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Chemorheological study of a polyfurfuryl alcohol resin system—Pre-gel curing stage

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ABSTRACT

The rheological and chemorheological behavior of a new biomass-based polyfurfuryl alcohol (FA) resin aimed to be used as a matrix in composite materials is studied in this work. The viscosity dependence on the shear rate and temperature of the resin is studied under steady and oscillatory conditions. The FA resin exhibits a Newtonian flow behavior within the shear rate range tested. The dependence of the viscosity of the uncured resin on temperature is measured and modeled. The flow activation energy, as calculated by the Arrhenius model, is 63.3 kJ mol^{-1}. The chemorheological study of the curing process showed that the flow activation energy of the resin is increased when the amount of catalyst is increased. Furthermore, the curing parameters of the FA resin using three amounts of catalyst of 2, 4, and 6% (w/w), are obtained by the Arrhenius model. The curing activation energy is found to be about 96 kJ mol^{-1} and with no dependence on the amount of catalyst. However, a significant difference of the logarithm of the pre-exponential curing parameter is found. This parameter increases from 28.9 to 30.7 when the amount of catalyst is increased from 2 to 6% (w/w). Based on the established values of the Arrhenius model parameters, predictions are made for the evolution of viscosity of the resin during isothermal curing with different temperatures, and different amounts of catalyst. This is of great importance in the design of the curing processes of the FA resin during development and improvement of composite manufacturing processes.

1. Introduction

The utilization of by-products from industrial processes is one of the most important issues in achieving the goal of sustainable growth. These by-products are even more interesting when they have a natural origin, such as biomass. Thus, in recent years a large increase in research on such biobased by-products has occurred globally, and with a particular focus on the development of new biobased polymers. In the field of thermosetting polymers, new resins have been developed from natural compounds traditionally considered as worthless industrial by-products. Many of these new resins are however only partially based on biobased by-products, e.g. lignins from wood have been used as part of the formulation of resins, such as novolac and resol resins (Alonso et al., 2004, 2001; Pérez et al., 2007). Only a few resins, such a polyfurfuryl alcohol (FA) (Dunlop and Peters, 1953), have been developed to be fully biobased. FA resin comes from the production of furfural from pentosan-rich biomass, such as sugar cane bagasse. Furfural is then processed into monofurfuryl alcohol, which subsequently is converted to the final FA resin through condensation reactions (Choura et al., 1996; Dunlop and Peters, 1953). The FA resin is primarily developed for being used as matrix in fiber-reinforced composite materials.

In general for all materials, optimal design of the manufacturing process is of importance in order to have the best possible materials performance (e.g. mechanical, thermal and acoustic), as well as to reduce the production costs. This is especially true for new materials, like biobased resins, that still have to be introduced into the market, and that therefore should appear as attractive alternative materials solutions for potential customers. High background knowledge of the physical and chemical properties of the materials is required in order to optimally design the particular manufacturing process. In the case of FA resin, one of the relevant processes is vacuum assisted resin transfer moulding, which is a widely used process for the manufacturing of composite materials with a thermosetting resin matrix. For this process, some of the important physical properties of the resin are the flow behavior and the viscosity dependence on temperature, in addition to the kinetics of the curing process.

The study of the curing kinetics of thermosetting resins through thermal analysis, such as differential scanning calorimetry (DSC), provides a fundamental understanding of the curing process.

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Rheometry, and other techniques like Fourier transform infrared spectroscopy, and nuclear magnetic resonance, complement the information obtained by thermal analysis. Rheometry can even replace DSC when the curing degree of the resin is monitored through the evolution of rheological parameters such as the generated torque or the elastic modulus of the resin (Auad et al., 2006; Domínguez et al., 2010b; Martin et al., 2000; Nichetti, 2004). Moreover, by rheometry, the most important transitions during curing of the resin: vitrification and gelation, can be identified. Gelation is of special importance during curing of a resin since it determines the point of irreversible transformation of the resin caused by the formation of an infinite molecular network. From this point, the resin starts behaving more as a solid than as a fluid. Gelation cannot be determined by DSC, and this is therefore an important advantage of rheology with respect to DSC. In addition, determination of the evolution of the chemorheological properties of the resin during its curing process, especially viscosity, is fundamental for the design and control of the manufacturing process. Furthermore, by implementing the chemorheological models in porosity growth models, they can be used to predict and control the porosity of the resin (Ledru et al., 2010).

The curing mechanisms of mono- and FA oligomers have been studied previously in the literature and a general mechanism was proposed by Dunlop and Peters (1953). This mechanism could however only explain the formation of linear chains. A more complete and complicated mechanism was proposed by Choura et al., and this mechanism was able to explain the branching and crosslinking of the FA resin as well as the color formation due to acid-catalyzed self-condensation of polyfurfuryl alcohol (Choura et al., 1996). The curing kinetics of FA resins have been studied in the literature mostly by thermal analysis techniques (Domínguez et al., 2012; Guigo et al., 2010), where a number of study has used different types of catalysts (e.g. Wewerka et al., 1969). However, the rheology and chemorheology of these systems and its dependency on the amount of catalyst have not been deeply studied in the literature.

In the present work, the flow behavior and the viscosity dependence on temperature of a FA resin are studied by rheology. The models of Andrade, Vogel–Taumman–Fulcher, Power-law and Williams–Landel–Ferry are applied on the measured viscosity values obtained at different temperatures. The Arrhenius chemorheological model is applied to analyze the evolution of the complex viscosity of the FA resin during the pre-gel curing stage, studied under isothermal conditions. The influence of the amount of catalyst added to the resin on the curing parameters was studied as well.

2. Theory

2.1. Rheology

The ideal viscous flow behavior of fluids is described by Newton's law: when a fluid moves under the influence of an external force, the shear stress (τ) is proportional to the shear stain rate ($\dot{\gamma}$). The constant of proportionality (η) is called the coefficient of viscosity, or the Newtonian viscosity. In nature, many fluids present however a flow behavior that deviates from the ideal Newtonian behavior. In the case of polymers, they usually present a shear-thinning rheological behavior, i.e. their steady viscosity reduces when the strain rate is increased, commonly described by models such as Power-law, and, Cross and Sisko models (Barnes, 2000). The rheological behavior of polymers is traditionally characterized by the steady viscosity and/or the complex viscosity. These viscosities are commonly related by the so-called Cox–Merz rule (Cox and Merz, 1958). The rheological behavior of polymers depends on structural factors, such as their molecular complexity, their molecular weight, and the presence of fillers in their formulation.

Over the years, there have been proposed and developed a series of models that predict the rheological behavior of fluids with temperature changes (Seeton, 2006). The most widely used model to describe the behavior of fluids with temperature is the Arrhenius model (also denoted as the Andrade model):

$$\eta^* = \eta^*_\infty \exp\left(\frac{\Delta E_\eta}{RT}\right) \tag{1}$$

where T is the temperature, η^* is the complex viscosity, η^*_∞ is the complex viscosity at $T = \infty$, R is the gas constant, and ΔE_η is the flow activation energy (i.e. the energy barrier to flow). For complex fluids, such as polymers, several models have been developed to correct the observed deviations from the temperature influenced viscosity behavior as predicted by the Andrade model. In the case of amorphous thermosetting polymers, some of the models used to predict the changes of complex viscosity at temperatures close to the glass transition temperature (T_g) (i.e. the temperature at which amorphous polymers transform from a rubbery to a glassy state) are: the Vogel–Taumman–Fulcher model (VTF) (Eq. (2)), and the Power-law model (Eq. (3)) (Recondo et al., 2006).

$$\eta^* = \eta^*_\infty \exp\left(\frac{B}{T - T_0}\right) \tag{2}$$

$$\eta^* = k\left(T - T_g\right)^{-m} \tag{3}$$

where T_0 is the temperature at which the relaxation time relevant to molecular displacements becomes infinite, B, k and m are constants to be estimated from a linearization of the models.

Finally, the most successful model for predicting the temperature dependence for viscous flow of polymers is the Williams–Landel–Ferry model (Williams et al., 1955). This model is suitable for modeling the viscosity dependence on temperature of polymers for the temperature range $T_g < T < T_g + 100\,K$. For temperatures above $T_g + 100\,K$ the Arrhenius model usually is the most recommended model. The WLF model is shown by Eq. (4) (using the complex viscosity instead of the steady viscosity):

$$\log\left(\frac{\eta^*}{\eta^*_g}\right) = -\frac{C_1\left(T - T_g\right)}{C_2 + \left(T - T_g\right)} \tag{4}$$

where η^* is the complex viscosity at temperature T, η^*_g is the complex viscosity at T_g, and C_1 and C_2 are constants that originally were considered to be constant for all polymers with values of 17.8 and 51.6 K, respectively. However, Ferry, one of the authors of the model, later on recommended the use of individual values determined for each polymer system instead of "universal values" (Ferry, 1980). In the present work, the method of reduced variables (C_{1r} and C_{2r}) is used to determine the values of the WLF model parameters (Peleg, 1992). A reference temperature (T_r) within the experimental range tested was used instead T_g and the values of C_{1r} and C_{2r} using a non-linear regression.

2.2. Chemorheology

The term used in the literature for the viscoelastic behavior of chemically reacting fluids is *chemorheology* (Tajima and Crozier, 1983). This covers the change in the viscosity of a thermosetting polymer caused by the chemical reactions that take place during curing. By monitoring the variation of chemorheological properties of a thermosetting polymer during curing, the growth of the molecular network, and the glass transition temperature (T_g) and gelation times at a given temperature can be obtained Halley and Mackay, 1996. The models commonly employed in the literature