



ELSEVIER

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Cure kinetics of epoxy/chicken eggshell biowaste composites: Isothermal calorimetric and chemorheological analyses

Mohammad Reza Saeb^{a,*}, Hadi Rastin^b, Milad Nonahal^b, Seyed Mohammad Reza Paran^c, Hossein Ali Khonakdar^d, Debora Puglia^e

^a Department of Resin and Additives, Institute for Color Science and Technology, P.O. Box 16765-654, Tehran, Iran

^b School of Chemical Engineering, College of Engineering, University of Tehran, P.O. Box 11155-4563, Tehran, Iran

^c Department of Polymer Processing, Iran Polymer and Petrochemical Institute, P.O. Box 14965-115, Tehran, Iran

^d Leibniz Institute of Polymer Research Dresden, Hohe Straße 6, D-01069, Dresden, Germany

^e University of Perugia, Department of Civil and Environmental Engineering, Strada di Pentima 4, 05100, Terni, Italy

ARTICLE INFO

Keywords:

Chicken eggshell
Epoxy
Calcium carbonate
Rheokinetic study
Isothermal DSC

ABSTRACT

Chicken eggshell (ES) is a biowaste powder comprising peptide functional groups and proteins, which give it potential to play the role of curing aid when added to the epoxy resin. In this work, pristine and terpolymer-modified ES (mES) were used in epoxy-based composites and their performance in network formation was compared with pristine calcium carbonate (CaCO₃) and terpolymer-modified CaCO₃ (mCaCO₃) additives, via comprehensive isothermal calorimetric and chemorheological analyses. The mechanism and progression of the crosslinking of identical composites containing very low amount of additives were also discussed. Rheokinetic evaluations revealed that, despite the almost identical chemical structure of the ES and CaCO₃, the former can more appropriately contribute to crosslinking reaction in the pristine form, since terpolymer modification causes a physical hindrance to its cure potential towards epoxy rings after surface modification. In the case of calorimetric studies, in contrast to nonisothermal cure kinetics, a more comprehensive image of the catalytic role of mES was identified in view of overall reaction order and apparent activation energy calculated for both types of systems.

1. Introduction

Epoxy is a well-known thermosetting resin possessing considerable beneficial properties such as sufficient adhesiveness, curing ability with various hardeners, superior mechanical and corrosion characteristics, that makes it one of the most widely used resins in surface coating industry [1–5]. However, its brittleness and poor impact strength have limited its use in coating and engineering composites applications [6,7]. In this regard, a great deal of efforts has been made to find an effective approach for toughening of epoxy. It has been revealed that introduction of second inorganic component into the epoxy matrix could substantially improve its impact strength [8,9]. Beyond the exceptional characteristics of nanomaterials as reinforcing agents in epoxy resin (namely high surface area, excellent mechanical and thermal properties), one should take into account that their use in practical and industrial scale is still far from perfect, because of their high expense and difficulties in their processing, due to high surface energy that causes agglomeration of nanoparticles [10,11]. By contrast, environmental concerns induce industrial centers to move forward

using new material with renewable resources. From this standpoint, an increasing attention has been directed toward the use of biowaste materials (such as husk ash, fly ash, bagasse) in polymeric industries, as potential alternatives for existing additives, because of their low cost, recyclability, biodegradability, and use of renewable resources [12–14].

Within different kinds of biowaste additives, widely available inexpensive chicken eggshell (ES) is a promising candidate as reinforcing agent in polymeric industries, due to its good mechanical characteristics such as acceptable toughness and impact strength [15]. However, over the last decades, landfill disposing of ES as by-product of egg processing industry has brought about serious environmental concerns [16]. From environmental problems and economic perspectives, biowaste ES has been recently applied in various applications areas, for instance for absorption of heavy metals [17,18], synthesis of hydroxyapatite [19] and sorption of CO₂ [20,21]. It is recognized that ES is composed of calcium carbonate (94%) with just 3–4% of organic materials including proteins, collagen, and sulfated polysaccharides, that makes it an excellent substituting material for mineral-based calcium

* Corresponding author.

E-mail addresses: saeb-mra@icrc.ac.ir, mrsaeb2008@gmail.com (M.R. Saeb).

<http://dx.doi.org/10.1016/j.porgcoat.2017.10.018>

Received 28 September 2017; Received in revised form 16 October 2017; Accepted 19 October 2017

Available online 02 November 2017

0300-9440/ © 2017 Elsevier B.V. All rights reserved.

carbonate (CaCO_3), such as chalk or calcite in polymer industries [22]. From structure features perspective, existing nanoporositities in ES structure are capable of forming strong interaction between polymeric matrix and ES, leading to improved mechanical properties. Toro et al. [23] compared performance of ES with commercial talc and calcium carbonate additives in improving mechanical characteristics, showing how ES is able to increase Young's modulus of PP matrix more than carbonate additives, as a result of better interfacial adhesion between PP and ES interfaces. Elsewhere, PP composites containing ES modified with stearic acid were prepared *via* melting extrusion and their mechanical and thermal properties were studied in detail [24]. It was found that mechanical properties of PP/ES composite were modified at low-strain by two times, while a deteriorating effect caused by ES was observed at higher strains. Kumar et al. [25], however, reported that the use of ES powders modified with isophthalic acid in PP composites improved mechanical properties compared to identical composites containing pristine ES or CaCO_3 . In another study on PP/ES composites [26], it was reported that ES modified by pimelic acid significantly improved the dispersion state of ES, as well as interfacial bonding between continuous and dispersed phases, causing a slight variation in tensile modulus but a noticeable increase in the value of impact strength by almost more than 200%. ES has been also used as reinforcing agent in thermosetting rubber [27,28]. Vulcanization features of acrylonitrile butadiene rubber, natural rubber and styrene butadiene rubber compounds in the presence of ES were comprehensively studied, showing decrease in the optimum curing time by incorporation of ES powder, irrespective of rubber type [28], while curing time was dependent on rubber type. In the case of epoxy thermosetting resin, Ji et al. [12] have shown that incorporation of 5 wt.% ES into the epoxy resin increased its impact strength by approximately two times compared to the neat epoxy, probably due to the presence of protein on the ES surface. Moreover, it was found that existing functional groups on ES surface could move forward curing reaction, acting as secondary curing agent in the improvement of interfacial bonding with epoxy resin [15].

It is well-established that ultimate properties of thermosetting materials are highly dictated by their curing characteristic, allowing one to control processing parameters. Moreover, study on cure kinetics of filled epoxy provides quantitative information regarding the effect of additive on microstructural features of 3D cured resin [29–31]. In a consecutive works, we investigated the cure kinetics of epoxy based nanocomposites filled with different kinds of nanomaterials such as graphene oxide [32], multi-walled carbon nanotubes (MWCNTs) [33,34] and magnetic nanoparticles [35] using calorimetric and rheokinetic analyses. Overall, it was found that curing mechanism cannot be individually detected by nonisothermal analysis, since the simultaneous change of temperature and rate constant makes it difficult to recognize the suitable model reaction. For example, in some previous works, we prepared epoxy-based nanocomposites containing various contents of MWCNTs [33,34]. Nonisothermal differential scanning calorimetry (DSC) analysis of cure kinetics provided useful information about the crosslinking of the epoxy in the presence of functionalized MWCNTs, but the use of chemorheological along with isothermal DSC analysis fulfilled in a complementary manner the role of MWCNTs as a secondary curing agent.

In our previous study, we comprehensively studied the cure kinetics of epoxy resin containing the ES modified by terpolymer of poly(N-vinyl-2-pyrrolidone-co-maleic acid-co-acrylic acid) through nonisothermal DSC analysis [15]. In this way, isoconversional methods including differential (Friedman) and integral (Ozawa and Kissinger–Akahira–Sunose) methods were employed to detect the effect of ES and CaCO_3 additives. Actually, nonisothermal analyses are based on dynamic heating programs over a specified temperature range; hence, the kinetic constants may experience a wide transition leading to poor accuracy of the resulting kinetic parameters obtained from kinetic models. It is believed that isothermal methods can provide some more insights into the network formation through complementary kinetic

parameters that allow for higher accuracies.

In this work, we aim to investigate the curing reaction of epoxy resin in the presence and absence of ES and CaCO_3 through isothermal calorimetric and rheological tests. In this way, autocatalytic and non-catalytic reaction models were considered on the basis of provided isothermal DSC data, showing how ES and CaCO_3 (in the pristine and modified form) have a completely different role in epoxy cure.

2. Experimental

2.1. Materials

In this work, epoxy resin under trade name of EPIKOTE (RIMR145) was provided by Momentive (USA) (epoxide equivalent weight of 170–210 g/eq.). Curing agent and catalyst used in this work were methyltetrahydrophthalic anhydride (EPIKURE-RIMH145) and EPIKURE catalyst (RIMC145), respectively. Chicken ES was obtained from local farms. The ALBAFIL[®] PCC CaCO_3 was supplied by CARY Co., USA. It should be noticed that in all prepared samples, additives were firstly washed and dried at 80 °C overnight and then grounded by milling (Retsch PM-400MA planetary ball mill with stabilized zirconia) for 6 h. Details of bare and modified ES (mES) and CaCO_3 have been reported in our previous work [15].

2.2. Preparation of epoxy-based nanocomposites

Pristine CaCO_3 and ES were modified with poly(N-vinyl-2-pyrrolidone-co-maleic acid-co-acrylic acid) terpolymer, to prevent aggregation of particles in the epoxy matrix, as discussed elsewhere [15]. Epoxy resin containing 0.1 and 0.3 wt.% of the pristine and modified CaCO_3 (or ES) were then mixed with curing agent in a weight ratio of 100:85.

2.3. Measurements and analyses

A Q2000 differential scanning calorimeter (DSC) (TA Instruments, New Castle, DE, USA) was employed to study the curing behavior of epoxy-based nanocomposites. In this regard, about 5 mg of each sample were placed in the aluminum cell and experienced heating from ambient temperature up to the isothermal temperature (120, 150, and 180 °C) by heating rate of 50 °C/min under nitrogen purge at 50 ml/min. According to the literature, curing reaction is completed once the heat flow curve level off. Rheological behavior of epoxy resin during curing reaction was traced by using Ares-G2 rheometer (TA). All tests were tested in their linear viscoelastic behavior, at 25 °C and fixed strain of 1%.

3. Results and discussion

3.1. Rheokinetic analysis of cure reaction

It is well-established that processing of thermosetting resin strongly depends on its rheological behavior, especially viscosity [36,37]. Understanding the interrelationship between curing characteristics and rheological behavior allow engineers to optimize cure parameters and consequently achieve desirable ultimate properties. Generally, contributing factors in curing reaction, such as temperature, flow characteristic, and conversion rate, dominantly control the viscosity behavior of thermoset resin [38,39].

Fig. 1 shows the variation of complex viscosity of blank epoxy resin as a function of curing time at two heating isothermal temperatures of 120 and 150 °C. It can be clearly observed that viscosity profile shifts, as expected, towards lower gel times upon increasing heating temperature from 120 to 150 °C. As a matter of fact, higher temperature means higher mobility for curing reaction moieties, raising the possibility of effective collision between particles [34]. Moreover, upon increasing heating temperature from 120–150 °C, ultimate viscosity

Download English Version:

<https://daneshyari.com/en/article/7106276>

Download Persian Version:

<https://daneshyari.com/article/7106276>

[Daneshyari.com](https://daneshyari.com)