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# Liquid rubber and silicon carbide nanofiber modified epoxy nanocomposites: Volume shrinkage, cure kinetics and properties

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## ABSTRACT

A cyclic anhydride cured epoxy modified with carboxyl-terminated poly (butadiene-co-acrylonitrile) liquid rubber (CTBN) and SiC nanofibers was developed by two different mixing strategies. In mixing method 1, SiC nanofibers were sonicated in epoxy/CTBN mixture, while in mixing method 2 the sonicated epoxy/SiC mixture was mechanically mixed with CTBN. The effects of liquid rubber, SiC nanofiber and their mixing methods on the cure shrinkage and cure kinetics of an epoxy/nadic methyl anhydride system were studied using pressure–volume–temperature (PVT) analysis. The influence of SiC nanofiber and mixing method on cross-linking induced phase separation were investigated by means of optical microscopy. The glass transition temperature ($T_g$) and the thermal stability of nanocomposites were evaluated. The epoxy/SiC/CTBN nanocomposite prepared by method 2 exhibited enhanced $T_g$ and thermal stability compared with neat epoxy and epoxy/CTBN blend. Moreover, improved impact strength was shown by epoxy/SiC/CTBN nanocomposites prepared by both methods, in comparison with epoxy/CTBN blend and epoxy/SiC nanocomposite. Additionally, fractographic analysis was carried out using scanning electron microscopy and a toughening mechanism for epoxy/SiC/CTBN nanocomposites was proposed.

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## 1. Introduction

Epoxy based thermosets play an important role as modern polymeric materials [1,2]. Epoxies tend to be rather brittle due to their high cross-link density and they are therefore inclined to fracture. The incorporation of thermoplastic/liquid rubber into epoxy is widely described in the literature as a way to improve the toughness of epoxy [3–7]. The losses in modulus and thermal properties due to the incorporation of such toughening agents are the major issues. During last few years, research has been focused on this aspect and nanofillers such as nanoclay, nanosilica, nanoscaled $TiO_2$ and carbon nanotubes (CNTs) were proposed to be used for maintaining mechanical and thermal properties of thermoplastic/liquid rubber modified epoxy [8–14]. The production of SiC one-dimensional nanostructures, such as nanofibers, nanowires, nanorods, and nanowhiskers, has been also widely studied in recent years due to its potential applications [15–17]. The outstanding mechanical properties of SiC nanofiber make this material a promising candidate for polymer–matrix composites. Up to now, few studies related to the enhancement of the mechanical properties of an epoxy matrix by the introduction of SiC nanowires have been conducted [18]. We have already reported the effectiveness of sonication process over high shear mixing for the dispersion of SiC nanofibers in epoxy [19]. One of our authors recently prepared and studied the mechanical properties of epoxy nanocomposites using SiC purified fibers and raw SiC branches [20].

It is well known that extensive shrinkage occurs during the cure of thermoset resins, caused by the polymerization and extensive crosslinking. The cure shrinkage reflects the decrease in the Van der Waals volume (and the associated excess volume) of the thermosetting polymer with conversion. Cure shrinkage has to be considered for its potentially serious consequences, depending on the application of the material. e.g., the shrinkage associated with the curing of thermoset resins contributes to poor surface quality.

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The presence of fillers and modifiers [21] influences the volume shrinkage behavior of epoxy resin. The compensation of the cure shrinkage of polyester resin by the addition of low profile additives was studied by Haider et al. [22]. Schubel et al. [23] investigated the potential use of nanoclay for the reduction of volumetric shrinkage in unsaturated polyester resin.

In pressure–volume–temperature (PVT) experiments, the specific volume at defined temperature and pressure as a function of time is measured. Modeling of cure shrinkage and kinetic studies of a simple epoxy resin system cured with an aromatic diamine 4,4′-methylene bis (3-chloro-2,6-diethylaniline) (MCDEA) were carried out by Ramos et al. [24]. PVT studies on epoxy/thermoplastic system were recently reported in literature, [25–27] also for systems containing inorganic filler [11]. Even if studies on toughening of epoxy by liquid rubber were extensively reported, the volume shrinkage studies on such systems are quite rare. As a pioneer work in this area, Borrajo et al. [28] studied the effect of cure shrinkage on the miscibility of a rubber with a thermosetting polymer. The volume shrinkage during cure reaction produces a slight decrease in the miscibility of the rubber in the thermosetting polymer, due to the reduction in the volume fractions of holes. Recently, one of the authors also studied the influence of a reactive rubber (CTBN) on the volume shrinkage behavior of epoxy resin [25] and compared it with the behavior of a non-reactive rubber (CTBN-ester) using PVT experiments. They observed that the reactive rubber is partially incorporated in the crosslinked epoxy phase and vice versa, reducing the degree of the undesirable shrinkage.

The approach of incorporating both soft rubber phase (liquid rubber/core–shell rubber) and rigid nanofiller into epoxy thermoset is attracting much interest during the past several years [29–32]. It is possible to tailor the multiple mechanical properties of epoxy matrix without compromising the desired thermal properties by carefully adjusting the soft and rigid phases. The promising properties offer by the resin systems containing both liquid rubber modifiers and nanofillers, led to the necessity to explore the volume shrinkage and cure behavior of these systems, thus to enable the use of these matrices for a given end use. To the best of our knowledge, this is the first report on the preparation of epoxy/SiC/CTBN nanocomposites. In this specific work, SiC nanofibers, the innovative component of proposed material, were synthesised via self-propagating high-temperature synthesis (SHS) technique. The aim of our study was to find a suitable mixing strategy to develop a novel rubber modified epoxy nanocomposite. The influence of liquid rubber, SiC nanofibers and mixing strategy on the volume shrinkage and cure behavior of epoxy resin system using PVT technique were analyzed. The influence of SiC nanofiber and mixing method on crosslink induced phase separation was followed. The glass transition temperatures ($T_g$), thermal stability, impact properties and toughening mechanisms of epoxy/SiC/CTBN nanocomposites were also evaluated.

## 2. Experimental

### 2.1. Materials

Silicon powder (Aldrich, 325 mesh, 99% purity) and PTFE (polytetrafluoroethylene) powder (Aldrich, 1 μ) were used as reducer and oxidant, respectively, for the preparation of SiC nanofiber. Diglycidyl ether of bisphenol A (Araldite GY 250) with an epoxide equivalent weight of approximately 183 g/eq was used. Nadic methyl anhydride (HY906) and benzyl dimethyl amine (DY062) as the curing agent and the accelerator, respectively, were provided by Huntsman Advanced Materials. Carboxyl terminated butadiene-co-acrylonitrile rubber (CTBN1300 × 8, $M_n = 3550$, acrylonitrile content = 18%), provided by Hypro Reactive Liquid Polymers, was used as the reactive liquid rubber.

### 2.2. Sample preparation

Synthesis of SiC nanofibers: The SiC nanofibers were synthesised via SHS technique [33]. The combustion synthesis, carried out in the modified calorimetric bomb, is a fast, simple, low-cost and environmentally friendly method for nanomaterial synthesis. The exothermic, self-sustainable process is initiated by resistive heating and terminated within few seconds. In case of SiC nanofibers, the starting homogenous mixture of reactants consisted of Si (<43 μm) and polytetrafluoroethylene (PTFE, 1 μm) powders. Initial pressure was equal to 1 MPa and the reaction was carried out under air atmosphere. Products were collected and purified by chemical (boiling in 30% KOH) and high temperature (600–650 °C) treatment. Fig. 1 presents SEM images of the raw product and the purified nanomaterial: it can be deduced that the diameter of nanofibers was mostly ca. 50 nm, while the length was several microns. Hence, we can consider that the aspect ratio of the nanomaterial was well above 100.

Epoxy/CTBN blend was prepared by mixing 15 phr (per hundred resin) of CTBN to the epoxy prepolymer for 10 min. Hardener and catalyst were added to the mixture of epoxy and CTBN and stirred with a glass rod for 10 min at room temperature. Epoxy/SiC nanocomposite were prepared dispersing 0.25 phr of SiC nanofibers in the epoxy for 30 min by using a IKA mechanical stirrer at 400 rpms, followed by a sonication step of 30 min by using the ultrasonic device UP400S equipped with the Sonotrode H7 (Hielscher Ultrasonics) at an amplitude of 20%. After degassing of the mixture in a vacuum chamber for 2 h, hardener and accelerator were added and stirred well with a glass rod for 10 min. Two mixing strategies were adopted for the preparation of epoxy/SiC/CTBN nanocomposites. Specifically, in mixing method 1, 0.25 phr of SiC nanofibers were dispersed in a mixture of epoxy and 15 phr CTBN for 30 min by mechanical mixing at 400 rpms, followed by sonication for 30 min at an amplitude of 20%. After a degassing phase of the mixture in vacuum chamber for 2 h, it was mixed with hardener and accelerators for 10 min. The samples prepared by using this method are designed as '$M_1$'. In mixing method 2, 0.25 phr of SiC nanofibers were dispersed in epoxy for 30 min, followed by mechanical mixing at 400 rpms and sonication for further 30 min at an amplitude of 20%. CTBN was then added to this mixture and stirred with a glass rod for 10 min. After degassing the mixture in vacuum chamber for 2 h, hardener and accelerator were added and mixed for 10 min at room temperature. The samples prepared by this method are designed as '$M_2$'.

The freshly prepared mixtures were immediately used for PVT analysis. The bulk samples for thermal, mechanical and morphological analysis were prepared by curing the mixtures according to the following cure schedule: 120 °C for 1 h, 150 °C for 1 h, and 180 °C for 2 h at room pressure in an oven.

### 2.3. Techniques

Specific volumes were measured using a fully automated GNOMIX high-pressure dilatometer. Ultrahigh-vacuum samples (ca. 1.5 mL) embedded in a nickel foil cup were loaded into the measuring cell that was completely filled with mercury as confining fluid. The sample was pressurized to 10 MPa and the curing reaction was analyzed by following the changes in the specific volume ($V_{sp}$) at 10 MPa, heating the sample to the desired temperature of 100 °C followed by isothermal curing for more than 6 h. Phase separation studies were carried out by observing a few milligrams of the samples between two glass slides using a Leitz laborlux 12 Pols optical microscope, while the sample was being cured in a Linkam CSS450 shearing cell. The Linkam cell was only used for heating and no shear was applied. Digital micrographs were taken at several times by means of a Hamamatsu TSU digital

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