In The Name of God

M. Sc. Thesis

Title of the Thesis:

Cure Behavior of Epoxy/ TiO$_2$ Nanocomposites

Supervisors:

Dr. Laleh Rajabi

Advisor:

M. Sc. Nasrin Rezaei

By:

Saeed Kaihani

January 2010

Razi University

Faculty of chemistry
Department of organic chemistry

M.Sc.Thesis

Title of the Thesis

Cure Behavior of Epoxy/ TiO$_2$ Nanocomposites

By:

Saeed Kaihani

Evaluated and approved by thesis committee:as……………..

Supervisor : Dr Laleh Rajabi   **Assistant professor**

advisor : M.Sc Nasrin Rezaei   **M.Sc**

Internal Examiner : Dr Nahid Shah Abadi   **Assistant professor**

External Examiner : Dr Kaivan Ghodrati   **Assistant professor**

January 2010

Acknowledgments:

Dedicated to:

My mother, father and dear wife

Abstract:

Nanocomposites using thermosetting polymers have not been studied so extensively. The objective of this research work was to study the curing kinetic of epoxy/TiO$_2$ nano composites. Effect of TiO$_2$ nano particles on the curing kinetics of epoxy/amine resin system has been investigated dynamically at four heating rates using TG/DTA.

Genetic algorithm was successfully used to calculate the fractional extent of conversion.

Each set of thermograms indicated the increase of the peak temperature with increasing the heating rate. The initial curing temperature and the peak exothermic temperature at four heating rates (5, 10, 15 and 20 $^\circ$C/min) have not been affected considerably due to the presence and varying the amount of nano TiO$_2$ particles, indicating that the presence of nano TiO$_2$ particles neither retarded nor accelerated the cure reaction of epoxy/amine system to a considerable extent.

The total curing reaction heat estimated from the area under the exothermic peak was dependant on the heating rate in all the resin systems studied. The ΔH values obtained, indicated the lowering of the extent of cure as a result of addition of lower amounts of TiO$_2$ nano particles.

The S shape of the α vs. T curves indicated that the TiO$_2$ containing systems studied follow an autocatalytic kinetics as the reference system (the neat epoxy system). On superposing the fractional conversion curves, almost equal deviation of the curves was observed from the reference curve (α at the heating rate of 20°C/min) in all the systems, suggesting the kinetic control mechanism throughout the cure reactions.

The presence of nano TiO$_2$ particles in various amounts did not seem to have caused any considerable barrier effect on the curing process of the resin systems studied.

Different multiple regression equations were tried in order to fit the values of the activation energy, where activation energy data fitted well in the cubic polynomial regression equations.

Plots of E$_a$ vs. α also indicated of the autocatalytic data mechanism followed by the nano TiO$_2$ containing composites.

Keywords: Titanium dioxide nano particles; Epoxy nanocomposites; Cure kinetics, TG/DTA.

LIST OF CONTENTS

Content	Page

Content   **Page**

List of Figures

Figures   **Page**

D

Figures **Page**

List of Tables

Tables   **page**

G

Chapter 1

General Introduction

1.1 Introduction

Advancements in material performance depend on the ability to synthesize new materials that exhibit enhanced properties, such as strength, fracture toughness, impact resistance, durability, etc. Nanocomposites are ideal materials to meet this challenge, as it has been shown that they have the potential to deliver the aforementioned properties oftentimes with minimal increase in weight; a luxury not always realized with conventional composites or metals. It should be pointed out, however, that the degree of enhancement of a particular property is highly dependent on the matrix/filler type system used, the extent of filler adhesion to the matrix, and the level of dispersion of the filler throughout the matrix. The advent of any new material inevitably leads to the need to characterize its properties and understand its behavior under different loading conditions. The response of materials to high strain rates is very important, as in practical engineering applications structural materials are subjected, either by design or by accident, to a variety of loading rates [1].

In the last five decades, breakthroughs have been made in our understanding of how to design organic polymer molecules to achieve desired properties and how to process polymers into preferred morphologies. The result has been a new generation of polymeric materials providing new levels of strength, stiffness, environmental stability, and load bearing capability coupled with elasticity and/or energy absorption. During this period polymer usage has been extended from non-structural to structural applications. Terms like "engineering plastics", and "advanced composites" have become part of our vocabulary. It is evident that material advances have been the keys to significant technology breakthrough throughout the human history. Today we are in the midst of a new revolution triggered by the onset of advanced composite materials. This new class of materials is characterized by the marriage of quite diverse individual components that work together to produce capabilities exceeds those of their separate elements. Their unique properties make them the materials for major technological advances [2].

The development of high performance composite materials is based on the concept of taking advantage of the stiffness and strength of high performance (but usually brittle) reinforcing agent by dispersing them in a usually softer matrix, which acts as a binder and transfers forces across the fiber matrix interface [3].

1.2 Nanotechnology and Nanomaterials

Nanotechnology deals with materials, structures, and device having dimensions of the order of one to hundreds of nanometers. This term covers the activities on design, manufacturing, manipulation, and testing or characterization of nanoscale objects [4].

Unique properties of nanoscale objects and nanostructured materials are expected to be the key to a wide range of exciting applications that can't be achieved by other methods. Nanotechnology promises to bring dramatic new developments in materials science, electronics, communication networks, biotechnology, medical science and environmental research [5]. It is expected to play an essential role in the life of the society in the 21 century.

One of the ideas of nanotechnology lies in assembling atoms and molecules into complex arrangements that have novel functions. This is the basis of a "bottom up" approach to manufacture and engineering nanoscale objects [6,7]. It includes, for example, arc-evaporation method of fabrication of carbon nanotubes, electrochemical synthesis methods, microwave plasma methods, and so on.

Another approach is termed "top down" approach. It usually refers to making nanoscale structures by machining or etching techniques [6,7]. Examples include ball milling or shock deformation, nanostructuring via friction and wear, etc. The bottom up approach is often more advanced but is typically also more expensive.

Nanostructured materials attract a great deal of attention in both academy and industry because of their potential applications in areas such as electronics, optics, catalysis, ceramics, magnetic data storage, and nanocomposites. Research on nanomaterials opens many new challenges both in fundamental science and technology. Nanomaterials are particularly attractive for applications in chemistry, electronics, high density magnetic recording media, sensors, and biotechnology. This is due to their novel material properties that differ from both the isolated atoms and the bulk phase [4,8].

Nanomaterials can be mainly classified in to three groups by their geometry, i.e., zero-dimensional materials (nanoparticles, nanoclusters, nanorods, nanotubes), and two-

dimensional materials (nanofilms) [6,7]. At presents, zero-dimensional nanoparticles and one-dimensional carbon nanotubes have received more attention compared to others.

The nanoparticles with characteristic dimensions of order of nanometers are easier to manufacture compared to other nanomaterials. Nanoparticles have already found applications in nanocomposites. One-dimensional nanotubes have recently attracted attention because of their intriguing properties that are not displayed by their bulk (three-dimensional) or particle (zero-dimensional) counterparts.

1.3 Polymer Nanocomposites

Nanomaterials can be classified into nanostructured materials and nanophase / nanoparticle materials. The former usually refer to condensed bulk materials that are made of grains (agglomerates), with grain sizes in the nanometer size range, whereas the latter are usually the dispersive nanoparticles. The nanometer size covers a wide range, from 1 nm to as large as 100 to 200 nm. To distinguish nanomaterials from bulk, it is crucial to demonstrate the unique properties of nanomaterials and their prospective impacts in science and technology. The introduction of inorganic nanoparticles as additives into polymer systems has resulted in polymer nanocomposites (PNCs) exhibiting multifunctional, high-performance polymer characteristics beyond what traditional filled polymeric materials possess. The development of these new materials will enable the circumvention of classic material performance trade-offs by accessing new properties and exploiting unique synergies between materials, that only occur when the length scale of morphology and the fundamental physics associated with a property coincide, i.e., on the nanoscale level. Multifunctional features attributable to polymer nanocomposites consisting of improved thermal resistance and/or flame resistance, moisture resistance, decreased permeability, charge dissipation, and chemical resistance. Through control/alteration of the additives at the nanoscale level, one is able to maximize property enhancement of selected polymer systems to meet or exceed the requirements of current military, aerospace, and commercial applications. The technical approach involves the incorporation of nanoparticles into selected polymer matrix systems whereby nanoparticles may be surface-treated to provide hydrophobic characteristics and enhanced inclusion into the hydrophobic polymer matrix. The reinforcement of polymers using fillers, whether inorganic or organic, is common in modern plastics. Polymer nanocomposites, or the more inclusive term, polymer nanostructured materials (PNMs), represent a radical alternative to

these traditional filled polymers or polymer compositions. In contrast to traditional polymer systems where reinforcement is on the order of microns, polymer nanocomposites are exemplified by discrete constituents on the order of a few nanometers. Uniform dispersion of these nano-sized fillers (nanoparticles) produces ultra large interfacial area per volume between the nanoparticle and the host polymer. The immense internal interfacial area and the nanoscopic dimensions between nanoparticles fundamentally differentiate polymer nanostructured composites from traditional filled plastics and composites. These material's characteristics simply imply that the overall performance of PNMs cannot be understood by simple scaling rules that apply to traditional polymer composites. Thus, new combinations of properties derived from the nanoscale structure of PNMs provide opportunities to circumvent traditional performance associated with conventional reinforced plastics, epitomizing the promise of PNMs.

Many examples can be found in the literature demonstrating substantial improvements in physical and mechanical properties. When using the term "nanocomposite" to describe properties comparisons, it is intended to relate to traditional unfilled and filled polymers and not fiber-reinforced polymer matrix composites. Polymer nanocomposites may provide matrix resins with "multi functionality", but they should not be considered in the near and intermediate term as a potential one for- one replacement for current state-of-the-art carbon fiber-reinforced polymer matrix composites. The value of PNM technology is not based solely on mechanical enhancements of the neat resin. Rather, its value comes from providing value-added properties not present in the neat resin, without sacrificing the inherent processibility and mechanical properties of the neat resin. Traditionally, the preparation of a blend or composite with multi functionality requires a trade-off between desired performance, mechanical properties, cost, and processibility. Development of materials with multi functionality, whether micron scale or nanoscale, must simultaneously balance four interdependent areas: constituent selection, processing, fabrication, and performance. Two main PNM processing methodologies have been developed: in-situ routes and exfoliation. Currently, exfoliation of layered silicates, carbon nanofiber/nanotubes, and polyhedral oligomeric silsesquioxanes (POSS®) in commodity and high-performance resins are the most investigated PNMs by government, academic, and industrial institutions all over the world [9].

Polymer nanocomposites (PNCs) consist of a polymeric material (e.g., thermoplastics, thermosets, or elastomers) and a reinforcing nanoscale material (nanoparticle). The nanoparticle has at least one dimension in nanometer scale. Polymer

nanocomposites show major improvements in mechanical properties, gas barrier properties, thermal stability, fire redundancy, and other areas. There are many factors that affect the polymer nanocomposite properties:

- Synthesis methods such as melt compounding, solvent blending, in-situ polymerization, and emulsion polymerization
- Polymer nanocomposite morphology
- Types of nanoparticles and their surface treatments
- Polymer matrix such as crystallinity, molecular weight, polymer chemistry, and Whether thermoplastic or hermosetting Understanding property improvement related to PNC properties is a very complex matter [10].

There are two main challenges to developing polymer nanostructured materials after the desired nanoparticle has been selected for the polymer of interest. First, the choice of nanoparticles requires an interfacial interaction and/or compatibility with the polymer matrix. Second, the proper processing technique should be selected to uniformly disperse and distribute the nanoparticles or nanoparticle aggregates within the polymer matrix.

In most cases, polymer nanostuctured materials exhibit multi functionality. Several of the functions of these materials are listed below:

- Thermal: increased thermal resistance, higher glass transition temperature (Tg) or heat deflection temperature (HDT), reduced coefficient of thermal expansion (CTE)
- Mechanical: increased modulus, strength, toughness, elongation (in some cases)
- Chemical: improved solvent resistance, improved moisture resistance
- Electrical: improved thermal conductivity, lower resistively (depends on the nanoparticles)
- Barrier: reduced oxygen, moisture transmission
- Optical: clear, transparency provided in selective systems
- Others: abrasion resistance, reduced shrinkage [11].

1.4 Epoxy Resins

Epoxy resins are formed from an oligomer containing at least two epoxide groups and a curing agent, usually either an amine compound or a diacid compound. A great variety of such resins is on the market. There are many monographs on epoxy resins available [12, 13].

The term "epoxy resin" describes a broad class of thermosetting polymers in which the primary cross linking occurs through the reaction of an epoxide group. In general, an epoxy resin