Effects of Nanoclays and Carbon Nanotubes on the Flow of Epoxy in Resin Transfer Molding: An Overview

Ayca Ertekin [1], R. Byron Pipes [2*], Lloyd A. Goettler [3]

[1, 2, 3] *Department of Polymer Engineering, College of Polymer Science and*
Polymer Engineering, University of Akron, Akron, OH, 44325
Ayca Ertekin: email: ae6@uakron.edu
Lloyd Goettler: email: lagoett@uakron.edu
** Corresponding Author: R. Byron Pipes: email: bpipes@uakron.edu*

SUMMARY: A concise overview of the state of the art of carbon nanotubes, nanoclays, their composites and resin transfer molding (RTM), with a particular emphasis on unsaturated flow in woven performs is presented. Experiments are proposed to develop understanding of the basics of the flow of epoxy resins, enriched with layered silicates and/or single wall carbon nanotubes (SWNT), through a porous media via RTM process.

KEY WORDS: Carbon nanotubes, nanoclays, resin transfer molding (RTM), unsaturated flow.

INTRODUCTION

The challenging advances in science and technology during the past few decades have led to a continuous demand for new, easy to manufacture, low-cost, and high performance materials and processes meeting increasingly stringent conditions of advanced technology applications. Due to the promising potential of nanoscale materials and composites, numerous studies have been conducted in nanotechnology research during the last two decades. Among many, two forms of polymer reinforcements in the nanometer range are nanoclays and carbon nanotubes. These nanoreinforcements have different geometric forms such that the clays are in platelet form with nano dimensions in thickness, while carbon nanotubes have diameters on the order of nanometers. Nanocomposites, made of nanoclays or so-called layered silicates as reinforcement, are reported to exhibit noticeably improved mechanical, thermal, optical and physico-chemical properties as compared to the pristine polymers or conventional composites. Other attractive features of nanoclay-based nanocomposites are increased modulus, strength, solvent and heat resistance, decreased gas permeability and improved flame retardancy [1-5]. Although the majority of the published studies have focused on nanocomposite property evaluation and synthesis [1-5], complete dispersion of nanoscale reinforcements in the polymer is still one of the most important and incompletely resolved issues in the manufacturing of nanocomposites [2-3]. Hence, the need for significant energy density to accomplish mixing suggests that chemical potential combined with mechanical mixing will be necessary for the dispersion of nanoreinforcements in polymers.

Likewise, several research groups [8-9] have indicated that carbon nanotubes (CNTs) possess outstanding thermal and electrical properties, low density, and small size with extraordinary resilience. The combination of remarkably high-aspect ratio, exceptional specific stiffness, strength, and high conductivity makes CNTs excellent candidates as fillers in polymer composites, especially for high technology applications, such as; data storage technology, electronic devices and sensors. Nonetheless, several studies [9] have emphasized the opportunity and challenge of controlling aspect ratio, polymer crystallinity, and dispersion [11, 13] in polymers at reasonable costs, to employ them or nanocomposites in commercial applications.

Resin transfer molding (RTM) is a versatile process capable of low cost, high volume and net shape manufacturing of polymer composites. During RTM, impregnation of a polymeric resin through a porous preform, generally in the form of carbon, glass or kevlar textile forms, is followed by a curing reaction either during the mold filling or after the injection is complete and the final product is removed from the mold after the cure cycle is completed. In some cases, postcuring is required to relieve residual stresses and to achieve the desired degree of cure. Numerous studies have been conducted on several aspects of RTM ranging from permeability predictions and measurements [17-20], optimization of heat transfer and cure [23-25], analysis of mold filling [21-22] to void formation during the past few decades. Currently, many research studies on RTM are focused on the development of process models and computer simulation tools for prediction of the flow and curing kinetics in the process.

In this overview, characteristic features of carbon nanotubes, nanoclays, and their nanocomposites will be summarized with a particular emphasis on the most critical issues observed in these nanoscale materials. Then, the basic concepts of polymeric flow in RTM will be discussed with a special attention on the “unsaturated flow” in the woven preforms. Finally, a set of experiments, enabling a combination of macroscopic length scale RTM process with nanometer length scale single walled carbon nanotubes or nanoclays will be discussed so as to explore the feasibility of using nanoreinforced-modified resin systems in RTM.

THEORETICAL BACKGROUND

Nanoclays and Polymer Nanocomposites

Polymer layered silicate nanocomposites (PLSN) can be considered as hybrid structures combining an organic phase (the polymer) with an inorganic phase (the silicate). The most widely used layered silicate, montmorillonite, is a crystalline, 2:1 layered clay mineral in which a central alumina octahedral sheet is sandwiched between two silica tetrahedral sheets. The characteristic features of clays are their high aspect ratio (≥ 1000) and capability to swell and exchange cations into their galleries. There are four processes to synthesize polymer-clay nanocomposites, namely, the solution approach; in-situ polymerization; melt intercalation and the sol-gel technique. Several researchers [1-5] have reported that three basic types of PLSN structures can be obtained depending on the method of preparation and the nature of components (i.e., type of layered silicate, type of organic cations and type of polymer matrix) employed. When the polymer chains enter between the silicate layers, intercalated structures in which a well ordered multilayer morphology such as polymeric and inorganic layers are observed.

If the silicate layers are completely and uniformly dispersed in a polymer matrix, exfoliated (delaminated) structures are observed. It is also indicated that both intercalated and exfoliated structures sometimes coexist in a polymer matrix, forming hybrid structures. XRD and TEM are the most commonly used characterization techniques for identifying the PLSN structures [1-4]. The intercalation of the polymer chains generally increases the interlayer spacing, causing a shift of the diffraction peak towards lower angle values. While XRD provides reliable information only for the intercalated structures, it can be deficient most of the times in differentiating exfoliated structures from disordered, agglomerated structures. TEM and atomic force microscopy (AFM) are also frequently used to characterize nanoparticle dispersion. The former requires meticulous sample preparation whereas the latter needs correct etching or cutting line free flat surfaces.

Carbon Nanotubes and Polymer Carbon Nanotube Composites

Carbon nanotubes (CNTs) are generally described as long and cylindrical fullerenes where the walls of the tubes are mono-atomic in thickness and have hexagonal graphitic structure. The atomic structure of CNTs is generally expressed by means of tube chirality, which is defined by chiral vector and chiral angle. The properties of CNTs strongly rely on the atomic arrangement of the graphine-like structure. The diameter of single-walled CNTs is determined by the chiral vector whereas the length results from a sustained growth process, generally 400-1000 nanometers for SWCN. [9]. CNTs can exist either in single-walled (SWNT) or in multi-walled (MWNT) forms. Detailed information about the structure, properties and processing of CNTs can be found in elsewhere [8, 9]. Terrones [9] emphasized that certain properties of CNTs are strongly dependent on crystalline structure and the number of defects. Thostenson et al. [8] stated that the most critical issue in the processing of CNT polymer composites is uniform s g Å F e polymer [11, 13, 16], the potential for nanotube/matrix interfacial bonding through functionalization of the CNT [13], wetting and alignment of the carbon nanotubes [14, 15] by the polymer matrix. While Wagner et al. [10] has shown that MWNTs embedded in a polymer matrix exhibit superior stress transfer efficiency of one order of magnitude larger than that of carbon fiber-polymer composites, Salvetat et al. [12] measured the axial and shear moduli of SWNTs by AFM and concluded that the slippage of the CNTs within the bundles caused a decrease in the moduli as the diameter of the tube bundles increased. Sandler et al. [16] showed that the electrical properties of nanocomposites are also strongly affected by CNTs such that only a modest volume fraction of CNTs produced conductivity in the polymers.

Unsaturated Flow Phenomenon in Resin Transfer Molding (RTM)

In conventional RTM studies, the flow of “unmodified” polymeric systems through the preforms has been analyzed by several mass, momentum and energy balance equations based on different strategies [23-25].

General approaches to describe the physics of the flow through porous media in LCM literature are based on global form of Darcy's Law, which describes macroscopic flow through porous media such as homogenous fibrous materials, as follows:

$$\mathbf{u} = -\frac{\mathbf{K}}{\mu}\nabla\mathbf{P} \tag{1}$$

where **u** is the volume-averaged velocity of resin in fibrous porous medium, **P** is the volume averaged pressure, **K** is the permeability tensor of the fibrous preform, and μ is resin viscosity. The flow of resin through a fibrous medium is typically treated as a single-phase flow in the existing RTM literature since the region behind the flow front is considered to be "fully saturated". Hence, the general trend in modeling the RTM flows is to use the macroscopic equation of continuity [23]:

$$\nabla \cdot \mathbf{u} = 0 \tag{2}$$

Nonetheless, Advani et al. [17], Pillai [24] and Lee et al. [18] reported that there often are obvious indications of incomplete saturation in woven, stitched or braided fibrous mats behind the resin front in RTM. In the same work, Pillai modeled the flow of resin through woven fiber mats in LCM as a dual-scale porous media where gap regions (~ 1 *mm*) and fiber tow regions (~ 10 μm) are treated as different phases. The volume averaging techniques have been adapted to derive the mass and momentum balance equations for the flow of resin in dual-scale porous media by many researchers [18, 23]. Pillai [24, 25] also proposed the idea of a sink term in the equation of continuity in the dual scale porous media. The sink term, S, refers to the rate of resin absorbed by fiber tows per unit volume owing to the delayed impregnation of fiber tows, as follows:

$$\nabla \cdot \mathbf{u} = -\mathbf{S} \tag{3}$$

It was argued that application of this equation along with Darcy's law successfully predicts the reduction of inlet pressure history observed in woven fiber preforms and explains the partial saturation behind the flow front and the degree of impregnation of fiber tows.

RESEARCH REQUIRED

Only a limited number of studies in the literature have investigated the unsaturated flow in dual-scale porous medium and there is a need for dimensionless parameters that quantify the degree of saturation in Darcy flow. Further, this need is particularly pronounced for multi-scale interactions of flows in dual-scale porous medium for nanoreinforced-modified resin systems. Thus, a fundamental understanding of how the presence of SWNTs or nanoclays influences the flow in dual-scale porous medium is mandatory. The first step in accomplishing this task is to study the changes in the thermoset polymer viscosity and cure kinetics that result from various degrees of dispersion of nanoreinforcements in epoxy composites.

Rheological, thermal, XRD and morphological (TEM) characterizations are required to assess polymer properties in both the liquid and solid phases. Moreover, development of chemorheological models will be essential to describe the simultaneous curing kinetics and viscosity changes with time.

CONCLUSIONS

Dual scale phenomena must be considered when nano-phase reinforcements are added to the low viscosity thermoset polymers employed in RTM. The enhanced physical properties of the polymeric matrix phase of the molded product in the presence of nanoreinforcements may be achieved at the expense of the flow characteristics of polymer. Yet, the understanding developed by research in this important field may well provide an opportunity to achieve multifunctionality of the composite matrix phase such as reduced permeability or enhanced thermal or electrical conductivity and thereby open many new opportunities for RTM in advanced products.

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