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Synthesis of silanized polyether urethane hybrid systems. Study of the curing process through hydrogen bonding interactions

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Abstract

Different types of silanized polyurethanes (SPUR) were prepared in two ways: the first type (a), by reacting a polyether diol with an isocyanatesilane and the second type (b) by reacting it with diisocyanate (IPDI) and afterwards with aminosilane. These systems are able to cure with atmospheric moisture and, as a consequence, a tridimensional hybrid structure is formed where the inorganic and organic phases are bonded with covalent bonds. The evolution of the curing process in both systems has been monitored by means of Fourier transform infrared spectroscopy, through the changes observed in the carbonyl stretching vibration region. The results obtained show that the SPURs of kind (b) present stronger hydrogen bonding interactions as a consequence of urea groups present in the final structure. Moreover, given the proximity of both urethane and urea groups to alkoxysilane end groups, during the alkoxysilane curing process these groups are forced to approximate themselves even further and therefore the reticulation process leads to an increase of the self association of urethane and urea groups.

Finally, DSC has been used to measure T_g values of the systems studied before and after the curing process. The obtained results have confirmed the main conclusions obtained in FTIR analysis.

Keywords: Organic–inorganic hybrid; Moisture curing process; FTIR

1. Introduction

Over the past decade, the synthesis and characterization of inorganic–organic hybrid materials have received considerable attention [1–8]. Hybrid materials exhibit the advantages of combining the properties of both organic polymers and inorganic ceramics. As an example, high modulus flexible polymers together with high thermal stability, characteristic of inorganic glasses, can be prepared.

In this way, in the last few years, alkoxysilane capped low molecular weight polyethers are experimenting great development because they have excellent adhesive properties [9–12]. Depending on the desired application, polymers with different mechanical properties can be obtained due to the versatility of the formulation. Moreover, due to their hybrid

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character, they present superior thermal and weathering resistance as well as better adhesive properties than traditional polyurethanes [13,14]. However, until 4–5 years ago, the synthesis of these systems was under patent and as result, the number of published papers in the literature is limited.

Most of the papers [1–5] published about organic/inorganic hybrid systems are based on the sol–gel process where an organosilane precursor is mixed with an organic matrix. It is generally accepted that the preferred hybrid structure is the one in which there is intimate crosslinking between organic and inorganic polymer networks. In the hybrid systems studied in our work, the silica phase, after curing, is strictly interconnected with the polymer matrix.

It is known that alkoxysilanes can undergo a moisture-curing process [6,7] as shown in Scheme 1. The alkoxy groups can react with water generating silanol and alcohol groups. The silanol groups can then condense to form siloxane groups with the elimination of water and alcohol. A silicon dioxide network is built after further hydrolysis and condensation reactions take place. This curing process is influenced by many factors such as pH, temperature, alkoxy group chemical nature and solvent. Among these factors, pH plays the key role. It is known [15] that under acid catalysis, hydrolysis is much faster than condensation. This leads to a three-dimensional network containing silanol residual groups, which can interact through the formation of hydrogen bonds. Due to these interactions the condensation degree obtained is not very high. Otherwise, under basic or organometallic catalysis, hydrolysis is very slow and is the step that limits the curing rate. The resulting three-dimensional network has not silanol residual groups, so higher condensation degree is obtained.

In our work two types of alkoxysilane capped polyethers have been prepared by reaction between a polyether diol with (a) an isocyanatesilane and (b) by reacting it with diisocyanate (IPDI) and afterwards with aminosilane. Both series have urethane groups in their structure, but only (b) has urea groups in addition to urethane. The presence of urea groups leads to a quite higher viscosity of this second kind of systems due to urea strong hydrogen bonding self association. The alkoxysilane end groups can undergo a moisture curing process giving rise to a hybrid material.

The aim of this work is to carry out a comparative study of the synthesis and curing process of the described systems using Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC).

For this purpose, we have studied hydrogen bonding association [16–19] present in the different systems as well as its evolution during the curing process by the analysis of the carbonyl stretching vibration region.

2. Experimental

2.1. Materials

Poly(propylene glycol) (PPG), isophorone diisocyanate (IPDI), *p*-toluene sulfonic acid (*p*-TSA), dibutyl tin dilaurate (DBTDL) and dibutyl tin diacetate (DBTDA) were purchased from Aldrich. 3-Trimethoxysilyl propyl isocyanate (TMSPI) was purchased from Osy/Crompton, and *N*-butyl 3-trimethoxysilyl propyl amine (b-TMSPA) was purchased from Degussa. All products were used as received.

2.2. Preparation of SPUR

SPUR polymers were synthesized in a 500 ml glass reactor equipped with a mechanical stirrer, a vacuum inlet and a manometer. A water bath was employed to heat the reaction system to the desired temperature. The two synthesized SPUR required a different synthetic method that is explained in the next section.

2.2.1. Synthesis of SPUR with 3-trimethoxysilyl propyl isocyanate (PPG425IS and PPG2000IS)

The reagents, PPG and TMSPI, in a 1/2 molar relation were fed into the flask reactor. The reaction

$$\equiv\text{Si–OR} + H_2O \longrightarrow \equiv\text{Si–OH} + \text{ROH} \qquad (1)$$

$$\equiv\text{Si–OH} + \equiv\text{Si–OH} \longrightarrow \equiv\text{Si–O–Si}\equiv + H_2O \qquad (2)$$

$$\equiv\text{Si–OR} + \equiv\text{Si–OH} \longrightarrow \equiv\text{Si–O–Si}\equiv + \text{ROH} \qquad (3)$$

Scheme 1. Alkoxysilanes moisture-curing process.