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Fabrication of carbon-based nanocomposite films by spin-coating process: An experimental and modeling study of the film thickness

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ABSTRACT

Spin-coating is used for the fabrication of nanocomposite thin films, consisting of carbon nanoparticles embedded in epoxy matrix, on Mylar substrate. The final thickness of the heat-cured film was measured as a function of the spinning speed and nanoparticle concentration. Multi-walled carbon nanotubes with carboxyl functionalization (MWCNT-COOH) or exfoliated graphite nanoplatelets (xGnP) were used as fillers. Experimental results were in good agreement with the predictions from a model that considered the rheology and flow behavior of the reinforced resin fluids on a rotating disk. The model was differentiated for Newtonian and non-Newtonian regime of the spinning polymer fluid. In case of non-Newtonian behavior of the epoxy resin at high particle concentrations, a semi-empirical approach was used to determine the model constants from rheology measurements. Results from this analysis also indicate how rheological and wetting properties of the nano-reinforced polymer fluids depend on the aspect ratio of the graphene nanoplatelets.

1. Introduction

Carbon-based nanocomposite films constitute a novel class of industrially applied coatings, which have received great attention due to their electrical, mechanical, thermal and optical properties [1–4]. Depending on the film composition and preparation methods, carbon nanocomposite films are used in a wide range of applications in different technological areas. In particular, such films find use in microelectronic devices [5,6], as substrates with novel biosensing or gas-sensing properties [7,8], in protective and optical coatings [9,10], and as radar absorbing or EMI shielding materials [11,12].

One of the crucial aspects in the fabrication of homogeneous nanocomposite films is to guarantee a uniform distribution of the nanoparticles inside the polymer matrix [13,14]. Besides filler dispersion, the deposition process of the films has a major effect on its overall properties. Spin-coating has become the predominant technique for the large-scale production of uniform and reproducible films with thickness of the order of micrometers and nanometers [15], in particular for microelectronic devices, solar cells and optical coatings [16–19]. In spite of their widespread industrial applications, a few analytical studies of the process for nanostructured polymer liquids can be found in the literature [20–22]. Spin-coating of polymer fluids is a complex process to model due to many mechanisms that are involved at the physical and chemical level. The final thickness and uniformity of the spin-coated films are known to depend on several process parameters, including rotational speed, solution concentration, fluid viscosity and density, and, when solvents are present, rate of solvent evaporation [23–25]. In the case of nano-reinforced polymer liquids, additional complexity in the behavior under spinning arises from the molecular interaction between the nanofillers and the polymer fluid. An accurate analysis of spin-coating for such fluids would allow for a better control of the process in its various applications.

Following the pioneering work of Emslie et al. [26], the analysis of spin-coating process can be performed considering the spreading of a thin axisymmetric film of viscous fluid on a rotating disk. In their work, Emslie et al. made the major assumption that the fluid exhibited Newtonian behavior, characterized by a linear relationship between shear stress and shear rate, and neglected the effect of several forces, such as Coriolis and gravitational forces, as well as spatial and temporal variations in concentration. The predictions of the flow pattern and of the final film thickness were therefore limited to ideal cases not involving suspensions with settling particles or highly viscous fluids. Later, Jenekhe and Schuldt

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analyzed the surface coating of non-Newtonian fluids during the process of spin-coating using numerical methods [27]. Numerical solutions for the film thickness profiles were obtained for non-Newtonian behavior described by power-law and Carreau constitutive equations. Results of this work unveiled that the final thickness and uniformity of films deposited by spin coating are dictated mainly by the fluid rheological properties, and not by the initial profile of the film. The effects of film inertia, disk acceleration, and interfacial shear due to the overlaying gas phase during spin coating were also investigated by numerical methods [28].

In this work, we study the fabrication of nanocomposite films by spin-coating of an epoxy resin reinforced with carbon nanoparticles on polymer substrate, followed by a heat cure cycle. In particular, this work is focused on Prime 20LV epoxy resin containing carboxy-functionalized multi-walled carbon nanotubes (MWCNT-COOH) or exfoliated graphite nanoplatelets (xGnP) at different loadings in the range 0.5–5 wt%. The spin-coating process is modeled considering the flow of a viscous fluid on a planar interface, and differentiating between Newtonian and non-Newtonian behavior of the nano-reinforced epoxy resin as determined in steady shear rheological experiments. The main objective is to predict the thickness of the spin-coated nanocomposite films considering also the non-linear behavior of nano-reinforced resin fluids at high particle concentration. A further objective is to investigate the effect of the geometry of the nanofillers on the rheological properties and wetting properties of the nanostructured epoxy resins on Mylar substrate.

2. Theoretical thickness of spin-coated films

The spin-coating process can be modeled considering the behavior of a liquid solution on a rotating disk substrate, and assuming that the liquid flows on the substrate only in the radial direction and is a function of time [29,30]. For viscous fluids ($Re \ll 1$) inertial effects other than centrifugal have a negligible influence on the rate of thinning of the fluid layer, and centrifugal forces can be considered constant during spinning [28]. In addition, the effect of interfacial shear on the thinning rate can be considered unimportant for moderate spinning times. In our analysis, we further neglect any effect due to solvent evaporation on the thinning rate of the spinning fluid, given the absence of solvents in the nano-reinforced epoxy resins. The film thicknesses that are measured and compared with the model predictions are those of the cured composites films, assuming that no volume shrinkage occurs during the curing and subsequent cooling steps. This assumption can be considered valid for epoxy matrices.

Using cylindrical coordinates (r, θ, z) with origin at the center of rotation and r and θ axes rotating with the plane with angular speed ω (Fig. 1), the Navier-Stokes equation for a Newtonian fluid (viscosity independent of shear rate) is:

$$\eta \frac{\partial^2 v_r}{\partial z^2} = -\rho r \omega^2 \quad (1)$$

where ρ is fluid density, η is fluid absolute viscosity, v_r is the fluid velocity in the direction of r and $\tau_{rz} = \eta \frac{\partial v_r}{\partial z}$ where τ_{rz} is the shear stress on the z face of a fluid element arising from fluid momentum in the y direction, z is the film thickness direction, and ω is the angular speed of the spin coater disk. Integrating and using suitable boundary condition of no-slip (v_r (r, θ, z) = 0 at z = 0) and free surface ($\frac{dv_r}{dz} = 0$ at $z = h$) we obtain [26]:

$$v_r(r,z) = \frac{\rho r \omega^2\, h^2}{\eta}\left[\frac{z}{h} - \frac{z^2}{2h^2}\right] \quad (2)$$

The radial flow Q is given by:

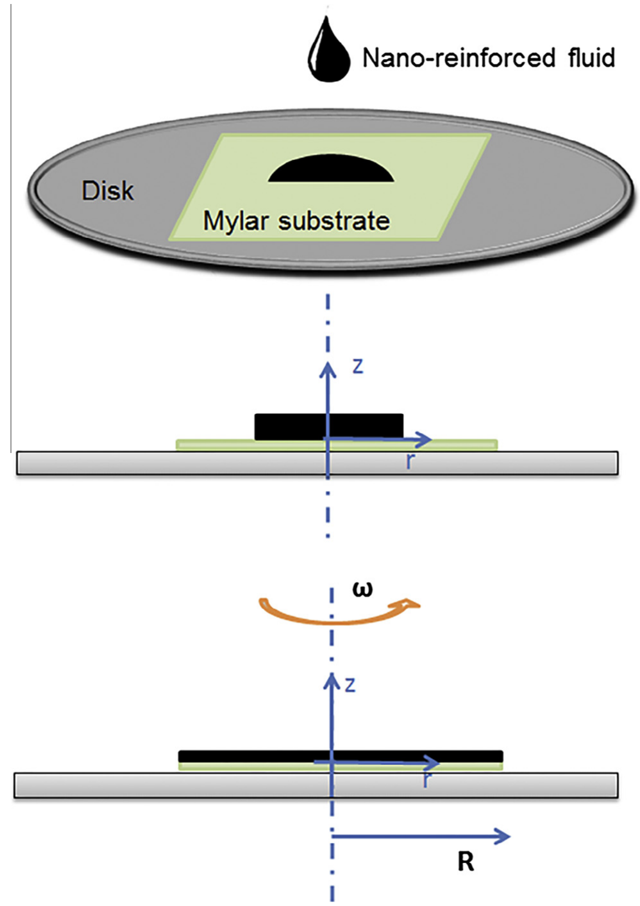

Fig. 1. Schematic of spin-coating process for the fabrication of nano-reinforced thin composite films. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$$Q = \int_0^h v_r dz = \frac{\rho r \omega^2 h^3}{3\eta} \quad (3)$$

Considering the variation of fluid thickness in time, the equation of continuity in radial direction becomes [30]:

$$\frac{\partial h}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}(rQ) = 0 \quad (4)$$

Replacing Eqs. (3) into (4), we obtain:

$$\frac{\partial h}{\partial t} = -C\left(\frac{1}{r}\right)\frac{\partial (r^2 h^3)}{\partial r} \quad (5)$$

where $C = \frac{\rho\omega^2}{3\eta}$. If we consider the time-dependent solution and that the film is uniform along the radial direction ($\frac{\partial h}{\partial r} = 0$), then integrating both sides between suitable limits, $h = h_0$ for $t = 0$ and $h = h_f$ for $t = t_{spin}$ (the selected duration of the spin-coating process), we obtain for a Newtonian fluid:

$$h_f = h_0 \left[\frac{1}{\frac{4\rho\omega^2 h_0^2 t_{spin}}{3\eta} + 1}\right]^{1/2} \quad (6)$$

For fluids exhibiting non-Newtonian behavior, the viscosity is a non-linear function of the shear rate ($\dot{\gamma}$), and a more complicated equation is required to describe it. A widespread model to describe the viscosity of fluids with shear-thinning behavior is the general four-parameter Carreau model [31,32], in which viscosity is related to $\dot{\gamma}$ by: