:

$$E_a = \frac{2.303 R c_1 c_2 T^2}{(c_2 + T - T_o)^2} \quad (8)$$

Table 6 summarizes the obtained apparent activation energy of pine oleoresin samples, as estimated from Equation 8. It should be pointed out that the Arrhenius model previously discussed describes temperature dependence of a material's viscosity in terms of a constant activation energy (E_a), whereas the WLF model describes an apparent activation energy E_a [28]. As can be seen in Table 6, for all samples the estimated apparent activation energy values increase with increasing tem-

perature, thus indicating temperature dependence for a_T in the experimental temperature range. The temperature dependence of shift factors at the different experimental temperatures could also reflect the effect of temperature on the viscoelastic properties of the oleoresin samples, thereby confirming their temperature sensitivity already indicated by application of the Arrhenius model. The successful application of the TTS principle and the WLF model to experimental data collected from pine oleoresins, despite the complex nature and composition (volatile and nonvolatile terpenes) of these fluids, is a novel and noteworthy finding.

4 CONCLUSION

Rheological evaluation of oleoresins collected from four different southern pine species confirmed that these compounds are structured fluids that exhibit viscoelastic behavior under small amplitude oscillatory shear deformation and flow conditions. To our knowledge, this is an original report of such behavior for pine oleoresins. The results described here suggest that species-dependent flow behaviors exist for the four pine species investigated. For example, oleoresin collected from slash pine exhibited Newtonian flow behavior whereas the longleaf and shortleaf pine oleoresin samples showed pseudoplastic behavior, but oleoresin sampled from loblolly pine behaved as Bingham fluid, requiring a yield stress of about 1.980 Pa to be exceeded before proceeding to flow. The viscosity of the studied oleoresins showed temperature dependence properties that were adequately described by the Arrhenius equation. The calculated flow activation energies of all the samples ranged from 153.5 kJ/mol to 219.7 kJ/mol; the viscosity of the fresh slash pine oleoresin sample was less sensitive to temperature changes compared to that of the fresh shortleaf and longleaf pine samples, which were the most affected by temperature changes. This trend was reversed after formation of macroscopic milky crystals in the oleoresin samples; viscosity of the slash pine oleoresin sample became the most sensitive to temperature changes (199.28-202.19 kJ/mol), whereas viscosity of the longleaf pine sample became the least temperature dependent (174.17-178.08 kJ/mol). Nevertheless, viscoelastic properties of the macro-crystallized pine oleoresin samples remained temperature-dependent and reversible. In addition, the TTS principle (or WLF equation) was successfully applied to data collected from oleoresin samples, and the results produced indicate that pine oleoresin displays behavior typical for a thermorheologically simple system over the temperature range of 25–65 °C, despite the complex composition of these compounds.

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The two types solid-liquid phase transitions observed for the four pine oleoresin species tested are compatible with different defensive mechanisms exhibited by southern pines to resist attack from its most important pest, the southern pine beetle. These include a chemical defense mechanism governed by temperature dependent physical properties of oleoresin (i.e. flow, viscosity, solid-liquid transitions) and a physical defensive mechanism, based on wound sealing, that involves formation of visual crystals apparently resulting from monoterpene evaporation. To our knowledge, the viscoelastic study described here is the first of its kind, leading us to conclude that the results described will provide a basis for a better understanding of the deformation and flow properties of pine oleoresins, and of their role in tree defense against attacks by insects and diseases.

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