European Polymer Journal 48 (2012) 1726–1733

Contents lists available at SciVerse ScienceDirect

European Polymer Journal

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

Macromolecular Nanotechnology

Preparation and characterization of rigid polyurethane–polyglycerol nanocomposite foams

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ARTICLE INFO

Article history:
Received 29 February 2012
Received in revised form 26 June 2012
Accepted 2 July 2012
Available online 9 July 2012

Keywords:
Polyurethane foams
Polyglycerol
Nanocomposite
Nanofiller
Montmorillonite
MMT

ABSTRACT

This work reports on the preparation of polyurethane–polyisocyanurate (PUR–PIR) foams containing different polyglycerols and layered silicate nanoclays. The rigid polyurethane foams were obtained in a laboratory scale, in a single step method, from a two-component system with a NCO to OH groups ratio equal to two. The reaction mixture consisted of the proper amounts of a commercial oligoetherpolyol, polyglycerol, catalysts, water, nanofiller, and polymeric diphenylmethane diisocyanate. The obtained foams containing 6% of one of three types of montmorillonite (MMT) (Cloisite 30B, Laponite RD, Bentonite) were characterized in terms of their structure, density, brittleness, compressive strength and thermal stability. The nanocomposite foams showed a higher number of cells with a smaller cell size in the presence of MMT, while the foams modified with nanofiller Cloisite 30B presented the best compressive strength and the best fire resistance.

1. Introduction

Considerable attention has been paid in the literature to develop an understanding of the structure–property relationships of polyurethanes (PUs), which has acquired significance because of the broad range of applications of these materials. Due to the wide range of possible compositions, PUs have found an extensive use in numerous commercial applications such as coatings, foams, adhesives, sealants, synthetic leathers, membranes, elastomers, etc. as well as in many biomedical applications. PUs constitute one of the most useful commercial classes of polymers which are widely used in both industry and everyday life [1]. The repeating unit in PUs is the urethane linkage produced from the reaction of an isocyanate (–NCO) with an alcohol (–OH). However, PUs also present some disadvantages, *i.a.* low thermal stability and in some cases not sufficient mechanical strength. To overcome these disadvantages, a huge effort has been devoted in recent years to the development of nanostructured polyurethane (PU)/montmorillonite (MMT) composites [2–6].

A good dispersion of the layered silicate has been found to improve the properties of the PU elastomer nanocomposites, such as the mechanical properties, the thermal stability and the gas permeability [3–7]. The dispersion of clays in the PU matrix has been improved by modification of MMT with active surfactants containing more than two hydroxyl groups [4].

Polyurethane foams (PUFs) account for the largest market among polymeric foams, estimated at nearly two billion kilograms in the US alone [8]. PU foams have a remarkably broad range of applications including thermal insulation, cushioning, buoyancy, energy absorption (packaging), etc. Their low density also allows the design of light, rigid components such as aircraft-interior panels,

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http://dx.doi.org/10.1016/j.eurpolymj.2012.07.001

structural shapes (transom cores, bulkhead core, stringers, motor mounts, etc.) in fiber-reinforced plastic (FRP) boat building, impact-limiters and crash-pads, composite foam cores, mold-patterns and plugs, sports-equipment core material, and composite tooling. The mechanical properties are essential considerations in such structural and semi-structural applications. Unlike thermoplastic foams, PU foams are formed by a reactive process in which polymerization and foam blowing occur simultaneously. The polymer structure must build up rapidly to support the fragile foam, but not so fast as to stop the bubble growth.

PUFs/clay nanocomposites are a comparatively new class of composite materials where at least one phase has dimensions in the nanosize range [9,10]. In these composites, clay has been reported to act as a cell opener [11,12] with ultrasonic treatment often giving homogeneous cell sizes and improved dimensional stability [3,13].

Polymer-MMT nanocomposites are the most common and the most investigated class of nanocomposites [14–19]. Because of the dispersion at the nanometer level, polymer–clay nanocomposites exhibit superior properties in comparison with the pure polymers or conventional composites; these properties include lightweight [20], high modulus, enhanced physical–mechanical strength [21,22], improved gas barrier [23], increased solvent resistance [24], improved thermal stability and flame retardancy [25,26]. Another impressive feature of nanocomposites and nano-filled composites is the concurrent improvement of multiple properties, in addition to the introduction of new functionalities [27]. The mechanical properties of nanocomposites are superior to the fiber-reinforced polymers because the enhancement from the inorganic layers occurs in the three dimensions rather than only in the dimension of the fiber [17,28]. Improvements in the thermal stability of polymer–clay nanocomposites are due to the nano-sized layers restricting the polymer molecular chain motion [29,30].

The present work reports the synthesis and characterization of rigid polyurethane foams based on nanoparticle-modified polyglycerol with a water and *n*-pentane mixture as the blowing agent. It aims to evaluate the effect of this renewable polyol and the nanofillers on the properties of the resulting rigid polyurethane foams.

2. Experimental

2.1. Materials

The polyols used in this study were Rokopol, a commercial polyetherol, and Pole, a polyglycerol: *Rokopol RF551-* (PCC Rokita, Poland), a general purpose sorbitol based polyether polyol recommended for the production of rigid polyurethane foams. The density of Rokopol RF551 at 25 °C equals 1.1 g/cm^3 with a typical hydroxyl number of 400–440 mg KOH/g of resin. The viscosity at 25 °C equals 5.842 Pa s. Its average molecular weight equals 600 g/mol. Polyglycerol (Pole) obtained by the polymerization of glycerol from bio-fuel production has a hydroxyl number of 190 mg KOH/g (Eco-innova, Poland). *NIAX Silicone SR-393* – a silicon based surfactant (Momentive, Czech Republic). Catalysts: K_{12} – 33% wt. solution of potassium acetate in ethylene glycol; *K Amin-* 2-[2-(Dimethylamino)ethoxy]ethanol (Sigma–Aldrich). Blowing agents: *n-Pentane Pure* – a clear colorless liquid, *n*-pentane content 99% (POCH, Poland); *Water–* distilled water. Isocyanate: -polymeric diphenylmethane – 4,4′-diisocyanate (pMDI) characterized by 31% of NCO groups, the density of pMDI (at 25 °C) is 1.22 g/cm^3. The commercial nanoclays used in this study were provided by southern clay products: *Cloisite® 30B* - a montmorillonite modified by methyl tallow bis-2-hydroxyethyl ammonium with a concentration of 90 meq/100 g clay; *Laponite® RD* - a synthetic layered silicate; *Bentonite* - an absorbent aluminium phyllosilicate, generally an impure clay consisting mostly of montmorillonite.

2.2. Preparation of foams

The rigid polyurethane foams were obtained in a laboratory scale in a single step method from a two-component (A and B) system with a NCO/OH ratio equal to two. The component A (polyol mixture) consisted of the proper amounts of oligoether - Rokopol RF 551 mixed with polyglycerol in various ratios (35 and 70 wt.% of polyglycerol), catalysts, water and nanofiller at 6%. It was prepared by vigorous stirring with a mechanical stirrer for 30 min followed by sonication using an ultrasonic homogenizer for 20 min. In the following step, the nanoparticulated polyol matrix was mixed at 3000 rpm for 10 s with component B (polyisocyanate, pMDI) at a predetermined mass ratio and the resulting reaction mixture was poured into an open metal mould with dimensions 100 × 100 × 50 mm^3. The following parameters were monitored: the start time which represents the time when the mixed components begin to increase in volume; the rise time which is the time when the foam reaches a maximum height, and the gelation time, which indicates the time when the surface of the foam stops being tacky to the touch. After demoulding, the PUF samples, were held at 60 °C for 24 h and cured at room temperature for another 24 h.

2.3. Characterization

After curing, the properties of the foams were determined according to the standard procedures.

The apparent density of the PUF samples was calculated in accordance to PN–EN ISO 845: 2000, as the ratio of the sample weight to the sample volume. The volume of the samples having a cubic shape was measured with a slide caliper having an accuracy of 0.1 mm. The samples were weighed using an electronic analytical balance with an accuracy of 0.1 mg.

FT–IR spectrophotometric analysis was performed in order to determine the structure of the foams. A Nicolet 8700 apparatus at a resolution of 4 cm^{-1} was used. The device was manufactured by Thermo Electron Corporation and equipped with a snap-Gold State II which allows for measurements in the reflection configuration mode.

The compression strength of the PUF samples was estimated in accordance to PN–EN ISO 604:2006. The samples of cubic shape and dimensions of 50 × 50 × 50 mm^3 were