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Gamma-rays initiated cationic polymerization of epoxy resins and their carbon nanotubes composites

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HIGHLIGHTS

- Epoxy resins were gamma-radiation cured in the presence of cationic initiator.
- Thermal treatment is necessary to complete radiation induced curing.
- Carbon nanotubes improve some mechanical properties of epoxy composites.
- Compatibility between carbon nanotubes and matrix was confirmed.

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ABSTRACT

Epoxy resins based on diglycidyl ether of bisphenol A (DGEBA) in the presence cationic initiator in the form of iodonium salt were exposed to gamma-rays in order to initiate curing process. The influence of the initiator concentration, dose rate, chemical structure of monomers and the presence of carbon nanotubes were determined on the basis of the recorded on-line thermal effects. The induction time of radiation curing increased with lowering concentration of the initiator and oxirane groups as well as with decreasing dose rates. As was confirmed by SEM images, carbon nanotubes were uniformly distributed over the matrix and closely surrounded by the macromolecules. Such a structure resulted from adsorption of the initiator on the filler surface what allowed to begin polymerization around nanoparticles and facilitated their incorporation into the matrix. As a consequence, the mechanical properties of the nanocomposites were improved.

1. Introduction

Development of curing by means of radiation processing is still important challenge for material science and engineering (Chapiro, 2002; Saunders et al., 2000; Berejka and Eberle, 2002; Ye et al., 2005). Potentially, the technology can be used in many branches of industry in structural applications and is a promising alternative for thermal curing. As is widely known, the thermal treatment introduces internal stress to the final product. This disadvantage might be eliminated by radiation processing which partly removes thermal stress in spite of the temperature enhancement resulting from exothermic polymerization. Many other advantages of radiation treatment were considered (Singh, 2001): reduction of processing time and elimination of hazardous volatile emission, increase in dimensional stability when the process occurs at moderate temperatures, relatively uniform curing due to limited gradient temperatures, etc. The expected benefit of the process involves improved characteristic of the final products which demonstrate excellent strength, stiffness and wear resistance. Developing other aspects of applied research, radiation induced curing of carbon fiber-reinforced composites as a new generation of materials for aerospace industry has been recently studied intensively by Coqueret and his group (Coqueret et al., 2009; Martin et al., 2014; Ranoux et al., 2012).

Radiation treatment is usually considered as a cold processing during which thermal effects are small and do not influence the final functionality of the products. Contrary to this usually legitimate assumption, radiation induced cationic polymerization is characterized by the substantial thermal effect which is a consequence of two phenomena: conversion of energy deposited into the heat (insignificant effect that rises temperature to less than 50 °C) and generation of heat during polymerization process which, in some cases, increases temperature to almost 300 °C.

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According to the analysis proposed by Coqueret et al. (2009) the second process initially is dominated by the combination of radicals in the viscous liquid which, with increasing conversion degree, is being replaced gradually by the monomolecular occlusion of residual active centers due to mobility restrictions.

The polymerization based on accelerator technique shows some limitations with respect to limited penetration of electron beam (EB) (Korenev, 2001). However, when gamma- or X-rays are applied as radiation sources, even thick products can be cured. Then, the radiation processing might be used for the large structures applied in aeronautic, transport industry or marine. According to Singh et al. the dose necessary to reach complete curing of the resins is about tenfold lower for gamma treatment than for EB irradiation (Singh et al., 1996). Generally, as curing involves chain reactions, the dose required for the process is usually lower than in the case of typical polymer crosslinking resulting from radical recombination. Gamma irradiation is considered as specially suitable for curing, however, due to low dose rates, the process is much time consuming than EB treatment. Thus, the reported research which utilizes gamma-rays can be regarded as the preliminary approach towards the treatment by X-rays generated upon EB conversion.

The paper presents the study on polymerization of various epoxy resins based on diglycidyl ether of bisphenol A (DGEBA) in the presence of iodonium salt. The nature of the components was selected basing on the characteristic of phenolic epoxides which exhibit high reactivity, elevated glass transition temperature and high modulus at high temperatures (Sui et al., 2003) contrary to products curing by multifunctional amine (Bernard et al., 2006). The process involving three dimensional curing was conducted using model epoxy resin and commercial products applying widely as a substrate for adhesives, electrical systems and electronics, as laminates, castings, fixtures, and others.

The thermal effect of radiation curing was monitored on-line by the detection of temperature changes and some results obtained were compared to the data recorded during heating of the samples in differential scanning calorimetry (DSC) apparatus. The influence of initiator concentration, dose rate, type of monomers and the presence of carbon nanotubes were determined. The aim of the studies was a clearer understanding polymerization induced by gamma-rays and assessment of pros and cons of the radiation method. Onium salt was used as an initiator since many previous papers reported that it demonstrates activity upon exposure not only to UV but also to ionizing radiation (Crivello, 1999; Degrand et al., 2003).

2. Materials and methods

2.1. Materials

The work was focused on the studies related to radiation-induced curing of epoxy resins and their composites basing on diglycidyl ether of bisphenol A (DGEBA) and its commercial derivatives as shown in Scheme 1. The characteristic of the resins is tabulated in Table 1.

Table 1
Characteristic of substrates according to manufacturer's Material Safety Data Sheets.

Oligomer	Viscosity at 25 °C [mPas]	Amount of epoxy groups [mol/100 g]	Density at 20 °C [g/cm^3]
DGEBA	[a]	0.588 (theoretically)	–
Epidian 6	10,000–15,000	0.510–0.540	1.15
Epidian 5	20,000–30,000	0.480–0.510	1.15
Epidian 52[b]	400–800	0.510–0.550	1.11–1.15

[a] Melting temperature: 40–44 °C.
[b] Epidian 5 doped with butylglycidyl ether.

Epidians were produced by “Organika-Sarzyna” Chemical Company. DGEBA was purchased from Sigma-Aldrich. Single wall carbon nanotubes (SWCNT) and multi wall carbon nanotubes (MWCNT) in the form of suspension in epoxy resins were obtained from the Nanomaterials Co, Warsaw, Poland. A cationic initiator [4 (1-methylethyl)phenyl][4-methylphenyl]iodonium tetrakis(pentafluorophenyl)borate salt (IPB), trade name Rhodorsil 2074, was purchased from Secant Chemicals Inc., USA. An iodonium salt IPB having poorly nucleophilic anion is considered as relatively effective and soluble in non-polar monomers, Scheme 2.

2.2. Preparation of epoxy resins and their composites; irradiation conditions

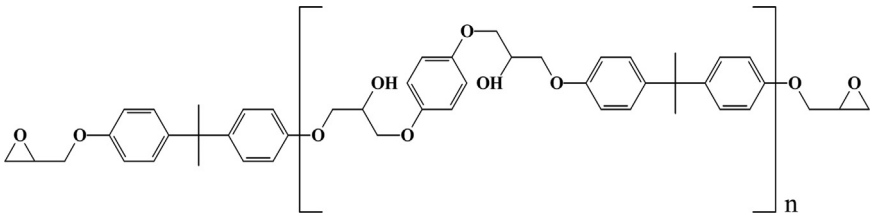
The initiator was dissolved in epoxy resins at 60–65 °C in an ultrasonic bath. Carbon nanofilers were dispersed in the matrix in the same way.

In situ polymerization was conducted by exposure of the resins to ionizing radiation. Gamma irradiation was performed in a Gamma Chamber 5000 at dose rates of 6.0 kGy/h, 3.0 kGy or 1.5 kGy using appropriate screens. The dose deposited was proportional to the exposition time. The temperature was monitored on-line by a thermocouple, wherein the thermocouple tip was fixed in the middle of the sample. Thermal effects were studied for 10 or 20 g samples closed in the glass vials insulated with polyurethane foam. The samples had a cylindrical shape with a diameter of 2 cm and a height of *c.a.* 3.2 cm.

For mechanical tests the specimens of the cross-section 10×4 mm^2 were casted in an aluminum mold and in such a form were gamma irradiated.

3. Methods

Thermal analysis was carried out using a TA Instruments differential scanning calorimeter (MDSC 2920). The measurements were performed under nitrogen at a heating/cooling rate of 10 °C/min. About 5 mg samples were placed in aluminum pans, closed with lids and inserted into the cell. During the first cycle of measurement the cell was heated from 0 °C to 250 °C, then was kept



Scheme 1. Formulae of epoxy compounds: for $n=0$ formula of diglycidyl ether of bisphenol A (DGEBA); for $n=0$ and 1 formula of Epidian 6; for $n=0$, 1 and 2 formula of Epidian 5 and Epidian 52 doped with butylglycidyl ether.