Facile Spray Coating in Preparing Anisotropic Composites

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ABSTRACT

Anisotropy has been taken advantage in composites to achieve specific mechanical, electrical, magnetic and other functional properties. In composite mechanics, orientation of fiber in polymer matrix will reinforce the composites to the greatest potential along loading direction. Here in this study, with specific dimensions and even dispersion quality, halloysite nanotubes (HNTs) have been studied regarding the orientation influence on mechanical properties in composites. Epoxy based composites including HNTs were prepared using spray coating method, with thin thickness as low as 5 μm. HNTs were aligned by the air flow and maintained by viscous polymers. Upon curing, the HNTs preserved their orientation perpendicular to the film direction, or, in other words, parallel to loading direction. Indentation tests in our previous report showed improvements in both modulus and hardness with higher HNTs orientation. The indentation modulus and hardness both increased by more than 60%. Based on the results from our research scratching tests using TriboIndenter and Atomic Force Microscopy also showed higher scratching resistance when HNTs were more aligned. Scanning Electron Microscopy and Dynamic Mechanical Analyzer have also proven the degree of orientation in some sense. This study is aimed to present the detailed inforamtion regarding the processing of successful particle alignment in final composites, and how the processing parameters influecne the final structural features.

Keywords: Spray coating, anisotropy, mechanical property, nanotubes

1 INTRODUCTION

Polymer composites have been used for structural applications. One method to reinforce the soft polymer matrix is to include stiff and strong nano-sized segments, such as carbon fillers of carbon nanotubes and graphene[1], inorganic particles of clay and metal oxides[2] and bio-fillers of cellulose and wood[3]. These fillers can also be categorized as one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) materials based on their dimensional and geometric features[4]. Among them, 1D nano-particles have been attractive mainly due to their anisotropic properties[5] and effective unidirectional reinforcement in polymers.

Introduction of nano-fillers into polymer matrix is an efficient way to reinforce the material[6]. Due to the usually low concentration and nano-scale size of nano-fillers, the transparency in final composite coatings is least influenced. The organic and inorganic fillers frequently used in academia and industries have been listed in reviewed in a lot of research[6]. It can be seen that the nano-fillers show much higher mechanical properties as compared to transparent polymers. In addition, the aspect ratio influences the stress transfer from nano-fillers to polymers, and in composite mechanics, the higher the value the more efficient in reinforcement[7]. Organic fillers of carbon nanotubes and graphene are the best in mechanical properties; nonetheless their barrier in transparency and the high cost are the disadvantages. Inorganic fillers (as summerized[6]) show decreasing cost from ITO to HNT, from $500 to $2 per kilogram. Considering the density of these fillers, HNT have the highest specific stiffness/hardness and lowest unit-volume price. This is also important since in composite mechanics, the mechanical stiffening/strengthening/hardening is proportional to volume percentage instead of weight percentage[8].

Halloysite nanotubes (HNTs), a naturally occurred clay mineral with one-dimensional hollow cylindrical structure, are exceptionally stiff and hard for their ceramic chemical composition[9]. The presence of hollow lumens in HNTs have also been extensively studied regarding their drug carrier/release properties[10] and nanoreactor potential[11]. Besides, HNTs has low surface charge and easily get dispersed in solvents and polymers of medium to high polarity. Significant mechanical and thermal improvements have been demonstrated in starch, chitosan, gelatin, cellulose, pectin, and polyvinyl alcohol[12]. However, to achieve their maxim potential the main challenge is to eliminate the random distribution of tube orientations. The misalignment of particles will cause inefficiency in stress transfer, and lead the properties of HNT filled nanocomposites to be far below theoretical predictions[6, 13]. For this reason, management of particle orientations to achieve desired macroscopic assembly of HNTs would be the focus of this contribution. This paper has mainly studied the parameters that will determine the final alignment of particles, and how theoretically influence the structural features. The alignment of particles at nano size levels have been proven from electron microscopy.

2 EXPERIMENTATION

Dragonite HNT clay was obtained from Applied Minerals (density 2.54±0.03 g·cm^{-3}, inner diameter 10-20 nm, outer diameter 40-60 nm, and aspect ratio ranges between 20 and 200. BET pore volume 20%, surface area up to 100 m^2·g^{-1}, refractive index 1.534). Epoxy 142-112 (purchased from Epoxy Technology, Inc., density 1.18 g·cm^{-3}) and acetone (purchased from VWR, density 0.79 g·cm^{-3}) were used as obtained. All the composite films were coated on glass slides with different viscosity levels.

The bulk rheological response of epoxy/acetone solutions was measured at 25 ^{o}C using a cone-and-plate (CP) geometry (2^o cone, 60 mm, and truncation gam 58µm, part #513606905) on the AR-G2. The steady shear viscosity of the solutions was measured at shear rates between 10 to 1000 s^{-1}.

A field-emission high-resolution scanning electron microscope (SEM) (Zeiss Supra 25, accelerating voltage 5 kV) was used to image the internal film structures. All samples were sputtered coated with a thin gold/ palladium layer (i.e., coating ranged from 15 to 20 nm) using a Gatan high-resolution ion beam coater for image analysis. To avoid the viscoelastic influence from epoxy, samples were fractured in liquid nitrogen (around -200 oC).

3 RESULTS AND DISCUSSIONS

The fluids of epoxy or epoxy/acetone mixtures all displayed Newtonian behavior, as shown in Figure 1. The orientation of the body will eventually be determined by inertia. Bodies with force and front-end symmetry are torque free when settling in Stokes flow, so that the toques due to inertia are unopposed. This results in an eventual broadside on orientation for all particles.

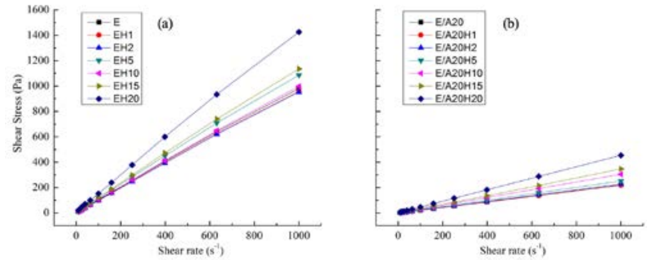

Figure 1 Shear stress as a function of shear rates for (a) Epoxy and (b) Epoxy/Acetone ratio of 20 based composites. Linear proportion between shear force and velocity change shows a Newtonian fluids feature. E/A10, E/A5 and E/A1 display the same Newtonian liquid behavior due to the presence of more acetone additions.

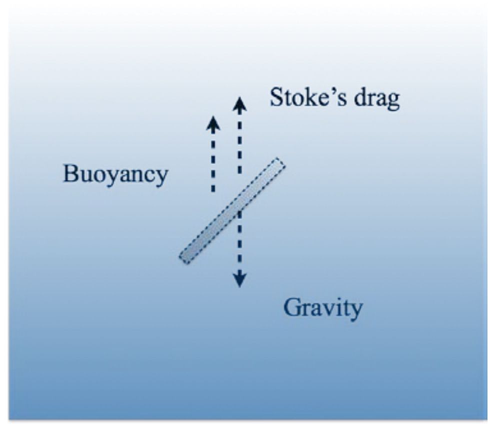

Figure 2 Relative flow motion past a falling particle in a fluid (i.e., a halloysite nanotube falling through the epoxy solution or melt), drag force, F_d, and force by gravity, F_g as well as buoyancy, F_b.

The sedimentation of the tubes at steady state is equivalent to the steady flow past a stationary long body. To simply the problem in study, the micromechanics analysis for a single particle was set-up and as plotted in Figure 2.

According to Stoke's Law, the force of viscosity on a small particle moving through a viscous fluid is given by[14],

$$F_d = 6\pi\mu R v$$

(Equation S1**)**

where F_d is the friction force, known as Stoke's drag, acting on the interface between the fluid and particle, μ is the dynamic viscosity, and in the liquid states studied here, they are mostly Newtonian fluids, and viscosity was taken as a constant from experimental measurements, R is the radius of the quasi-radius of the object, v is the flow velocity relative to the object.

The single particle sedimentation procedure was analyzed by the equation of motion,

$$F_{sedimentation} = m\dot{v}$$
$$= F_d - (F_g - F_b)$$
$$= 6\pi\mu Rv - (\rho_{particle} - \rho_{fluid}) \cdot g \cdot \frac{4}{3}\pi R^3$$

(Equation S2**)**

where $\rho_{particle}$ and ρ_{fluid} are the density of the particle and the fluid, respectively, and g is the gravitational acceleration.

Integration on both sides gives,

$$\int_{t_0}^{t_\infty} m\dot{v}\, dt = m(v_\infty - v_0)$$
$$= \int_{t_0}^{t_\infty} [6\pi\mu Rv - (\rho_{particle} - \rho_{fluid}) \cdot g \cdot \frac{4}{3}\pi R^3]\, dt$$
$$= \int_{t_0}^{t_\infty} [6\pi\mu Rv]\, dt - \int_{t_0}^{t_\infty} [(\rho_{particle} - \rho_{fluid}) \cdot g \cdot \frac{4}{3}\pi R^3]\, dt$$

(Equation S3**)**

To calculate the stability time, t_∞, parameters of v_0 and v_∞ are needed. The initial injection velocity, v_0, can be obtained,

$$v_0 t_{spray} \cdot \pi r_{gun}^2 = V_{spray}$$

(Equation S4**)**

where t_{spray} is the time consumed for spraying out of specific fluidic volume V_{spray}, and r_{gun} is the radius of spraying gun.

At equilibrium states, the excess forces of gravity and buoyancy will keep a balance with Stoke's drag,

$$F_d = F_g - F_b = (\rho_{particle} - \rho_{fluid}) \cdot g \cdot \frac{4}{3}\pi R^3$$

(Equation S5**)**

The resulting equilibrium velocity, v_∞, will be given by from Equations S1 and S5,

$$v_\infty = \frac{2}{9}\frac{(\rho_{particle} - \rho_{fluid})}{\mu} \cdot g \cdot R^2$$

(Equation S6**)**

Taking all the equations above, the calculated particle settling time was plotted in Figure 3. It can seen that the increases of time in the processing technique actually allows more time relaxation before being cured. This is also one important reason why we have well aligned particles from more viscous sprayed suspensions.

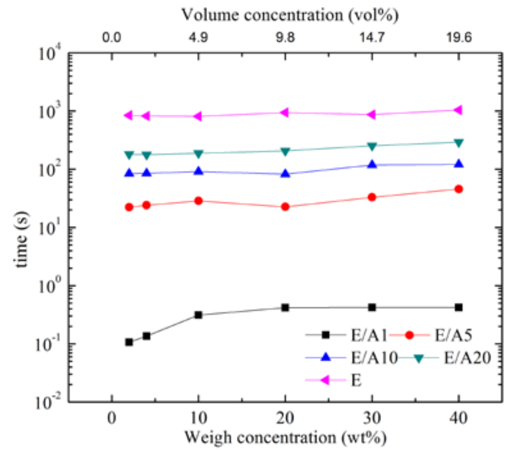

Figure 3 Sedimentation time for mixtures of various viscosities.

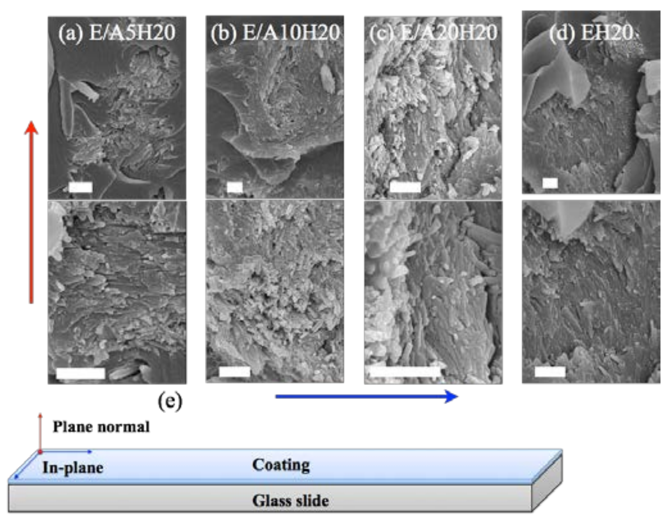

Figure 4 Viscosity influence on particle alignment in (a) E/A5H20, (b) E/A10H20, (c)E/A20H20 and (d) EH20. Viscosity increase from a to d signifies a higher constraining effect, which will retain the shear flow assisted HNT alignment. All concentrations of HNT are 20 wt% to exclude concentration influences.

To examine the viscosity and concentration influences on HNT alignment in spray coating, SEM imaging in composites were conducted (Figure 4). It can be seen that with the increase of viscosity, the alignment of HNT was improved. The addition of acetone decreased the viscosity, and improved the ease of processing; unsurprisingly, the decreased viscosity reduced the constraining of HNTs and cannot retain the orientation induced by the aerodynamic flow. As shown in Figure 7, when samples change from epoxy/acetone ratio of 5 to pure epoxy, the alignment of HNT in most fracture surface alters from lying within plane to being parallel to the plane-normal direction.

4 CONCLUSION

The epoxy/HNT composites were prepared using coating method. This procedure takes advantage of hydrodynamic flow to align the particles; while the presence of viscosity retains the HNT orientations. The measuremtn of viscosity was found to have a correponding relationship to particle alignment. The key in this technique to well control the viscosity and also the processing time before all samples are cured.

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