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Shear induced orientation of phase segregated block copolymer/epoxy blends

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ABSTRACT

In this work a phase segregated blend system consisting of a block copolymer (BCP) and epoxy matrix with cylindrical morphology is considered. Transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS) investigations reveal that long-ranged ordered nanostructures can be obtained under certain preparation conditions. The pre-shearing conditions are the most important factors in order to obtain regular structures.

1. Introduction

Materials with long ranged ordered and/or highly oriented nanostructures are interesting for a broad variety of applications such as electronic, biomedical, optical or photovoltaic devices [1–8], for instance. Next to materials with highly anisotropic properties the controlled arrangement or deposition of nanoparticles is possible. The exploitation of self-ordering capabilities of block copolymers (BCP) is one of the most promising routes for the manufacturing of thin films but also bulk materials with organized structures in the tens of nanometers range [9,10]. Depending on the processing conditions, materials with different nanostructures such as spherical, cylindrical or lamellar morphology can be produced.

The self-organization is based on the immiscibility of the different blocks [11–14]. Due to the chemical bonds between the blocks the size of the separated phases is restricted. In the ordered state the shape of nanostructures mainly depends on the Flory–Huggins interaction parameters and the polymerization degrees of the block segments. In the disordered state which is present at temperatures above the order to disorder temperature T_{ODT} or in solutions below the order to disorder concentration c_{ODT}, for instance, no phase separation occurs.

The concept of nanostructuring can also be exploited by blending BCP with other polymers. Two main strategies can be followed to achieve nanostructured thermoset/BCP systems: amphiphilic block copolymers with one block miscible with the thermosetting matrix, or reactive block copolymers containing functional groups in one

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block that react with the thermosetting matrix [15–18]. Recently, it has been shown by Carrasco et al. [19] that a blend system consisting of an amphiphilic PS-b-P2VP block copolymer and epoxy resin exhibits microphase separation. With the variation of BCP content lamellar and cylindrical morphologies have been obtained. Differential scanning calorimetry (DSC) indicates the partial miscibility of the P2VP block in the epoxy resin.

Usually BCP tend to form isotropic morphologies. To obtain long ranged ordered systems different strategies have been developed such as large amplitude oscillatory shearing (LAOS) [20–23], droplet pinning [24], melt-extrusion [25], graphoepitaxy [26], infiltration in anodic aluminum oxide [27], growing on nanopatterned substrates [28] or electric field alignment [29]. Depending on the materials properties and processing parameters the alignment direction might be controlled. In case of LAOS it has been found that orientation of a lamellar morphology can be modified by adjusting the temperature T, strain γ, frequency f or molecular weight of the polymer [20,30–32].

This article focuses on the rheological orientation of a blend system with cylindrical morphology consisting of PS-b-P2VP and epoxy resin. Thereby, the effect of different shear conditions will be discussed by means of transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS) investigations.

2. Materials and methods

2.1. Sample preparation

Unless otherwise stated, all chemicals were used without further purification.

Polystyrene-*block*-Poly(vinyl pyridine) (PS-b-P2VP) (Mn = 32500-b-7800 kg/mol, Mw/Mn = 1.05) was purchased from Polymer Source Inc. Anhydrous THF was purchased from Sigma–Aldrich GmbH. Epoxy curing system consisting of an epoxy prepolymer, diglycidyl ether of bisphenol A, DGEBA (ref. ARALDITE LY 556), an anhydride hardener, methyl tetrahydrophtalic anhydride, MTHPA (ref. ARADUR 917) and an imidazole accelerator, 1-methyl imidazole (ref. Accelerator DY 070) were purchased from Huntsmann and kindly provided by CIDETEC.

2.2. Rheology

Alignment and curing have been carried out by means of an ARES rheometer (TA instruments) equipped with parallel plate tools of 25 mm diameter. The sample thickness has been adjusted to approximately 1 mm.

In order to align the blend morphology two different strategies have been preceded: oscillatory and continuous pre-shearing. The pre-shearing experiments have been carried out for 4 h at 25 °C, and after the pre-shearing step the samples have been cured. The curing process has been performed in a two-step process, in a first step the temperature of the system was increased from 5 °C to 80 °C at 5 °C/min and the maintained during 2 h at 80 °C. Then, in the second step, the temperature was increased from 80 °C to 100 °C at 5 °C/min at maintained at this temperature for 2 h. As during curing process, first gelation of the epoxy network and then vitrification took place, the applied strain during the curing process was continuously autoadjusted not reaching a maximum torque of 400 g/cm and preserving the structure. After the curing process, the samples have been quenched to room temperature and the samples have been carefully extracted from the shearing tools to obtain the full tablets for further investigations. The corresponding viewing directions are depicted in Fig. 1.

2.3. Transmission electron microscopy

Transmission electron microscopy (TEM) analysis was performed to investigate the morphology of the blend system. For this purpose a ZEISS Libra200 FE TEM operated at 200 kV has been employed. The thin sections with a thickness of approximately 70 nm have been prepared by means of a microtome Leica UC6. Diamond knives (Diatome) have been used for trimming (model cryotrim 45°) and wet sectioning (model cryo 35° with a boat). The slices were deposited on copper grids (400 mesh Cu, Agar) and stained with iodine (I_2, Aldrich) for 4 h in a closed vessel saturated with vapors of the staining agent.

2.4. Small angle X-ray scattering

Small angle X-ray scattering (SAXS) has been employed to gain information about the anisotropy and order in larger samples volumes. For this purpose an X-ray source (with a rotating anode to generate a beam with a diameter of 0.3 mm at the sample) Rigaku MicroMax 007 with a wavelength of 1.54 Å (Cu Kα) has been used. The scattering patterns have been recorded by means of a 2-dimensional area detector (MARCCD). The sample-to-detector distance has been adjusted to approximately 160 cm and calibrated with silver behenate. The present SAXS patterns reported have been acquired from the normal and tangential directions at distance between 11 and 12 mm from the shear axis (outer radius, see Fig. 1).

3. Results and discussion

In order to achieve highly oriented cylinders within PS-b-P2VP/epoxy blend systems at first, information about

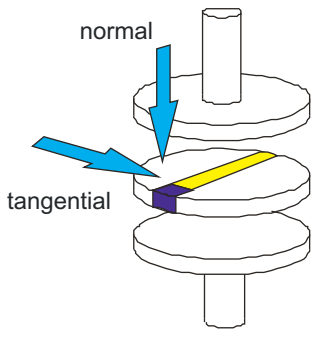

Fig. 1. Viewing directions for TEM and SAXS investigations.