Visible Light Induced Cationic Polymerization of Epoxides by Using Multiwalled Carbon Nanotubes

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The visible light induced cationic polymerization of epoxides can be achieved by means of multiwalled carbon nanotubes (MWCNTs), which act as visible light photoinitiators via a radical-induced cationic photopolymerization process. When MWCNTs are irradiated with longer wavelengths (above 400 nm), they generate carbon radicals, by means of hydrogen abstraction from the epoxy monomer; these radicals are oxidized in the presence of iodonium salt to a carbocation that is sufficiently reactive to start the cationic ring-opening polymerization of an epoxy monomer. These mechanisms have been supported by electron paramagnetic resonance analysis.

1. Introduction

Photoinitiated polymerization processes continue to attract interest due to their potential applications in coatings, adhesives, inks, printing plates, optical wave-guides, and microelectronics.[1] By applying a large variety of photoinitiaiting systems and a combination of different monomers, various complex polymer architectures, such as block and graft copolymers[2] as well as hyperbranched polymers,[3,4] can be prepared. New photochemical methodologies have recently been developed to obtain polymers with a controlled molecular weight, structure, and functionality.[5,6] Photopolymerizations can be initiated in various ways, such as through radical, cationic, or even anionic processes. Many photoinitiating systems that act at a UV, visible,[7] or even near IR region[8–12] have been developed. Since UV wavelengths require higher energy and can cause skin and eye damage,[13] there is a great deal of interest in extending the photoactivation of polymerizations to the visible range. Although photoinitiated free radical polymerization is at a more advanced state, many efforts have also been made to develop visible light photoinitiating for the cationic mode, since many industrially important monomers, such as epoxides and vinyl ethers, can only be polymerized by a cationic mechanism that is insensitive to oxygen inhibition.

General strategies to conduct cationic polymerization at the visible range involve the oxidation[14] of free radicals by onium salts (also called free-radical promoted cationic polymerization), the formation of charge transfer complexes,[15] and electron transfer reaction[16] within the exciplexes of polynuclear aromatic compounds and onium salts. Lalevee et al. have shown that various dyes,[17] silanes,[18] and polythiophenes[19] can efficiently induce a reduction in onium salts, even at a visible range.

Carbon nanotubes (CNTs), which were first discovered by Iijima,[20] are nano-objects that are characterized by peculiar electronic properties as a function of their structure.[21] In fact, a change in chirality can transform CNTs into a semiconductor with large electronic gap properties.[22] Their semiconductor-type behavior could be exploited in photochemistry to produce an electron–hole pair or an exciton during the irradiation of multiwalled carbon nanotubes (MWCNTs).

It has already been reported in literature that ultrasmall semiconductor particles,[23] as well as magnetite nanoparticles,[24] are able to generate radicals upon photoexcitation, a process that can start the radical polymerization of vinyl monomers. In a recent paper, we have reported the use of CNTs as radical generators upon UV-irradiation. In that paper, a high efficiency of the photoinitiating system was evidenced,[25] as a result of a very fast acrylic double bond conversion, which can even be achieved in the presence of a carbon filler. The initiation mechanism is based on the reactions of electrons and holes generated in conduction (cb) and valence (vb), respectively, in analogy with the general behavior of CNTs. The overall mechanism is presented in **Scheme 1**A. Both electrons and holes can participate in the generation of initiating radicals. Conceptually similar visible light photoinitiated radical polymerization, based on the generation of electrons and holes, obtained using mesoporous carbon nitride, was also described.

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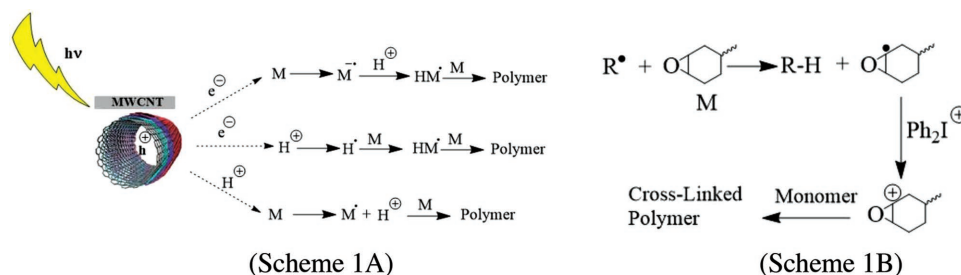E-mail: marco.sangermano@polito.it

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Scheme 1. A) Visible light initiated radical polymerization by means of MWCNTs. B) Oxidation of the radicals formed by visible light irradiation of MWCNT following hydrogen abstraction.

As cationic polymerizations can successfully be initiated by the redox process, which involves photochemically generated radicals and iodonium salts,[26] it seemed appropriate to trigger cationic polymerization epoxy using MWCNTs.

Herein, we describe a novel methodology for the cationic polymerization of epoxides through visible light generated electrons and holes from MWCNTs, followed by electron transfer reactions with iodonium salt. The proposed mechanism has been evaluated and confirmed by means of electron paramagnetic resonance (EPR) analysis. The obtained cross-linked films were characterized by thermomechanical properties.

2. Experimental Section

2.1. Materials

3,4-epoxycyclohexylmethyl-3,-4-epoxycyclohexane carboxylate and p (octyloxyphenyl) phenyliodonium hexafluoroantimonate (PI, ABCR) were purchased from EEC, Aldrich. MWCNTs NC 7000 multiwall carbon nanotubes were purchased from Nanocyl S.A. and employed without further purification.

2.2. Sample Preparation

The CNT fillers were dispersed at a ratio between 0.05 and 0.3 wt% in the epoxy resin and mixed with a high-shear homogenizer (Ultra-Turrax, IKA) at 30 000 rpm for 5 min. After mixing, the iodonium salt photoinitiator agent was added to each formulation at 3 wt%. The different formulations were coated onto a polypropylene substrate by means of a wire-wound applicator (film thickness 100 µm). The films were cured with a visible lamp (Hamamatsu LC8, with a visible bulb and a cut-off filter below 400 nm, equipped with an 8 mm light guide) under nitrogen.

2.3. Characterization

The photopolymerization process was followed by the measurement of the epoxy group conversion, which was conducted by means of Fourier-transform infrared (FT-IR) spectroscopy during irradiation, employing a Thermo-Nicolet 5700 instrument. The total epoxy conversion was calculated by monitoring the decrease in the absorbance of the epoxy group between

780 and 820 cm^{-1}. The formulations were coated on SiC (film thickness 25 µm), and FT-IR spectra were collected before and after irradiation. The films were cured with a visible lamp (Hamamatsu LC8, with a visible bulb and a cut-off filter below 400 nm, equipped with an 8 mm light guide).

EPR analysis[27] was performed at room temperature, on a Bruker ESR 300E spectrophotometer, in the presence of the 5,5-dimethyl-1-pirroline-N-oxide (DMPO) spin-trap. MWCNTs were irradiated for 60 min with visible light, then 17×10^{-3} M DMPO was added. The reaction mixture was irradiated again for 2 min and the EPR spectrum was recorded immediately after the end of irradiation. Measurements were carried out in quartz capillary tubes, and the following parameters were used: a microwave frequency of 9.78 GHz, a power of 5 mW, a modulation frequency of 100 kHz, a modulation amplitude of 0.4 Gauss, and a time constant of 40 ms. Simulated spectra were obtained by means of the WinSim software.[28]

Dynamic mechanical thermal analysis (DMTA) was performed on the photocured samples using an MK III Rheometrics Scientific Instrument, at a frequency of 4 Hz, in the tensile configuration with 5 K min^{-1}. The storage modulus, E', and the loss factor, $\tan\delta$, were measured from room temperature up to the temperature at which the rubbery state was attained. The T_g value was assumed as the maximum of the loss factor curve ($\tan\delta$).

3. Results and Discussion

In this work, we have investigated the efficiency of MWCNTs to act as visible light photoinitiators for the cationic photopolymerization of an epoxy monomer, namely 3,4-epoxycyclohexylmethyl-3,-4-epoxycyclohexane carboxylate (EEC), through a radical induced cationic polymerization mechanism. Because of the two epoxy groups, this monomer, in suitable conditions, can readily be cross-linked and ultimately used to form networks.

An aliquot of 3 wt% of iodonium salt was added to the epoxy formulation containing MWCNT at 0.05, 0.1, and 0.3 wt% as a cationic oxidant and irradiated with visible light above 400 nm; iodonium salt is transparent at this irradiation wavelength. However, upon irradiation, the formulations containing the CNT rapidly cross-linked and formed solid tack-free films, thus confirming the promoting effect of MWCNT.

Conversion during irradiation was evaluated by means of FT-IR analysis, following the broad peak at 815–780 cm^{-1} belonging to the epoxy group, which decreased after 30 min

Table 1. The effect of the MWCNT concentration on the visible light initiated cationic polymerization of EEC at $\lambda > 400$ nm.

MWCNT [wt%]	Oct-Ph$_2$I$^+$PF$_6^-$ [wt%]	Irradiation time [min]	Conversion[a] [%]
0.05	3	30	75
0.1	3	30	58
0.3	3	30	50

[a]Determined by IR spectra.

of irradiation, with an overall conversion of 75% of the epoxy group. The lowered conversions attained high concentrations of MWCNT (**Table 1**), may be due to the screening effect or the favored coupling of the thus formed radicals.

In the process, the radicals formed upon irradiation of MWCNT can abstract hydrogen from the epoxy ring of the monomer to generate oxidizable radicals, as demonstrated by Crivello.[29] These electron donating radicals can readily be oxidized by iodonium salts to generate the corresponding cationic species, which are capable of further propagating to essentially yield networks due to the bifunctional nature of the monomer (Scheme 1B).
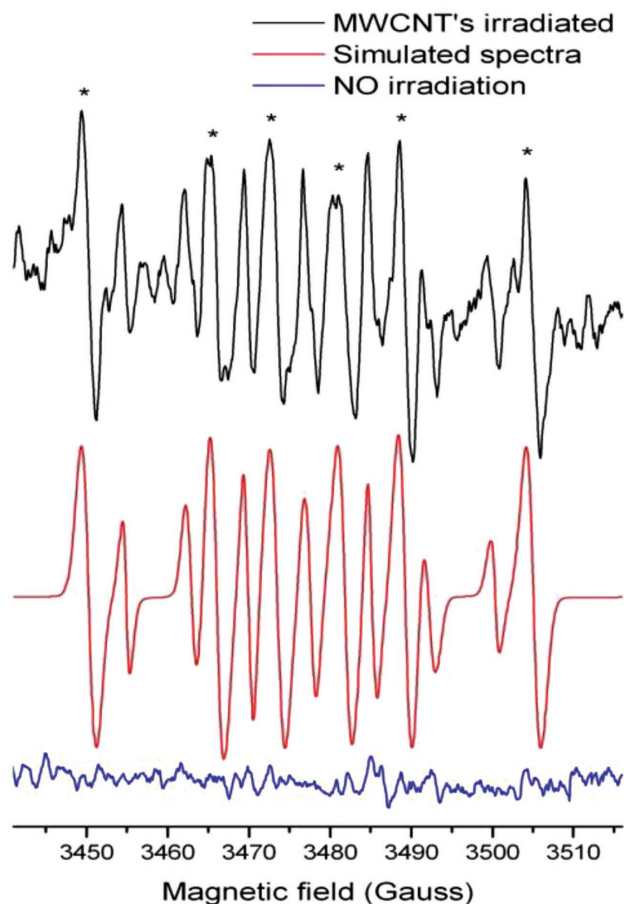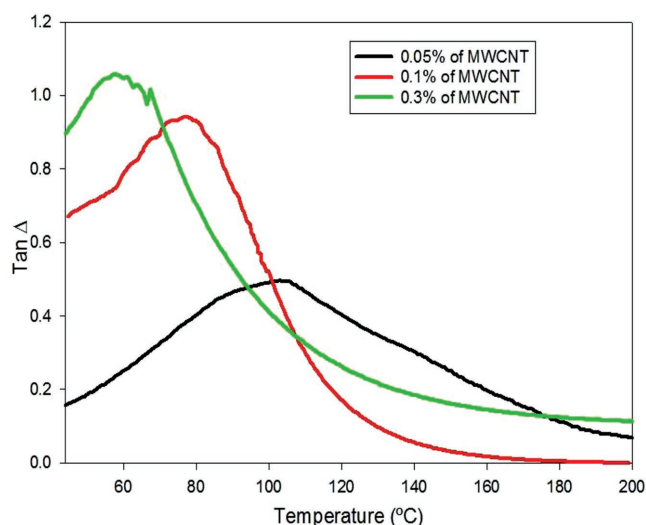
Figure 2. Tanδ curves registered by means of DMTA of the photocross-linked epoxy films obtained from the formulations containing 0.05, 0.1, and 0.3 wt% of MWCNT and 3 wt% of iodonium salt photoinitiator. The formulations were irradiated by means of visible light with a lamp cut-off at 400 nm.

In order to gain more insight into the mechanism, EPR studies were conducted (EPR spectra reported in **Figure 1**). Thus, a water suspension of MWCNTs, irradiated with visible-light in the presence of DMPO, led both to the formation of the typical DMPO–OH radical species, previously observed by Wu et al.[30] after UV irradiation of MWCNTs, and the C-centered radical, characterized[31] by a six-line pattern with $a_N = 15.7$ Gs and $a_H = 23.2$ Gs.

The effect of the amount of MWCNT on the thermomechanical properties was also investigated by means of DMTA. As can be seen from **Figure 2**, as the content of the MWCNT is increased, a significant decrease in T_g occurs, with a shift in the maximum of the tanδ curves toward a lower temperature. This observation, arising from the lower cross-link density, is in complete agreement with the FT-IR analysis (wide ante).

4. Conclusions

We have here demonstrated the ability of MWCNT to act as visible light photoinitiators via a radical induced cationic photopolymerization of epoxy monomers. We have shown that when MWCNTs are irradiated with longer wavelengths (above 400 nm), they generate carbon radicals by means of hydrogen abstraction from the epoxy monomer; these radicals are oxidized, in the presence of an iodonium salt until they are sufficiently carbocation reactive to start the cationic ring-opening polymerization of epoxy monomer. This mechanism has been supported by EPR analysis, and it has been shown that if the MWCNT content is increased, a possible shielding effect occurs, which induces a decrease in the epoxy group conversion, with a consequent decrease in the cross-linking density and T_g of the cured films.

Figure 1. EPR spectra of the MCWNT water suspension irradiated in a solar simulator in the presence of DMPO (* indicates the lines attributable to the C-centred radical).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

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