



Structure-property relationships in solvent free adhesives derived from castor oil

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ABSTRACT

A method to prepare solvent free castor oil (CO) based polyurethane (PU) adhesives with different ratios of CO and hexamethylene diisocyanate (HMDI) has been developed and the relationships between the microstructure and mechanical properties investigated. Solvent free castor oil-based PU adhesives were synthesized by promoting the reaction between castor oil and HMDI, at room conditions, and by varying the CO/HMDI weight ratio in the range 1:0.032–1:0.32 wt%. The curing of these adhesives did not require any external stimuli such as heat or irradiation treatment and once cured at room temperature they were stable up to 140 °C and water-resistant. A multi-technique approach was used to characterize so-obtained adhesives. The adhesion energy in metal–metal contact was evaluated as a function of the debonding velocity (V_d) through tack experiments. The mechanical properties were influenced by the –NCO/–OH ratio, which varies the crosslinking density in the adhesives. Moreover, the structure–mechanical property relationship was explored and the inter-correlation between the storage modulus (G'), adhesion energy (E_{ad}) and correlation length (ξ) detailed, with both G' , E_{ad} increasing while ξ decreased. These solvent-free bio-based adhesives showed capability to adhere different substrates such as wood, paper, textile, and metal, which makes them promising candidates in different industrial and commercial applications.

1. Introduction

Polyurethanes (PU) derived from different sources have been used in many industrial applications as adhesives, coatings, paints, lubricants, thermoplastic elastomers, and foams (Ebnesajjad and Landrock, 2015; Engels et al., 2013; Lambuth, 1989). The suitability in such a wide range of applications is due in part to the potential of modifying the physical and chemical properties of the basic building blocks (Frisch, 2002). In recent years, the preparation of such polyurethanes from renewable resources and the replacement of synthetic polymers have gained the attention of researchers across the world. Naturally occurring vegetable oils are currently the prominent focus of both academic and industrial research and development into renewable resources (Donnelly et al., 1991; Zhang et al., 2015). During the past few decades, castor oil has been widely investigated as a potential source material for the preparation of polyurethanes. It is a naturally occurring, environmental friendly and inexpensive material that contains secondary hydroxyl groups in the predominant ricinoleic fatty

acid (80–95% in the fatty acid profile) that are available for functionalization. Adhesives based on naturally sourced materials have been developed in recent years to replace traditional formulations and overcome disadvantages such as toxicity, use of organic solvents, material cost, and degradability (Donnelly et al., 1991; Zuber et al., 2015). Such volatile, solvent-free adhesives can be produced by using natural resources at low prices whilst being biodegradable and are therefore highly sought after when compared to those produced from petrochemical derived products. Polyurethanes based on biodegradable polyols (Howard, 2002), and particularly biopolymers containing urethane linkages (Gallego et al., 2015; Ratajska and Boryniec, 1998), are considered largely biodegradable materials. In recent years, some polyurethane prepolymers based on castor oil and isocyanates were synthesized and characterized as adhesives and coatings (Gurunathan et al., 2015; Silva et al., 2010; Somani et al., 2004, 2003; Tenorio-Alfonso et al., 2018). However, the basic understanding and elucidation of the structural-mechanical properties and adhesiveness by varying the isocyanate concentration of such materials have not been investigated

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in great detail. Basically, these types of prepolymers are reactive products containing terminal isocyanate groups (–NCO) able to interact with another polymer containing active hydroxyl group (–OH) known as polyols or polyamines. This reaction leads to the formation of new polyurethane bonds. There are several factors such as composition of polyol and isocyanates, reaction temperature, and size of the isocyanate compounds which significantly affects the final physical and chemical properties of polyurethanes (Borrero-López et al., 2017; Gallego et al., 2014). The use of vegetable oils in combination with diisocyanate crosslinkers may provide a different degree of physical interactions (intra and inter molecular) which may also contribute to the final physical properties of polyurethane such as adhesiveness, thermal stability, curing time, etc. However, the micro- and molecular structure of these materials is a key element to understand their effectiveness as adhesives. Therefore, it is necessary to comprehend the rationale controlling the structure and then the final properties so to detail the microstructure-mechanical properties relationship in such adhesives derived from natural resources. In this study, model adhesive formulations based on castor oil, as a source of polyols, and HMDI, as crosslinker, were prepared and fully characterized to detail the effect of the crosslinking density on the final microstructure and adhesiveness. The aim of this investigation was to disclose the relationship between the structure and functional properties of such complex systems.

2. Materials and methods

2.1. Materials

Castor oil (211 cSt at 40 °C, Guinama, Spain) was used as received without any purification. 1,6-hexamethylene diisocyanate (HMDI, purum grade, 98.0%), triethylamine ($\geq 99.5\%$), and all other solvents were purchased from Sigma-Aldrich and used without further purification.

2.2. Preparation of adhesives

The adhesives were prepared by means of a simple methodology to crosslink the castor oil molecules with HMDI under mild reaction conditions. For example, the adhesive CO-75 was prepared as follows: first, 75.66 g of castor oil was dissolved in toluene (35 ml) at room temperature followed by agitation for 20 min to form a homogeneous solution. Triethylamine was then added in excess (6.35 ml) to the reaction mixture followed by drop wise addition of 24.34 g of HMDI. After complete addition of HMDI, the mixture was stirred for 2 days at room temperature. The toluene from the crude product was removed under vacuum by rota-evaporator at 65–70 °C for 15–20 min to obtain a viscous liquid. The curing of all adhesives was performed by keeping the samples in open air at room conditions (temperature: 25 °C \pm 2 °C; relative humidity: 63% \pm 3%) for the time required for the complete reaction of all free isocyanates. Generally, the curing time was dependent on the amount of HMDI added in the composition and was ranging in between 24 and 48 h (data not shown). The same experimental set-up was used to prepare all CO-based adhesives with the different CO/HMDI weight ratios studied. Table 1 includes the different CO/HMDI weight ratios and the corresponding –NCO/–OH mole ratios according to the CO fatty acid profile previously reported (Quinchia et al., 2010), as well as the codes applied for each sample. Some of the adhesives prepared are shown in Fig. S1 of the Supporting Information (ESI).

2.3. Measurements

2.3.1. ATR-FTIR measurements

Fourier transformation infrared spectroscopy (FTIR) was used to determine the functional groups of synthesized adhesives. The spectra were obtained by using FTIR-4200 spectrometer (JASCO) with the wavenumber range from 400 to 4000 cm^{-1} , at a resolution of 4 cm^{-1} ,

Table 1
Composition of CO-HMDI adhesives.

Composition		Nomenclature	CO/HMDI	Isocyanate index	Yield
CO (g)	HMDI (g)		weight ratio	(–NCO/–OH mole ratio) ^a	(wt%)
96.88	3.12	CO-97	1:0.032	0.14	95
95.40	4.60	CO-95	1:0.048	0.21	96
92.55	7.45	CO-92	1:0.081	0.36	97
86.15	13.85	CO-86	1:0.161	0.71	96
75.66	24.34	CO-75	1:0.321	1.43	96

^a According to the CO fatty acid profile reported in Quinchia et al. (2010), i.e. 82.5%ricinoleic acid.

in transmission mode. Samples were placed directly on an attenuated total reflectance (ATR) accessory provided with monolithic diamond crystal.

2.3.2. Thermogravimetric analysis (TGA)

Measurements of thermal stability and degradation were carried out by means of TGA. The experiments were carried out under constant nitrogen purging using a model Q-50 (TA Instruments, DE, USA) thermogravimetric analyser. Typically, ~ 10 mg of sample were placed on a platinum pan and heated from 30 °C to 600 °C, at a heating rate of 10 °C/min.

2.3.3. Rheology

The rheological measurements were investigated with a controlled-stress MARS rheometer (Thermo Haake, Germany) using parallel plate–plate geometry (35 mm). Small-amplitude oscillatory shear (SAOS) measurements inside the linear viscoelastic range were carried out after removal of toluene i.e. before curing (BC) and after curing (AC) of the adhesives. Both viscous (before curing) and solid-like (after curing) samples were placed directly between the plate–plate geometry prior to gap adjustment. Frequency-sweep experiments were performed in the range of 0.01–20 Hz. Initial stress-sweep tests were carried out to determine the linear viscoelasticity range for each sample. All the experiments were performed at 25 °C.

2.3.4. Probe tack experiments

The tack tests (adhesion tests) were carried out in a Shimadzu AG-IS Universal Testing Machine (Japan), using a 500 N load cell and smooth steel plate–plate geometries (35 mm), at 25 °C. Tests were performed using two initial gaps (0.5 and 0.1 mm) between the plates and debonding speeds (V_d) of 1 and 5 mm/s for each gap. The contact time between adhesive and surface was always 1 min for all probe tack measurements performed just to ensure a good contact with the plate surface. The required normal force for debonding was measured as a function of time.

2.3.5. Small angle X-ray scattering (SAXS)

SAXS measurements were performed using a HECUS, S3-MICRO Kratky-type camera equipped with a position sensitive, 50 M OED detector comprising of 1024 channels, 54 μm in width. An ultra-brilliant point microfocus X-ray source (GENIX-Fox 3D, Xenocs, Grenoble) provided Cu K α radiation with a wavelength, λ , of 1.542 Å at a maximum power of 50 W. A sample-to-detector distance of 281 mm allowed for a measurable q-range between 0.01 and 0.54 Å⁻¹ (where q, the scattering vector, is given by $q = 4\pi/\lambda \sin \theta$, and 2θ is the scattering angle). The S3-MICRO camera was calibrated using silver behenate ($d = 58.38$ Å) (Raftery and Gilles, 1995) and kept under vacuum to reduce scattering from air. Samples were placed into demountable cells with Kapton film windows giving a sample thickness of 1 mm. Measurements were performed at a temperature of 25 °C and controlled by a Peltier element with an accuracy of 0.1 °C. Raw scattering data were

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