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Silica-nanocomposites of photo-crosslinkable poly(urethane)s based on poly(ε-caprolactone) and coumarin

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ABSTRACT

Photo-reversible nanocomposites of polyurethanes (PUs) based on coumarin (CD) and poly(ε-caprolactone) (PCL), with different molecular weights (PCL530, PCL2000) were developed. High molecular weight PUs were loaded with three different amounts of fumed silica nanoparticles (SiNPs) (1, 3 and 5 wt%) to improve their physical, mechanical, thermal and photo-chemical properties. The incorporation of SiNPs and the interaction with the PU matrix was confirmed by FTIR, while their dispersion was observed by Field Emission Scanning Electron Microscopy (FE-SEM). The thermal stability of PU nanocomposites was improved due to the positive interaction of SiNPs with PU matrix. The incorporation of SiNPs leads to the formation of more thermal stable semicrystalline structure. Stress-strain experiments showed an increase on Young's modulus. Surprisingly, the photo-reversible ability of nanocomposites measured by UV–vis exhibited faster photo-dimerization process in PCL2000-PUs based nanocomposites than in PCL530-PUs ones, contrarily to the behavior of PUs without SiNPs. These nanocomposites are promising systems to design versatile and sustainable coatings with improved thermal stability and tunable mechanical performance.

1. Introduction

The surface properties of diverse materials can be improved by finishing them with coatings to provide different behavior, such as higher mechanical performance, suitable gloss or water resistance [1]. In this context, the use of biodegradable polyurethanes has gained considerable attention for sustainable coating purposes in several industrial fields such as automotive finishing, due to their extraordinary properties, i.e. easy application, room temperature curing process, superior elasticity, among others. Biodegradable aliphatic polyesters, such as poly(ε-caprolactone) (PCL), can be used to design and to synthesize poly(urethane)s by their polycondensation with an isocyanate offering the opportunity to easily tailor their structure and final properties through a designed synthesis [2]. PCL is a biodegradable polymer that presents good elasticity. It can be copolymerized or blended to take advantages of a synergistic combination with other polymers [3–5] and, in the form of diol, it can also be used to obtain sustainable polyurethanes with tailored physical properties [6,7].

On the other side, coumarins are natural compounds extracted from renewable resources [8]. The use of coumarin derivatives have gained interest in polymer science due to their applications in several fields such as medicine [9,10], electro optical [11,12], pharmacy [13–15], antimicrobial systems [16–18] or smart coatings [19]. Particularly, one of the most interesting applications of coumarin derivatives is their use as backbone in polyurethanes for coatings [18], especially in engineering [20]. This topic has gained

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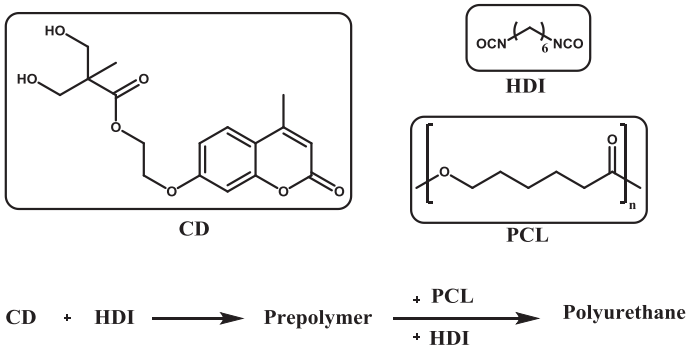

Scheme 1. Synthesis of PU based on PCL and coumarin.

attention during the last years [21–23], due to the unique reversible photochemistry of coumarins. In this sense, photochemistry instability of coumarin molecules are highly studied [24], since they are able to photodimerize by the formation of a cyclobutane ring, resulting from a [2π + 2π]-cycloaddition caused by UV light irradiation at wavelengths longer than 300 nm, while upon irradiation at wavelengths shorter than 300 nm the photocleavage of coumarin molecules takes place [25–28]. Thus, it is expected that the process of UV irradiation of polyurethane matrices containing coumarin moieties at wavelengths higher than 300 nm will produce crosslinked polymeric matrices. Meanwhile, the UV irradiation at wavelengths lower than 300 will render the original polyurethane. From a sustainable point of view, photo-reversible materials are also interesting as they facilitate the recycling process of the usually difficult to reuse crosslinked materials [29].

Due to the fact that a good mechanical strength is required in coating applications, a new approach is growing up in the sustainable polyurethane coatings field, focused on the development of biodegradable nanocomposites; low amounts of nanofillers can produce an enhancement in the thermo-mechanical performance of biodegradable polymers. Among others, silica-nanoparticles have gained considerable attention due to their hardness, permeability, chemical stability [30], low toxicity [25,31], antireflection properties [32] and low cost. In fact, silica is one of the most employed additives in the polymer industry, for example in the fabrication of concrete, as thickening agents, adsorbents or desiccants [33–35]. SiNPs have been widely used in the development of PU-based nanocomposites for several applications such as permeation membranes [36,37], adhesives [38], shape memory materials [39], coatings [38,40] or super hydrophobic surfaces [41].

In a previous work, PUs based on PCL-coumarin were successfully obtained starting from a coumarin diol-hexamethylene diisocianate (CD-HDI) pre-polymer. The PCL-coumarin based PUs synthesis was optimized and it was verified that the use of the CD-HDI pre-polymer increased the reactivity of CD leading to PUs with high molecular weights and a low polydispersity index (Scheme 1).

The final PUs properties were tailored by varying the ratio of hard to soft segments. With this purpose, the hard segment content was regulated by varying the pre-polymer content during the PU synthesis to obtain PUs with 5, 15 and 25 mol% of CD, while the PCL length was varied (PCL M_n = 530 g mol^{-1} and PCL M_n = 2000 g mol^{-1}) to regulate the proportion of the soft segments. PU530s, with lower crystallinity, offered higher photo-dimerization yields than PU2000s [7].

In the present work, we prepared silica-based nanocomposites by loading the PU matrices with three different amounts of SiNPs (1, 3 and 5 wt%) with the main purpose to increase the thermal stability and to improve the mechanical performance of the previous developed PUs. Since the main objective of this research is to develop high performance photo-reversible crosslinked nanocomposite coatings, the photo-dimerization and photo-cleavage processes were studied by UV–vis spectroscopy.

Nanocomposites were irradiated with two different incident wavelengths of light: 365 nm to induce the dimerization of coumarin, and 254 nm for the photo-cleavage. The effect of nano-silica on the mechanical and thermal properties was studied for PU samples with and without coumarin, as well as for non-irradiated nanocomposites and their corresponding crosslinked materials.

2. Experimental section

2.1. Materials

2,2-Bis(hydroxymethyl)propionic acid, *p*-toluenesulfonic acid (PTSA), 1,4-dioxane, 2,2-dimethoxypropane, N,N′-dicyclohexylcarbodiimide (DCC), dichloromethane (DCM), ethyl acetoacetate, resorcinol, 2-bromoethanol, ethyl acetate, 4-(dimethylamino) pyridine (DMAP), triethylamine (TEA), potassium carbonate, Dowex H^+ resin, poly(ε-caprolactone) diol (M_n = 530 g mol^{-1}), poly (ε-caprolactone) (PCL) diol (M_n = 2000 g mol^{-1}), stannous octoate ($Sn(Oct)_2$), hexamethylenediisocianate (HDI), 1,2-dichloroethane (DCE), N,N-dimethylformamide (DMF) HPLC grade and lithium bromide (LiBr) were supplied by Sigma-Aldrich. Acetone, DMF, *n*-hexane, chloroform, ethanol and methanol, were supplied by Scharlau. Sulfuric acid (98%), ammonia (30%) and sodium chloride were supplied by Panreac. Sodium bisulfate was supplied by Fluka and anhydrous magnesium sulfate ($MgSO_4$) was supplied by Quality Chemicals. Thin liquid chromatography (TLC) silica gel 60 F_{254} aluminum sheets (20 × 20 cm) were purchased from Merck. Fumed silica dioxide nanopowder (primary particle average size: 7–14 nm) was purchased from Interchim Innovations. All the products were used as received.