Materials Chemistry and Physics 182 (2016) 110–118

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Multifunctional highly aligned graphite nanoplatelet-polyether imide composite in film form

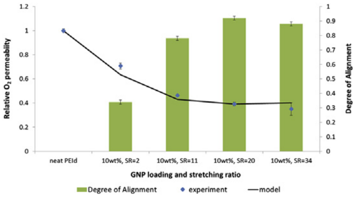
Huang Wu*, Lawrence T. Drzal

Composite Materials and Structures Center, Michigan State University, East Lansing, MI 48624, USA

HIGHLIGHTS

- PEId-GNP composite films are fabricated through melt film extrusion.
- Filler alignment of the composite films and its causes are studied.
- Property-filler alignment relation is revealed.
- Annealing is proved to change the filler alignment and film properties.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 25 November 2015
Received in revised form
20 June 2016
Accepted 9 July 2016
Available online 8 August 2016

Keywords:
Annealing
Electron microscopy
Mechanical properties
Composite materials

ABSTRACT

The objective of this research is to investigate the effect of adding graphite nanoplatelet (GNP) particles into polyether imide film. Extruded films were produced with various amounts of GNP and different degrees of post-extrusion stretching. A uniform high degree of alignment of the GNP particles along both machine direction (stretching) and transverse direction was obtained under high stretching ratios. Tensile properties including tensile modulus, strength and elongation were investigated. O_2 permeability was reduced with the increase of GNP loading and stretching ratio of the film. The Bharadwaj model was applied to predict the permeability. Information of degree of alignment was obtained through analyzing SEM images in image-processing software and used with the Bharadwaj model, resulting in good agreement with experimental data. Annealing of the stretched films under 340 °C showed a significant improvement of both electrical and thermal conductivity in the film direction.

Published by Elsevier B.V.

1. Introduction

Polymer nanocomposite films have drawn more and more attention because of their unique multifunctional properties and the possibility to be incorporated into other structural or functional materials. Polyether imide (PEId, Ultem resin, Sabic IP) is a thermoplastic material which has high chemical and thermal resistance, good flame resistance and low smoke generation [1]. Major applications of PEId are as a structural material for confined space, including high-floor office, airplanes and submarines. Just like the other thermoplastic based materials, PEId can offer lighter and more durable solutions as alternatives to metal and alloys, but falls short in properties like thermal and electrical conductivity and barrier properties to small molecules. Meanwhile, a group of nanofillers such as carbon nanotubes (CNT) [2], nanoclay [3] and nano graphite [4] are considered to be efficient in providing such multifunctionality to their composites. Among those fillers, the graphite nanoplatelet (GNP) combines electrical and thermal conductivity similar to CNT and two-dimensional morphology similar to nanosilicates, resulting in the capability of meeting most of the requirements if incorporated into composites.

In a composite reinforced by anisotropic fillers, the alignment of the filler is usually the key to performance of the composite. Lan

---

* Corresponding author. Present address: 433 Building, The Dow Chemical Company, Midland, MI 48667, USA.

E-mail addresses: huang.wu.84@gmail.com (H. Wu), drzal@egr.msu.edu (L.T. Drzal).

http://dx.doi.org/10.1016/j.matchemphys.2016.07.011
0254-0584/Published by Elsevier B.V.

et al. [5] designed a clay-epoxy thermoset composite with sub-ambient Tg to allow alignment of clay particles under strain. Analogous to this system would be stretching the thermoplastic nanocomposite material above Tg to obtain high alignment such as by a blown film process. Zenkiewicz et al. [6] reported the dependence of blowing ratio on the barrier properties of clay/PLA film. It is found that higher blowing ratio would lead to lower permeability by oxygen, water vapor and carbon dioxide. TEM images shown by the author verified that the particles tend to be more aligned under higher blowing ratio. However, not all the properties can benefit from alignment. Kim et al. [7] proposed a schematic that describes electrical conductivity changes due to the transition of graphite particles from the aligned state to the un-aligned state. Similar results are also discussed in Ref. [8]. Adequate post-treatment would be necessary to alter the alignment of fillers in order to achieve optimized and balanced performance.

Although film-form GNP has been widely studied as a promising material [9–13], most of the processing methods are still limited to lab scale. The goal of this research is to fabricate unidirectional-stretched GNP/PEId film through extrusion and film casting, which is an industrial scalable process, along with tuning its properties with annealing to optimize the multifunctionality of the resulting composite. Stretching ratios from low to high were applied to obtain composite film with different degrees of alignment of the GNP particles. Tensile properties, electrical and thermal conductivity and barrier to oxygen transport have been measured. The effect of annealing the film under above glass transition temperature of the polymer was also explored. Degree of alignment of the GNP particles was characterized to provide insights of the mechanism of electrical conductivity improvement of the annealed films.

2. Experimentation

2.1. Materials

Polyetherimide (PEI, Ultem 1010) was provided by Sabic Americas, Inc. (Houston, TX). GNP-5 was provided by XG Sciences Inc. (East Lansing, MI). The GNP particles have an average diameter of 3.9 μm with a specific surface area of 40 m^2/g and an average thickness of 25 nm.

2.2. Material processing

2.2.1. Melt-extrusion and film casting

Melt-extrusion was carried on Leistritz twin-screw extruder (MIC27/6L-48D). The screws were in the co-rotation mode. The shearing provided by co-rotating screws can help separate the filler particles and result in a better dispersion than counter-rotation. Barrel temperatures were set to 310 °C with a melt temperature at 340 °C. The die pressure was at around 5.5 MPa with screw speed set at 150 rpm. GNP was fed at a side feeder at 1/3 screw length away from the main feeder where the polymer was fed. The melt was extruded through a film die and then stretched and collected by a three-roll film collector, whose rolls were heated to 160 °C by oil to get uniform, wrinkle-free film. Trial runs were conducted to optimize the roll temperature, from which it was found that higher temperatures resulted in higher occurrence of un-uniform thickness across the film, while lower roll temperatures caused wrinkles and un-uniform skin for the composite films. 160 °C was chosen as the films produced under this temperature appeared to maintain good uniformity without wrinkles consistently.

In the experiment setup, the stretching ratio was controlled by fixing the material feeding speed and changing the speed of the three roll stack. The stretching ratio (SR) then is calculated as:

$$\mathrm{SR} = \frac{\text{Die Opening Thickness (DOT)} \times \text{Die Opensing Width (DOW)}}{\text{Film Thickness (FT)} \times \text{Film Width (FW)}}$$

The die opening width was 152 mm and the films were collected at 1, 4, 8 and 16 fpm three-roll speed. Film dimension and SR value are listed in Table 1.

2.2.2. Annealing of extrusion cast film

The extrusion cast film was also annealed under 340 °C in a hot press. To keep the dimensions to the same as those of the un-annealed sample, a piece of aluminum foil with 150 μm thickness was used as the spacer. A square hole with the same dimension as the GNP/PEId film was cut on the aluminum foil. The foil, along with the sample in the hole, was sandwiched by two sheets of PTFE film and two steel plates. The whole set-up was then placed in the pre-heated 340 °C hot press (CARVER Laboratory Press, Model 2731, Fred S. Carver INC.). A pressure of 23 MPa was applied immediately and held for 1 h. After that, water cooling was applied to the hot press to cool the sample.

The change in thickness dimension after 1 h annealing is shown in Table 2. Note that the samples used for annealing were the central part of the extrusion cast film with all the edges trimmed off, so the thickness is slightly different from Table 1.

2.2.3. Melt-extrusion and compression molding

GNP-5 and PEId were also melt-blended and extruded as strands with the same twin-screw extruder setup as used for film and then cut into pellets. An aluminum foil with a round hole cut in the center was used as mold. The composite pellets were piled at the center of the hole and then compressed into ~150 μm thick films at 340 °C.

2.3. Characterization

2.3.1. Electrical conductivity measurement

The resistance of GNP/PEI composite films was measured in two directions: the through-plane direction which is across the thickness of the sample and in-plane direction which is the stretching direction for extrusion cast films and the radius direction for compression molded films. The resistance value was then converted into resistivity by taking into account the sample dimensions.

2.3.2. Thermal diffusivity and thermal conductivity

Thermal diffusivity of the GNP/PEId composite films was measured by laser flash method (LFA 447 NanoFlash, Netzsch) in through-plane direction. The heat capacity Cp was determined by Differential Scanning Calorimetry (DSC, TA Instruments) and the density of the samples was calculated by the rule of mixtures. Thermal conductivity was calculated by multiplying thermal diffusivity by Cp and density.

2.3.3. Scanning electron microscope (SEM) observation

SEM was used to observe the morphology of the samples at high vacuum mode. The composite film samples were cut and mounted in a cast epoxy holder (manufacture: LECO, St. Joseph, MI). Then the surface was polished with #4000 grit finish, 1 μm alumina powder/water slurry on a LECO LP20 polisher and then 0.05 μm alumina powder/water slurry on a Buehler Vibromet polisher (Lake Bluff, IL) for 2 h. The polished surface was etched by plasma in a chamber filled with O_2 at room temperature and 0.283 torr. A 10 nm gold layer was also sputter coated to the surface for observation. For extrusion cast films, cross-sections of both stretching direction (machine direction, MD, corresponding cross-section is yz-plane)