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Research paper

Anisotropic clay–polystyrene nanocomposites: Synthesis, characterization and mechanical properties

Henrik Mauroy [a,*], Tomás S. Plivelic [b], Jussi-Petteri Suuronen [c], Fredrik S. Hage [d], Jon Otto Fossum [e], Kenneth D. Knudsen [a,e,**]

[a] Physics Department, Institute for Energy Technology, P.O. Box 40, N-2027 Kjeller, Norway
[b] MAX IV Laboratory, Lund University, P.O. Box 118, SE-221 00 Lund, Sweden
[c] Department of Physics, Division of Materials Physics, University of Helsinki, P.O.B. 64, FI-00014, Finland
[d] SuperSTEM Laboratory, SciTech Daresbury, Keckwick Lane, Daresbury WA4 4AD, United Kingdom
[e] Department of Physics, Norwegian University of Science and Technology, Hoegskoleringen 5, N-7491 Trondheim, Norway

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ABSTRACT

Recent studies on clay–polymer nanocomposites have shown prominent improvements in thermal and mechanical properties with the addition of quite small amounts of nanometer sized clay particles. The present work presents characterization of anisotropic clay–polystyrene nanocomposites synthesized via a guided self-assembly technique, employing electric fields to align the clay particles into chain-like structures inside the polymer matrix. Four different kinds of surface modified clay were used as particle additives, namely Hectorite, Laponite, Na-Montmorillonite and Li-Fluorohectorite. The microstructure of the nanocomposites was examined with wide angle X-ray scattering (WAXS), X-ray computed microtomography (XMT) and transmission electron microscopy (TEM). Thermogravimetric analysis (TGA) was further employed to examine the high-temperature resilience of the nanocomposites before determination of the mechanical properties during compression. The results showed that the nanocomposites were of the intercalated type with the clay dispersed as ~15–70 nm thick crystallites which in turn aggregated into micrometer sized particles. Alignment of the clay particles into chains inside the polymer matrix led to differences in mechanical properties compared to nanocomposites having a random orientation of the clay particles. In particular the aligned polystyrene–fluorohectorite nanocomposite displayed large improvements compared to its non-aligned counterpart. It was also observed that differences in yield strength depended on the compression direction.

1. Introduction

Anisotropy in the mechanical properties can be a desired quality of modern polymeric composite materials where high strength along a particular direction is wanted. This can be in e.g. light bicycle frames (Liu and Wu, 2010), automotive car suspensions (Richard, 2003), cross bows (Virk et al., 2009), or even in large aircrafts (Kelly, 2008; Chawla, 2012). These materials are made of sheets of woven or braided high-strength fibers (e.g. glass, carbon or polyaramides) embedded in a polymer matrix (Gibson, 2010; Jose and Joseph, 2012). The fabrication of today's state-of-the-art polymer composites are still using macroscopic fibers with thicknesses in the millimeter range and lengths measured in centimeters or meters. To enhance these materials further, better control of the structure of the reinforcing fibers on the micro and nano scale is needed.

In the present work a novel concept circumventing the conventional top-down approach has been investigated. Here a guided self-assembly technique, which orients the reinforcing filler particles, has been developed. In this case an external electric field orients organoclay nanoparticles into an anisotropic pattern inside a polymer matrix. Clay–polymer nanocomposites (CPN), without preferred orientation of the filler particles, have earlier shown improvements in the physical properties at surprisingly low nanoparticle weight fractions of 1–5 wt.% (Kojima et al., 1993; Haraguchi and Takehisa, 2002). This is due to the large aspect ratio of exfoliated clay layers and their large surface area (Utracki, 2004; Moczo and Pukanszky, 2008). These interesting properties, combined with anisotropy, are likely to result in new types of materials with highly specialized properties. The present work investigated the synthesis and characterization of CPNs where the organoclay particles were permanently aligned into chains inside a polystyrene matrix.

The guided self-assembly was performed by applying an alternating electric field to the monomer-clay dispersion in order to manipulate the

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* Corresponding author. Tel.: +47 45 26 45 50; fax: +47 63 81 63 56.

** Correspondence to: K.D. Knudsen, Department of Physics, Norwegian University of Science and Technology, Hoegskoleringen 5, N-7491 Trondheim, Norway. Tel.: +47 45 26 45 50; fax: +47 63 81 63 56.

E-mail addresses: henrik.mauroy@ife.no (H. Mauroy), kenneth.knudsen@ife.no (K.D. Knudsen).

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orientation of the clay particles, which consisted of aggregates of multilayered crystallites.

Inside an electric field (Fig. 1) clay particles are electrically polarized along the silica sheets (Fossum et al., 2006; Rozynek et al., 2012), i.e. the stacking direction (plate normal) **n** is perpendicular to the direction of the electric field (Castberg et al., 2012). The polarization results in chain formation by the clay particles due to attractive forces between positively and negatively charged parts. An effective polarization of the clay only occurs when the dielectric constant of the matrix is lower than that of the clay (Wang et al., 2009), as is the case for styrene with respect to the clays employed in this work.

In the presented work two batches of samples, for each of the four types of organoclay, were made in parallel: one with alignment and one without. All samples were examined by wide angle X-ray scattering (WAXS), X-ray computed microtomography (XMT), transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). Furthermore, the mechanical properties of all nanocomposites were measured and the impact of their morphology is discussed.

2. Experimental

2.1. Materials

Styrene monomer (≥99%), benzoyl peroxide (Luperox® A75, 25% water), and cetyltrimethylammonium bromide (CTAB) (≥98%) were purchased from Sigma-Aldrich and used without further purification. The synthetic clay, Laponite XLG (Lap) was kindly donated by Andreas Jennow AB, and the synthetic clay Li-Fluorohectorite (FHt), was purchased from Corning Inc. Two natural clays, Na-Montmorillonite SWy-2 (Mt) and Hectorite SHCa-1 (Ht), were purchased from The Clay Minerals Society Repository.

2.2. Preparation/synthesis

The clays were surface modified using CTAB through a simple cation-exchange process: where the ammonium cation of CTAB replaced the inorganic interlayer cations. A detailed description of this procedure can be found in Mauroy et al. (2013). In terms of nomenclature, the four clays were labeled org-X, where X is the type of clay (i.e. org-Ht corresponds to the surface treated Hectorite clay, etc.). The cation exchange capacity (CEC) for each clay type (Kaviratna et al., 1996; The Clay Minerals Society) is listed in Table 1. The basal spacing (d_{001}), measured by WAXS prior to and after surface modification is also listed in Table 1, in addition to the weight fraction of surfactant, measured by TGA.

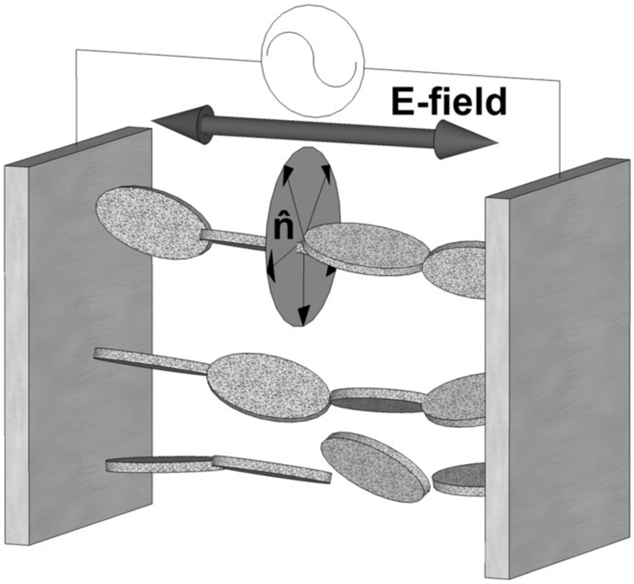

Fig. 1. Schematic illustration of how the clay particles or crystallites align inside an electric field.

Clay–polystyrene nanocomposites with two different clay concentrations, 1 and 3 wt.%, were prepared with in situ free radical polymerization of polystyrene (PS) inside sealed square-shaped glass capillaries with an inner cross section of 1.0 mm × 1.0 mm. A more detailed description of this process can be found in Mauroy et al. (2013). The capillaries were immersed (standing upright) in silicone oil, and kept at 95 °C to polymerize for 5 days. A parallel batch of CPNs having aligned clay particles was also prepared. Prior to polymerization, these samples were placed between two parallel flat electrodes, immersed in the silicone oil, and oriented with the capillary walls parallel to the electrodes. An alternating voltage of 3000 V was applied over the electrodes, producing an electric field (E-field) of 625 V/mm, which was the maximum field achievable with the present setup. The polymerized nanocomposites, now shaped as ~4 cm long square rods, were carefully pulled out of the capillaries and labeled PSXw, where X and w indicate the type of clay and the weight percent of clay, respectively. An additional letter "E" was added if the sample was prepared inside an E-field.

2.3. Characterization

2.3.1. Wide angle X-ray scattering (WAXS)

WAXS experiments were performed at beamline I911-4 of the MAX-lab synchrotron facility in Lund, Sweden (Labrador et al., 2013). All data were collected at a wavelength of 0.91 Å with a sample-to-detector distance of 481 mm or 1900 mm, corresponding to a q-range of about 1–10 nm^{-1} or 0.1–3 nm^{-1}, respectively. Here q is the magnitude of the scattering vector and is defined as $q = (4\pi / \lambda) sin\theta$, where λ is the wavelength and 2θ is the scattering angle. The beam size at the sample position was approximately 300 × 300 microns, and the detector used was a two-dimensional CCD (165 mm diameter from Mar Research, Inc). The samples were analyzed with the X-ray beam perpendicular to the direction of E-field alignment (see Fig. 2).

Data treatment was done using the software FIT2D (Hammersley et al., 1996) and customized Matlab® routines. The data were normalized with respect to the transmitted intensity using a photodiode located inside the beam-stop. Broadening of the clay 001 reflection was used to give a rough estimate of the thickness of the layer stacking (clay crystallite), L, by employing the Scherrer formula (Patterson, 1939), $L = (K \times \lambda) / (FWHM \times cos\theta)$, where K (~0.9) is a numerical constant, λ is the X-ray wavelength, $FWHM$ is the full width at half maximum of the 001 Bragg reflection, and 2θ is the Bragg angle. The average number of layers in each particle was calculated by dividing the thickness L by the d_{001}-value of the dispersed org-clay particles.

2.3.2. X-ray microtomography (XMT)

X-ray computed microtomography was carried out with a voxel size of around 0.9 μm using a custom-built Nanotom 180 NF XMT setup

Table 1
Selected properties for the clays and organoclays.

Clay type[a]	CEC (meq/100 g)[b]	Pure clay d_{001}-value[c] (nm)	Org-clay d_{001}-value[c] (nm)	Weight fraction of surfactant in the organoclay[c] (%)
Ht	44	1.1	1.9	35
Lap	47	1.3	1.5	36
Mt	76	1.2	2.0	36
FHt	120	1.2	3.1	40

[a] Ht = Hectorite, Lap = Laponite, Mt = Montmorillonite and FHt = Fluorohectorite.
[b] Ht, Mt see (The Clay Minerals Society); Lap, FHt see (Kaviratna et al., 1996).
[c] (Mauroy et al., 2013).