Industrial Crops and Products 72 (2015) 125–132

Contents lists available at ScienceDirect

Industrial Crops and Products

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

Toughened polyester cellulose nanocomposites: Effects of cellulose nanocrystals and liquid epoxidized natural rubber on morphology and mechanical properties

Hanieh Kargarzadeh[a], Rasha M. Sheltami[a,c], Ishak Ahmad[a,*], Ibrahim Abdullah[a], Alain Dufresne[b]

[a] Faculty of Science and Technology, School of Chemical Sciences and Food Technology, Polymer Research Center (PORCE), Universiti Kebangsan Malaysia (UKM), 43600 Bangi, Selangor, Malaysia
[b] The International School of Paper, Print Media and Biomaterials (PAGORA), Grenoble Institute of Technology, BP65, 38402 Saint Martin d'He'res Cedex, France
[c] Chemistry Department, Faculty of Science, University of Benghazi, Benghazi, Libya

ARTICLE INFO

Article history:
Received 17 September 2014
Received in revised form
14 November 2014
Accepted 22 December 2014
Available online 14 January 2015

Keywords:
Blend
Unsaturated polyester resin
Cellulose nanocrystal
Liquid epoxidized natural rubber
Nanocomposite
Toughness

ABSTRACT

Unsaturated polyester resin (UPR) has been modified with a liquid epoxidized natural rubber (LENR). The addition of LENR improves the toughness, but it is inevitably accompanied by a significant loss in stiffness, yield strength, and thermal resistance. Incorporation of a rigid material into the LENR–UPR blend, such as cellulose nanocrystal (CNC), provided a ternary polyester nanocomposites with desire mechanical properties. In the present work, the effects of different CNC and LENR content on the nanocomposite morphology and mechanical properties were examined. Morphological studies revealed that the size of the rubber particles is independent of the rubber content due to the chemical interaction of rubber and matrix; however, the size of the LENR particles increased with increasing CNC content. Tensile tests indicated that the blend's tensile strength and elastic modulus could be further improved by incorporation of the CNCs. The high crystallinity and surface area of CNCs were the main factors for improvement of tensile properties of the blend. Moreover, the impact energy of the UPR improved when it was modified with the LENR, and even further improvement was achieved with the CNC addition to form nanocomposites. Dynamic mechanical thermal analysis (DMTA) showed that the storage modulus of nanocomposites with 1.5 wt% rubber content was lower than those with 4.5 wt% LENR; however, both samples showed a higher storage modulus than the neat UPR and the unfilled blend. The glass transition temperature (T_g) of the UPR decreased with the LENR addition, but improved with the addition of CNCs. The nanocomposites prepared with a higher LENR content displayed better mechanical properties than those with low LENR content.

1. Introduction

Unsaturated polyester resins (UPRs) is one of the most popular thermoset materials used as a matrix for composites, electronic equipment, containers, automobiles, and cultured marble because of its clarity and excellent chemical and corrosion resistance. The major drawback of UPRs is that they are brittle with poor impact resistance in the cured state. Therefore, toughening UPRs has been the subject of intense investigation throughout the world (Kargarzadeh et al., 2014; Thomas et al., 2013).

The most common technique for toughening brittle UPR is incorporating a dispersed elastomeric phase in the resin. In this process, a rubber is initially miscible with the resin and a curing agent. When the reaction begins, the rubber generally forms an initial copolymer with the resin before phase separation, resulting in the cured thermosetting polymer possessing a dispersed rubbery phase. The addition of a rubber modifier improves the fracture toughness, but it is inevitably accompanied by a significant loss in stiffness, yield

Abbreviations: UPR, unsaturated polyester resin; LENR, liquid epoxidized natural rubber; CNC, cellulose nanocrystal; MEKPO, methyl ethyl ketone peroxide; T_g, glass transition temperature; ENR, epoxidized natural rubber; DMTA, dynamic mechanical thermal analysis; FESEM, field emission scanning electron microscope; TEM, transmission electron microscopy; CTBN, carboxyl-terminated butadiene-co-acrylonitrile.

* Corresponding author. Tel.: +603 8921 5431/5424; fax: +603 8921 5410.
E-mail addresses: hanieh.kargar@gmail.com (H. Kargarzadeh), gading@ukm.edu.my (I. Ahmad).

http://dx.doi.org/10.1016/j.indcrop.2014.12.052
0926-6690/

strength, and thermal resistance. This is not unexpected, as the elastic modulus of the toughness modifier is significantly lower than that of the thermosetting matrix (Kargarzadeh et al., 2014). Therefore, rigid inorganic nanoparticles, such as silica, clay, and carbon have been used to toughen polyester without adversely affecting the elastic modulus. Although the polyester nanocomposites show better balance properties, the toughening effect of the inorganic nanoparticles was not so prominent compare with the liquid rubber (Afina et al., 2013; Vijayan et al., 2012; Xu et al., 2013).

Cellulose nanocrystals (CNCs) are a very important biopolymer that have attracted a great deal of interest in the nanocomposite field, due to their high modulus, strength, low density, high crystallinity, high surface area, unique optical properties, and their renewability and environmental friendly (Dufresne, 2012; Habibi et al., 2010). CNCs have been widely used as a reinforcement for a variety of thermoplastic and thermoset polymeric matrices. However, reports on the preparation of CNC-reinforced thermosetting matrices are relatively rare. There have been only a few researchers who have reported utilizing CNCs in an epoxy resin (Tang and Weder, 2010; Xu et al., 2013), but to the best of our knowledge, no report has been found on using an unsaturated polyester as the matrix to produce a CNC-reinforced, rubber-modified thermoset.

In this study, liquid epoxidized natural rubber (LENR) was used to modify the UPR, an orthophthalic polyester resin containing 30% styrene, and then, the resulting material was combined with CNCs. Both, LENR and CNC have been prepared from natural source and they are good candidates to replace synthetic liquid rubbers and inorganic fillers to toughen UPR while keeping desirable mechanical properties. The objective of this research was to investigate the effects of the LENR and CNC content on the morphology and mechanical properties of the nanocomposites. In particular, the dispersion of the rubber particles and CNCs, along with extensive discussion on the matrix interaction and toughening mechanism of both the blends and the nanocomposites was evaluated.

2. Materials and methods

2.1. Materials and chemicals

Raw kenaf (*Hibiscus cannabinus*) bast fibers, from which CNCs were prepared, were supplied by KFI Sdn. Bhd. (Malaysia). The UPR was supplied by Revertex Sdn. Bhd. (Malaysia). All other chemicals used were purchased from SYSTERM, Classic Chemicals Sdn. Bhd. (Malaysia). LENR was prepared in our laboratory by photosensitized degradation of dried epoxidized natural rubber (ENR) (Abdullah and Zakaria, 1989; Kargarzadeh et al., 2015).

2.1.2. Cellulose nanocrystal preparation

Colloidal suspensions of cellulose nanocrystals (CNC) in water were prepared from sulfuric acid hydrolysis of cellulose extracted from kenaf bast fiber as reported in our previous work (Kargarzadeh et al., 2012).

2.1.3. Preparation of LENR-modified UPR blend

To prepare the rubber-modified UPR, LENR was added to the UPR and mixed using an electrical stirrer for approximately 3 h. After that, methyl ethyl ketone peroxide (MEKPO) initiator at a 1.5 wt% concentration was added and stirred for 2 min. The mixture was poured into a 3-mm-thick aluminum mold and cured at room temperature for 24 h. The rubber content was varied between 1.5 and 6% (w/w) (Kargarzadeh et al., 2015).

2.1.4. Nanocomposite processing

Freeze-dried CNC were dispersed in styrene by using an ultrasonicator for 30 min in an ice bath. The CNC suspension in styrene was mixed with the UPR and sonicated for 30 min. The resulting mixture was stirred with a mechanical stirrer and heated at 60 °C until the excess styrene evaporated. The mixture was then cooled to room temperature, the LENR was added to the UPR–CNC and mixed for approximately 2 h before the initiator (1.5% concentration relative to the resin) was added and stirred for 2 min. The final mixture was poured into molds and cured at room temperature for 24 h. Different percentages of CNC loading (2, 4 and 6 wt%) were prepared. The nanocomposites using the CNC will be referred to as CNC–LENR–UPR. Two different nanocomposites were prepared, with 1.5 and 4.5 wt% LENR content, chosen on the basis of the mechanical properties (blend with 1.5 wt% LENR indicated higher tensile strength and 4.5 wt% LENR performed higher impact energy).

2.2. Characterization

2.2.1. Microscopy

The fractured surface morphologies of the LENR–UPR blend and the CNC–LENR–UPR nanocomposites were investigated using a Zeiss Supra 55VP field emission scanning electron microscope (FESEM). All samples were sputter-coated with gold prior to observation to prevent charge build up. In the case of the blend, its rubber phase was extracted using toluene for 12 h under ambient conditions.

Transmission electron microscopy (TEM) was conducted using a Philips CM30 microscope to investigate the morphology of the CNC–LENR–UPR nanocomposite. A thin film (70 nm) of this nanocomposite was prepared using cryo-ultramicrotomy (Leica EM, FC6) under liquid nitrogen.

2.2.2. Tensile test

Tensile tests of the samples were performed using an Instron Universal Testing Machine, model 5567 according to the ASTM D-638-91 standard test methods for examining the tensile properties of the unsaturated polyester at a 5 mm/min crosshead speed. The specimens were cut from the cured sheets to a $160 \times 13 \times 3$ mm size, with the shown values taken from an average of 10 measurements.

2.2.3. Impact test

The impact strength of unnotched specimens was measured following the ASTM D4812 impact resistance of plastic test. The tests were run using a RAY-RAN digital universal pendulum impact system at room temperature, for an average of 10 samples.

2.2.4. Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical thermal analysis was performed using a TA Instruments, DMTA instrument model Q 800 according to the ASTM D4065. The purpose of this test was to determine the storage modulus (E'), tan delta (δ), and glass transition temperature (T_g) of the samples. The peak in the tan delta vs. temperature thermogram was taken as T_g. Measurements were taken from −100 to 150 °C at a 5 °C/min heating rate and a 1 Hz fixed frequency. A single cantilever mode was used for the $35 \times 13 \times 3$ mm samples, with values taken from an average of 4 specimens.

3. Results and discussion

3.1. LENR-modified UPR

3.1.1. Morphological analysis

Fig. 1 shows the typical micrograph of a neat UPR and rubber-modified polyesters. The neat UPR displayed a smooth and glassy fractured surface with ripples, demonstrative of its poor impact strength (Ahmad and Hassan, 2010; Kargarzadeh et al., 2015). However, the fractured surface of the LENR–UPR blend [Fig. 1(b–d)]