



# Photo-crosslinkable polyurethanes reinforced with coumarin modified silica nanoparticles for photo-responsive coatings

Cástor Salgado, Marina P. Arrieta\*, Laura Peponi, Daniel López, Marta Fernández-García\*

Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC), C/ Juan de la Cierva 3, 28006 Madrid, Spain

## ARTICLE INFO

### Keywords:

Polyurethane  
PCL  
Modified silica nanoparticles  
Coumarin  
Photo-crosslinking

## ABSTRACT

Coumarin and poly-ε-(caprolactone) diol (PCL)-based polyurethanes (PUs), were reinforced with modified silica nanoparticles (mSiNPs), in which a novel coumarin molecule was synthesized. The behavior as photo-responsive coatings of these materials was studied. The silica nanoparticles (SiNPs) modification was analyzed by infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and UV spectroscopy. The yield of photo-crosslinking in nanocomposites loaded with mSiNPs was studied by UV–vis spectroscopy, which showed higher conversion degree than nanocomposites with unmodified SiNPs and non-reinforced PUs. The dispersion of mSiNPs on segregated microdomains was observed by transmission electron microscopy (TEM). The presence of coumarin grafted on the SiNPs surface (mSiNPs) leads to an improvement on the thermal stability of PU matrix. Meanwhile, they were able to maintain the mechanical performance before and after the irradiation process mainly due to the improved nanofiller-matrix interaction. Contact angle measurements were also assayed to study the hydrophobicity changes on the surface of modified nanocomposites. The observed phase segregation was associated with the mechanical and thermal properties of the materials and the photo-crosslinking of coumarin moieties bring to the final material high responsiveness to be employed as photo-switchable coatings.

## 1. Introduction

One of the most employed materials in the industry are polyurethanes (PUs) owing to their versatile properties, which can provide to these materials a widely range of applications: furniture insulation [1], adhesives [2], elastomeric foams and coatings [3]. In particular, its use as sustainable coating is gaining attention in several industrial fields mainly due to their easy application, room temperature curing process, superior elasticity, among others [4]. One of the most interesting things of PUs is that their morphology can be regulated during the synthesis. Usually, PU moieties are formed by two different segments: hard segments (HS) and soft segments (SS). HS are mainly constituted by the urethane linkage between an isocyanate and a chain extender; meanwhile macromolecular diols like PCL or poly(ethylene glycol) (PEG) conform the SS. Phase distribution on PUs depends on the molecular weight ( $M_n$ ), HS nature, relationship between HS/SS [5] and SS crystallization degree [6]. These features determine the morphology and the final properties of PUs. For instance, HS are able to aggregate in ordered hard domains (HD) restraining the motion of SS chains, influencing their mechanical and thermal properties, among others [7]. In this sense, Kalajahi et al. found a reduction of phase separation degree by increasing the length of the chain extender [8].

Biodegradable polymers have gained an important role in last decades in the industrial sector for the development of sustainable coatings for several applications [9]. PCL-based PUs have been widely studied systems in last years, because of their good physical properties such as a great elasticity and good transparency, their easy processing as well as an inherent biodegradability [10,11]. In this sense, the ability to be disintegrated after their useful life in different media, including composting, represents an interesting environmentally friendly end-life option [12,13]. Despite these advantages, the applications of PCL-based PUs as coatings are still limited due to their low mechanical resistance. Thus, improvements in surface and bulk mechanical properties are highly desirable.

One interesting way to increase not only the mechanical performance, but also the thermal properties of these systems is by tuning their structure. Many researchers are focussed on the incorporation of chain extenders to improve these properties of PUs, among others [7,8]. Photo-responsive polymers show a great development in recent years due to their many advantages [14,15] since they use solar irradiation, which is a renewable, cheap and clean energy. In this sense, coumarin derivatives are certainly synthesizable systems, which can provide antioxidant activity and photo-responsive properties to the final material [16–18]. As shown in Fig. 1, when a material containing coumarin

\* Corresponding authors.

E-mail addresses: [marrieta@ictp.csic.es](mailto:marrieta@ictp.csic.es) (M.P. Arrieta), [martafg@ictp.csic.es](mailto:martafg@ictp.csic.es) (M. Fernández-García).

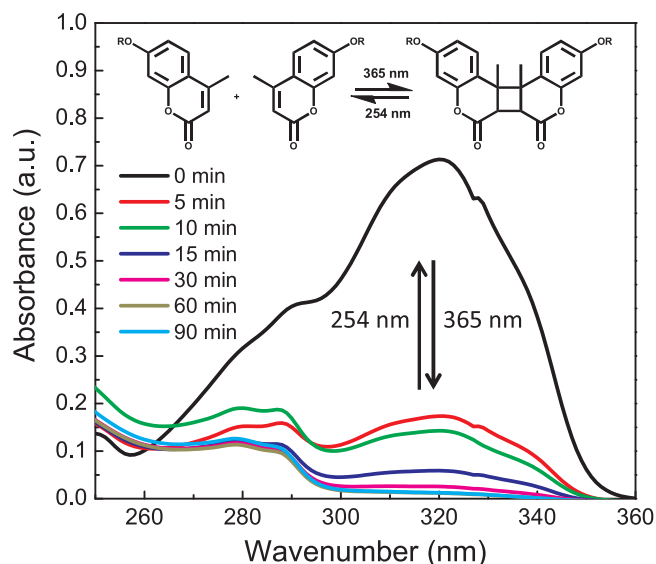


Fig. 1. Photo-dimerization and cleavage process of coumarin and the UV-vis spectra of a coumarin solution in  $\text{CHCl}_3$  during the photo-dimerization process at different irradiation times.

moieties is subjected to UV-irradiation with wavelengths near to 365 nm, a photo-dimerization process is produced between the alkene groups of coumarin molecules through a [2+2] photo-cycloaddition rearrangement [4]. This is a reversible reaction, produced when coumarin dimers are irradiated at 254 nm. The progress of the photo-dimerization reaction is well studied by UV-vis spectroscopy, by following the increase/decrease of the absorption band of coumarin double bond at 320 nm [19,20]. By using coumarin as chain extender in PUs moieties, thermal and mechanical properties can be improved, while coumarin provides its photo-responsiveness properties to the final material [16,21–23].

The use of nano-reinforcements to improve the mechanical properties of biodegradable polymers for coating applications represents a promising method without influencing the transparency when their dispersion is optimal. In fact, nanoparticles are able to improve several properties of the final nanocomposites including the mechanical, thermal, viscoelastic or abrasion resistance. The mechanical properties depend not only on the components but also on the phase morphology, such as separated microstructures where an elastomer and the filler are dispersed in the polymer matrix separately [24]. Fumed silica is an inorganic and amorphous particle, and it is one of the most employed nano-fillers at industrial level. It is a low-price material obtained as by-product of silicon. Silica nanoparticles (SiNPs) have been used to reinforce several PUs by different authors [25–27] and recently our group have improved the photo-dimerization and photo-cleavage yields of PCL-coumarin based PUs by reinforcing the polymeric matrix with SiNPs [4].

Optimal nano-filler dispersion is the main challenge in the development of nanocomposites. An interesting way to improve the

dispersion of nanoparticles into the polymeric matrix is the physical or chemical modification of nanoparticles surface to improve the interaction between the polymer matrix and the nano-fillers [28,29]. Silane coupling agents, such as (3-aminopropyl)triethoxysilane (APTES), are widely used to chemically modify SiNPs because of their good interaction with fumed silica [30,31]. Thus, the chemical functionalization of silica nanoparticles allows the improvement of their dispersion into the polymeric matrix leading to a final nanocomposite with enhanced performance.

In this work, fumed silica was chemically modified with APTES as coupling agent linked to a novel synthesized coumarin derivative. The new obtained modified silica nanoparticles (mSiNPs) were dispersed into the PCL-coumarin based PU-matrix to study its interaction with the segmented PU and its influence on the mechanical, thermal and photo-responsive properties. The development of these materials is an interesting way to achieve a family of PU-based coatings with tunable properties.

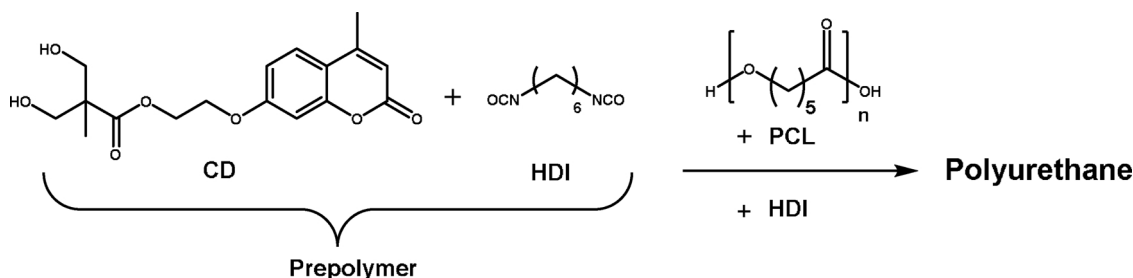
## 2. Experimental section

### 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  $\text{H}^+$  resin, poly( $\epsilon$ -caprolactone) diol ( $M_n = 530 \text{ g mol}^{-1}$ ), poly( $\epsilon$ -caprolactone) (PCL) diol ( $M_n = 2000 \text{ g mol}^{-1}$ ), stannous octoate ( $\text{Sn}(\text{Oct})_2$ ), hexamethylenediisocyanate (HDI), 1,2-dichloroethane (DCE), *N,N*-dimethylformamide (DMF), HPLC grade lithium bromide (LiBr) and (3-aminopropyl)triethoxysilane (APTES) 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 and succinic anhydride was supplied by Fluka and anhydrous magnesium sulfate ( $\text{MgSO}_4$ ) was supplied by Quality Chemicals. Thin liquid chromatography (TLC) silica gel 60  $F_{254}$  aluminum sheets ( $20 \times 20 \text{ cm}$ ) 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.

### 2.2. Synthesis of polyurethanes

The synthesis of PCL-coumarin were obtained starting from a coumarin diol-hexamethylene diisocyanate (CD-HDI) pre-polymer and further reacted with either PCL 530 ( $M_n = 530 \text{ g mol}^{-1}$ ), or PCL 2000 ( $M_n = 2000 \text{ g mol}^{-1}$ ) (Scheme 1) following the procedure described in a previous work [21]. In a two-necked rounded flask, 0.1 eq. of coumarin diol (CD) obtained according to Seane-Rivero et al. [32] were dissolved in 20 mL of DCE. Afterward, HDI (0.1 eq.) was added dropwise and stirred for two hours. After pre-polymer formation, the adequate amount of HDI (0.9 eq.), PCL diol (0.9 eq.) and  $\text{Sn}(\text{Oct})_2$  catalyst



Scheme 1. Synthesis of polyurethane based on both PCL and coumarin.

Download English Version:

<https://daneshyari.com/en/article/7105296>

Download Persian Version:

<https://daneshyari.com/article/7105296>

[Daneshyari.com](https://daneshyari.com)