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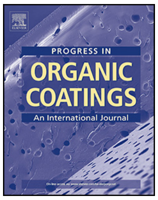

Improvement of the water-vapor barrier properties of an uv-cured epoxy coating containing graphite oxide nanoplatelets

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ABSTRACT

In this paper we investigated the improvement of water-vapor barrier properties of an UV-cured epoxy film containing graphite oxide nanoplatelets. Graphene platelets were successfully dispersed in the epoxy resin and cured by UV-irradiation. Good performances in increasing water vapor barrier properties at a very low filler loading are obtained: the permeability decreased of about 40% with a 0.5 wt.% of GOx and of about 60% with a 1.0 wt.% of GOx. These good results are attributed to a homogeneous filler dispersion, as clearly shown by TEM microscopy.

1. Introduction

Polymeric films are largely used in the packaging and coating industry with the stringent requirement of high oxygen and water vapor barrier properties. Because of their relatively high permeability for gases or water vapor, pristine polymers are not suitable materials for these purposes. Industrial applicants cope with this problem by using laminated films, which consist of many components such as functional polymers (mainly silanes or fluorinated compounds) and aluminum foils [1]. Among the different strategies suggested in the literature, the preparation of nanocomposite materials is one of the most promising methods for improving gas barrier properties [2,3].

Polymer/clay nanocomposites represent an effective strategy to decrease gas permeability [4–6]. In particular, the presence of the layered clay fillers can induce a significant decrease in both oxygen and moisture permeability. A strong reduction in oxygen permeability upon the incorporation of organoclay into PE was reported by Osman et al. [7,8]. Avella et al. suggested that the introduction of calcium carbonate nanoparticles drastically reduced the permeability of oxygen and carbon dioxide for polypropylene nanocomposites [9]. Similar results were also achieved by dispersing clays in thermosets [10] and in vulcanized rubbers [11]. The incorporation of fillers in platelet shape generates a structure able to hinder penetrant diffusion and thus decrease the permeability of the material [12]. In this case, the tortuous diffusion path model may be applied to the composite.

More recently, graphene and its derivative nanosheets have been considered as potential fillers for gas barrier membranes due to their diffusion hindering effect [13–18]. Therefore, lamellar structure of graphene are an interesting alternative to the use of organoclays fillers to enhance the gas barrier properties of polymeric matrices. In this context, Vitale et al. investigated the effect on water vapor barrier properties of graphene nanoplatelets in an UV-curable perfluoropolyether methacrylic oligomer. They found an increase of the water vapor barrier properties of this polymer at very low filler amounts [19].

The present study focuses on the improvement of the water vapor barrier properties of an UV-cured cycloaliphatic epoxy matrix containing graphene oxide nanoplatelets. The choice of the filler is related to its lamellar morphology which could generate a tortuous diffusion path able to hinder penetrant diffusion and thus decrease the gas permeability of the material. In particular, the tortuous path induced by the graphene sheets should act on the kinetic of the water vapor diffusion through the polymeric films, thereby improving its barrier behavior. Furthermore, the graphite oxide shows a good compatibility with the epoxy resin due to the presence of the polar functional groups on its surface.

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2. Experimental

2.1. Materials

The UV-curable epoxy resin was the bis-cycloaliphatic diepoxy resin 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexyl carboxylate (**CE**) and the triphenylsulfonium hexafluoroantimonate ($Ph_3S^+SbF_6^-$) was used as photoinitiator. Both products were purchased from Sigma-Aldrich and used as received without any further purification.

Graphite oxide (**GOx**) was obtained using natural graphite flakes (purum powder ≤ 0.1 mm, Sigma-Aldrich) following the Brödie method. GOx produced through this method has led to the formation of single layers or stacks of up to 7 sheets with hydroxyl, carbonyl and epoxy groups on their surface [12].

2.2. Sample preparation

Graphite oxide was directly dispersed, in the range between 0.5 and 1.0 wt.%, into the UV-curable epoxy resin using an IKA Ultraturrax at 30000 rpm for 5 min. The mixtures were then placed in an ultrasonic bath for 60 min. The photoinitiator was added just before UV-irradiation in a proportion of 2 wt.% with respect to the resin. The formulations were coated on different substrates (e.g. PET for permeability test) and UV-irradiated for 1 min (the light irradiance on the sample surface was 60 mW/cm^2). Freestanding films with a thickness ranging from 100 to 250 μm were prepared for DMTA analysis.

2.3. Sample characterization

The progress of the photopolymerization process was followed by FT-IR in a Thermo-Nicolet 5700 spectrophotometer. The spectra were obtained co-adding 7 individual scans at 8 cm^{-1} of resolution. 25 μm-thickness films were coated on silicon wafers and simultaneously exposed to a UV-beam (Hamamatsu LC8 portable UV-lamp), with an irradiance of 60 mW/cm^2 for 3 min to induce polymerization, and to the IR-beam, to make an in-situ evaluation of the extent of reaction. The conversion of the epoxy group was followed by monitoring the decrease in the absorbance of the epoxy groups centered at 750 cm^{-1} and normalized by the carbonyl peak centered at around 1700 cm^{-1}. The conversion curves as a function of irradiation time is the average result of 3 runs for each sample.

Gel content values of the cured coatings were obtained by measuring the weight loss after 24 h in chloroform at room temperature (ASTM D2765-84).

UV–visible spectroscopy measurements were performed using a Varian-Cary 5000 spectrophotometer.

Dynamic-mechanical thermal analyses (DMTA) were performed on a Triton Technology DMA (Mettler-Toledo) at 1 Hz frequency in a tensile configuration. The storage modulus, E', and the loss factor, tan δ, were measured from 30 °C to the temperature at which the plateau of rubbery state was observed. The Tg value was assumed as the maximum of the loss factor curve. The samples were prepared by placing the corresponding formulation in a silanized glass template, cured in the UV lamp to obtain specimens with dimensions of about 2 × 0.5 × 0.1 cm.

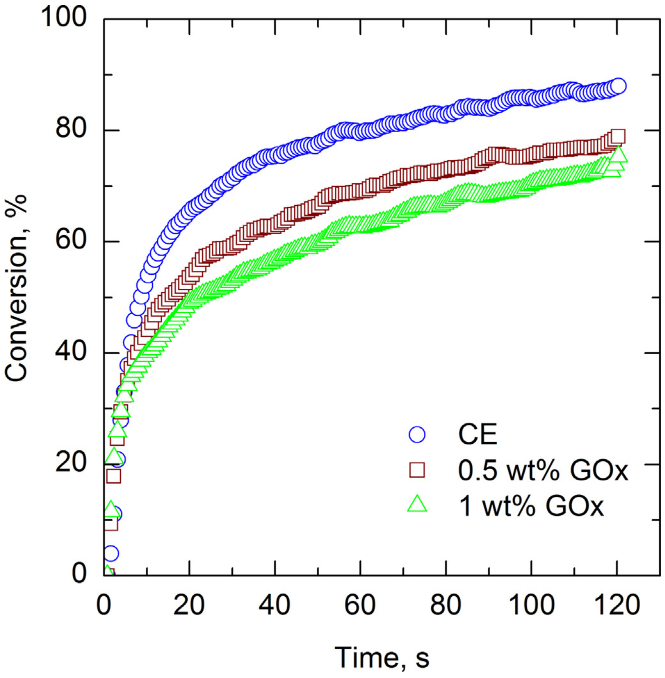

Fig. 1. Real-time FT-IR conversion curves as a function of irradiation time for the pristine CE resin (○) and for the epoxy resin formulations containing 0.5 (□) and 1.0 (△) wt.% of the graphite oxide. Iradiance on the sample surface 35 mW/cm^2. Film thickness 25 μm.

Water vapor permeability specimens were prepared by coating a PET substrate (thickness 15 μm) with either the pristine epoxy resin or the resin containing the graphite nanoplatelets. Afterwards, the obtained specimens were mounted on an EXTRASOLUTION MultiPerm® instrument with a surface reducing frame in order to realize an exposed surface of 2.27 cm^{-2}. Analyses were performed following the DIN 53122 standard, using a pressure of 1 atm, a temperature of 25 °C, and a 100% humidity level.

TEM analyses were performed on microtomized samples in a 300 keV transmission electron microscope Philips CM30. TEM micrographs were processed with a slow scan CCD camera and analyzed with a Digital Micrograph program.

3. Results and discussion

In this study, the dispersion of graphite nanoplatelets filler in a cycloaliphatic epoxy resin (CE) is investigated with the aim to improve the water vapor barrier properties of the crosslinked films. Fig. 1 reports the RT-FTIR conversion curves obtained from the photopolymerization process at different graphite oxide amounts.

Table 1
Properties of UV-cured films.

Sample	Conversion (%)[a]	Gel content (%)[b]	T% (@ 510 nm)[c]	Tg (°C)[d]	WVTR (g/m^{2}24 h)[e]
CE	89	99	100	193	16,9
CE + 0.5 wt.% GOx	79	98	96	205	10,2
CE + 1.0 wt.% GOx	75	99	92	214	7,4

[a] measured by RT-FTIR analysis.
[b] measured on crosslinked films ASTM D2765-84.
[c] measured on crosslinked films with UV–vis spectrophotometer.
[d] maximum of tanδ peak of DMTA analysis.
[e] measured with permeometer DIN 53122.

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