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Oriented array of polyethylene-*block*-poly(ethylene oxide) nanoplatelets in unsaturated polyesters cross-linked coatings

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ABSTRACT

Transparent coatings of cross-linked unsaturated polyester (UP) containing staggered platelets of polyethylene-*block*-poly(ethylene oxide) with their normal perpendicular to the substrate have been readily prepared by a solvent assisted spin-coating method. For this purpose, homogeneous liquid dispersions of block copolymer platelets in liquid UP resin have been prepared using a selective solvent, deposited onto flat substrates by spin-coating and converted into a transparent solid layer by photochemical cross-linking. Although such stratified morphology has been already reported for inorganic nanoplatelets (typically clay particles), we report for the fist time the formation of such stratified morphology in fully organic system. The shear-induced origin of this organization has been confirmed by the rheological properties of the uncured systems where a pronounced non-Newtonian behavior has been observed.

1. Introduction

The incorporation of a second dispersed phase in polymer matrices is a common way to modify their properties (thermal, mechanical, optical…). Depending on the weakness of the host polymer matrix, a great variety of inclusions, inorganic or organic, has been progressively employed over the last 20 years. The developments of nanoscience and processing techniques both enabled the size of these inclusions to approach the nanometer regime (i.e. materials with at least one dimension in the range 1–100 nm). In such nano-composites, the interfacial area is significantly augmented and compared to the host polymer, advanced properties are rapidly reached, generally at low loading, which in turn confers many advantages such as easy processability (even in the form of thin cover) or transparency [1].

Among the various manners to obtain nanosized inclusions, the use of block copolymers in thermoset resin has shown a great deal of interest [2,3]. In this case, the dispersed phase is also organic and consists in self-assembly of block copolymers. Such nanostructured domains are obtained by combining a network-forming liquid precursor (thermoset system like epoxy, unsaturated polyester, polyurethane, phenoplast) and block copolymers. Among the important literature on the subject, three main procedures are reported. In the first type, self-organized mesophases are formed prior to curing by combining nonreactive amphiphilic block copolymer and a network-forming liquid precursor that selectively mixes the blocks of the copolymer. Further curing fixes the initial morphology [4]. A second typical approach involves a reactive block polymer that forms nanoscale domains upon curing [5]. The third type corresponds to block copolymers where all the blocks are miscible. The polymerization induces a microphase separation of one block that provokes the nanostructuration [6].

Using the first of these three later approaches, we have previously reported the preparation of nanostructured polymers obtained from the self-association structures of

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low molecular weight polyethylene-*block*-poly(ethylene oxide) block copolymers (PE-*b*-PEO, 1400 g·mol^{-1}) dispersed in a liquid unsaturated polyester resin (UP) [7]. Due to the selective mixing of the poly(ethylene oxide) (PEO) block with UP, PE-*b*-PEO displayed amphiphilic properties at room temperature and formed self-organized mesophases prior to curing. Curing the system under appropriate conditions leads to the formation of crystalline platelets which are morphologies rarely encountered for polymer blends. The platelets, composed of a crystalline polyethylene (PE) core covered on both sides by PEO domains, present a high aspect ratio (6 nm thick, 500 nm–1 μm long). They are homogeneously dispersed and randomly oriented in the cured matrix. This shape is unusual for polymer blends systems but is common for inorganic nano-composites containing inclusions like clay [8], polyhedral oligomeric silsesquioxanes (POSS) [9], alumina [10] which morphologies and properties are well documented. The dispersion of platelets-like structures results in remarkable properties enhancement thanks to geometrical effects, but is extremely dependent on the orientation of the fillers. For example, in mimicking natural biological materials such as bones or nacre, unidirectional arrangements of platelets in a polymer matrix improves the mechanical properties [11,12]. On the model of their inorganic counterparts where stratified morphology has been already reported [13], the aim of this work is to complete such polymeric sheets orientation within the liquid blends (i.e. prior to curing) and to study its origin. For this purpose, we focused on the preparation of blends of PE-*b*-PEO and UP with low viscosity by a solvent assisted procedure in order to prepare, by spin coating, coatings where an anisotropic orientation of the nanoplatelets is expected. A study of the morphology of the cross-linked coatings, using AFM and TEM, is presented and correlated to rheological measurements of the blends.

2. Experimental

2.1. Materials

PE-*b*-PEO, polyethylene-*block*-poly(ethylene oxide), was purchased from Sigma–Aldrich and used without further purification (M_n = 1400 g·mol^{-1}, 50 wt.% ethylene oxide). Unsaturated polyester (UP) resin was provided by DSM Composite Resins (Palapreg P18-03) and contains 65.5 wt.% unsaturated polyester (UP) and 34.5 wt.% styrene. The C=C molar ratio (styrene)/(UP) in the prepared formulations was adjusted to a value of 1 wt.% by adding styrene. Lauroyl peroxide (97%) and 2,2-dimethoxy-2-phenylacetophenon (99%) were purchased from Sigma–Aldrich and respectively used, without further purification, as free radical polymerization initiator and photo-initiator.

2.2. Coatings preparation

Coatings of cross-linked UP/PE-*b*-PEO blends were prepared by spin-coating dispersions of PE-*b*-PEO in UP resin onto glass or mica substrates. These dispersions were prepared in tetrahydrofuran (THF). In a first step PE-*b*-PEO was dispersed in the organic solvent by sonication for 1 h at room temperature. UP resin was then added to the mixture and sonicated for another 1 h. Photochemical free radical initiator (2,2-dimethoxy-2-phenylacetophenon) was finally added and the mixture was sonicated for 15 min. In all the preparations, the mass of solvent and the total amount of polymer (i.e. UP resin and PE-*b*-PEO) were kept constant (25 and 5 g respectively) in order to insure a constant value of the solid content in the solution (17 wt.%). The content of free radical initiator was 1 wt.% with respect to the amount of UP resin only. In a typical preparation, to 1 g of PE-*b*-PEO dispersed in 25 g of THF is added 4 g of resin and 0.04 g of initiator (UP and PE-*b*-PEO contents are in this case in the ratio 80/20). The solution was then deposited onto glass substrates or freshly cleaved mica sheets (1 cm^2) by spin-coating at 2800 rpm for 30 s, leading to a transparent coating with a thickness ranging from 2 to 3 μm. Due to the low value of the vapor pressure of styrene at room temperature (P_{Styrene} = 5 mmHg; P_{THF} = 162 mm Hg), its evaporation is expected to very low during the spin coating process. The coating was then subsequently exposed to a photochemical curing, 15 min at 365 nm (VL-4.LC UV filtered lamp, 8 W, I = 265 μW/cm^2 at 15 cm). This photochemical curing was performed immediately after spin coating in order to avoid the styrene evaporation that would occur during the storage in the uncured state.

2.3. Coatings characterization

Optical microscopy was performed on a Olympus BX51 microscope. AFM (tapping mode) was carried out with a Nanoscope III (Digital Instruments). For TEM, coatings onto mica substrates were included into a liquid resin (Agar 100, Agar Scientific), cured for 48 h at 60 °C, microtomed to a thickness of about 80 nm on a Ultracut E Reichert-Jung, placed on TEM grids and stained in RuO4 vapors [14]. TEM was performed on a Philips CM20 with a LaB$_6$ filament, using an accelerating voltage of 200 kV.

2.4. Rheology

For the rheological tests, the UP/PE-*b*-PEO blends were prepared following the procedure described in our previous work [7]. Briefly, it consists in blending the UP and PE-*b*-PEO in the molten state (T > 120 °C) followed by a slow cooling, down to the room temperature, under vigorous mixing for favoring a homogeneous dispersion of the self-organized structures in the liquid resin. Uncured blends containing 1–10 wt.% of PE-*b*-PEO were prepared following this protocol. Steady-shear measurements were performed on Kinexus rehometer (Malvern) with a cone-and-plate geometry (40 mm, 1° angle).

3. Results and discussion

3.1. Solvent assisted preparation of PE-b-PEO dispersion in UP resin

Following the protocol described in our previous work [7], liquid blends composed of UP resin containing