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An experimental study of dynamic behaviour of graphite–polycarbonatediol polyurethane composites for protective coatings

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ABSTRACT

Segmented polycarbonatediol polyurethane (PUPH) has been synthesized and modified with different amounts of graphite conductive filler (from 0 to 50 wt%). Thermal and dynamical thermal analysis of the composites clearly indicates changes in the polyurethane relaxations upon addition of graphite. Broadband dielectric spectroscopy has been used to study the dielectric properties of the (PUPH) and one composite in the frequency range from 10^{-2} to 10^{7} Hz and in the temperature window of −140 to 170 °C. Relaxation processes associated with different molecular motions and conductivity phenomena (Maxwell–Wagner–Sillars and electrode polarization) are discussed and related to the graphite content.

1. Introduction

In recent years, electrically conductive polymers have attracted a lot of attention because of their wide possible applications. Since polymers are, in general, insulating materials, many efforts have been directed to improve their electrical conductivity [1–3]. Electrically insulating polymers such as polyurethane can be specifically modified in order to increase its conductivity by dispersing conductive fillers [4,5]. Polycarbonatediol polyurethanes are widely used as protective coatings for materials that are subjected to environmental degradation. The excellent properties of polyurethanes such as high impact resistance, high elasticity, resistance to corrosion, sunlight, oxidation or weather conditions, make these polymers very useful as protective coatings [6,7]. Another important property for coatings is the electrical conductivity. Conductive metals lack of properties such as elasticity and corrosion resistance. In contrast, insulating polymeric materials behave as conductive ones by the addition of conductive particles, show good mechanical properties and are easy to mold. Carbon materials such as carbon nanotubes (CNTs) have been used to increase the electrical properties of polymer matrices [8]. However, CTNs are very expensive for large-scale applications. Other conductive fillers such as graphite and its variants are being used to provide electrical conductive properties to polymeric matrices [9,10]. Graphite is very cheap, abundant, has an elevated electrical conductivity (10^{4} S cm^{-1}) and increases the mechanical properties of polymers having a reinforcing effect on the polymeric material [10]. The drawback is the difficult dispersion of the graphite in the polymer matrix. This fact can be overcome by modifying its surface. For example, graphite can be expanded by chemical oxidation and thermal shock in order to increase the size of channels, improving thus the interaction with the polymer matrix [11]. In this work, polyurethane has been synthesized and modified with different amounts of expanded graphite (EG) as a conductive filler. The composites characterization has been carried out by means of thermogravimetric analysis, differential scanning calorimetry, wide angle X-ray diffraction, dynamic mechanical analysis and broadband dielectric spectroscopy. The main goal of the present work is the study of these materials as potential candidates for coating applications.

2. Experimental

2.1. Materials

Polyhexamethylene–pentamethylene carbonatediol, PH100, was obtained from UBE Chem Eur. (Castellón, Spain). 4-4′-Diphenylmethane diisocyanate, butanediol, natural graphite powder of size <20 μm, N,N-dimethylacetamide, nitric acid and sulfuric acid were purchased from Sigma–Aldrich Co. (Madrid, Spain).

2.2. Preparation of expanded graphite

Expanded graphite was obtained by the method of chemical oxidation [11]. The natural graphite was dried at 75 °C in a vacuum oven for 10 h. Then, it was blended for 12 h with a 3:1 sulfuric and nitric mixture in order to form the graphite inserted compound. The nitric acid was used as an oxidizer and the sulfuric acid as an intercalating agent. The mixture was stirred from time to time to

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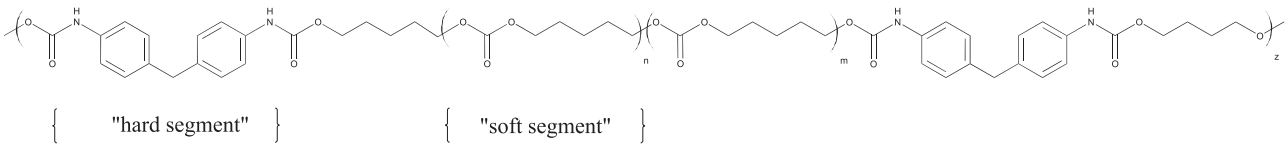

Fig. 1. Scheme of the chemical structure of the segmented polyurethane in soft and hard segments.

get an uniform intercalation of the sulfuric into the graphite flakes. After that, the mixture was washed to obtain a neutral pH, then was filtered and the resulting material was dried at 60 °C in vacuum for 5 h. Afterwards it was subjected to a thermal shock at 800 °C for 20 s in order to form the expanded graphite.

2.3. Preparation of segmented polycarbonatediol polyurethane (PUPH)

Polyurethane solutions were obtained by a standard polymerization method based on the two-step process in dimethylacetamide [12]. In the first step one equivalent of polycarbonatediol PH100 was inserted in the reactor, previously dried for 24 h at 100 °C, with three equivalents of 4,4′-diphenylmethane diisocyanate. The reaction was carried out at 70 °C for 2 h under argon atmosphere. The second step corresponds to the addition of the chain extender, butanediol. Two equivalents of butanediol were added to obtain a viscous amber polyurethane solution with approximately 25 wt% in solid content. The solution was stored for 24 h in order to remove the bubbles produced in the synthesis process. Fig. 1 shows a scheme of the chemical structure of PUPH.

2.4. Preparation of composites

Different weight fractions of expanded graphite, from 0 to 50 wt%, were introduced in the PUPH solution. In order to disaggregate the flakes and to obtain a stable dispersion, the blend was sonicated in an ultrasonic bath for 1 h and was stirred vigorously for 5 h, respectively. The suspensions were cast on glass slides which were previously washed in an ultrasonic bath with distilled water and later with acetone in order to eliminate the water. The polyurethane/expanded graphite composites (PUPH/EG) coated glasses were kept at 70 °C during 12 h. Films were prepared with dimensions of (4 cm × 2.7 cm) and with a thickness that ranged between 200 and 250 μm. An image of the PUPH and PUPH/EG solutions is shown in Fig. 2.

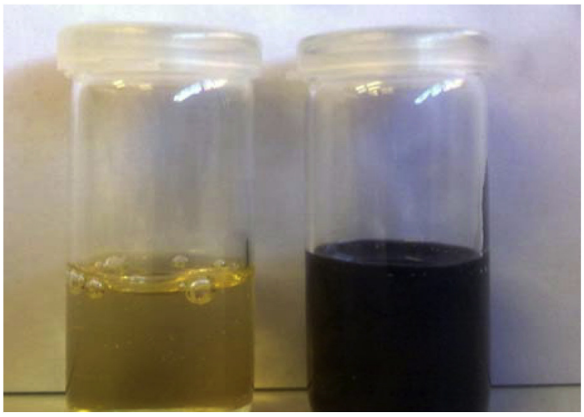

Fig. 2. PUPH solution (left) and PUPH/EG solutions (right).

3. Characterization

3.1. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on a Setaram Setsys 16/18 TGA-ATD analyzer. The samples were analyzed in platinum pans at a heating–cooling rate of 10 °C/min from 30 to 1000 °C under oxygen atmosphere. Samples masses ranged from 7 to 10 mg.

3.2. Differential scanning calorimetry measurements

Differential scanning calorimetry (DSC) study was performed on a Q-20 differential scanning calorimeter from TA Instruments calibrated with indium. The measurements were carried out in the range of −90 to 220 °C at a heating rate of 20 °C/min under nitrogen atmosphere. A second run (to delete the thermal history) was used for the thermal characterization of the films.

3.3. X-ray characterization

The wide angle X-ray diffraction (WAXRD) was acquired on a Bruker AXS D5005 diffractometer. The samples were scanned at 4 °C/min using Cu K_α radiation (λ = 0.15418 nm) at a filament voltage of 40 kV and a current of 20 mA. The diffraction scans were collected within the range of 2θ = 5–80° with a 2θ step of 0.01°.

3.4. Dynamic mechanical measurements

Dynamic mechanical measurements (DMA) were performed on a 2980 dynamic mechanical analyzer (TA instruments). The temperature range went from −100 to 180 °C by using rectangular samples of dimension (16.540 mm × 6.000 mm × 0.250 mm). Measurements were carried out at 3 °C/min heating rate and at a frequency of 1 Hz.

3.5. Dielectric measurements

The experimental dielectric behavior (DRS) of PUPH and PUPH/15EG films was studied with a Novocontrol Broadband Dielectric Spectrometer (Hundsagen, Germany) consisting of an Alpha analyzer to carry out measurements from 5×10^{-2} to 3×10^{6} Hz. The measurements were carried out in inert N_2 atmosphere between −150 and 150 °C. The temperature was controlled by a nitrogen jet (QUATRO from Novocontrol) with a temperature error of 0.1 °C during each single sweep in frequency. Molded disc shaped samples of about 200 μm thickness and 20 mm diameter were used. The experimental uncertainty was better than 5% in all cases.

4. Results and discussion

Thermogravimetric analysis was carried out in order to analyze the effect of expanded graphite insertion on the stability of the polyurethane films. This analysis allows the evaluation of changes in weight as a function of temperature in a controlled atmosphere. Fig. 3 shows the TGA thermograms obtained for each film and Table 1 collects the characteristic temperatures of the degradation processes in the materials under study. T_{on} is the temperature