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Elaboration, morphology and properties of renewable thermoplastics blends, based on polyamide and polyurethane synthesized from dimer fatty acids

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ABSTRACT

Two different thermoplastics, polyurethane (TPU) and polyamide (DAPA), have been elaborated by polymerisation from dimers of fatty acids. Since the addition of DAPA into the TPU matrix brings different positive impacts such as a higher biobased content and a lower density of the final system, different multiphase systems have been elaborated by blending both biobased polymers. Different polymers ratios have been mixed in controlled thermo-mechanical conditions. The analysis of the corresponding thermal properties allows to investigate the miscibility and interactions between both phases. Rheological measurements (melt) and mechanical tests (solid state) were also used to understand better the "morphology-properties" relationships of these biobased systems. An increase of the mechanical performances (Young's modulus, yield stresses) were observed as DAPA content increases in the systems. For specific ratios, a co-continuous structure was observed by electronic microscopy after selective extraction. Simple models have been used to simulate the mechanical properties of these systems *vs.* the polymers contents.

1. Introduction

Nowadays, the use of renewable bio-based carbon feedstock is highly taken into consideration because it offers the intrinsic value of a reduced carbon footprint and an improved life cycle analysis (LCA), in agreement with a sustainable development. That is why forthcoming chemicals and materials for daily uses are obtained more and more from the biomass, through different chemical and/or biochemical (white biotech) processes [1]. These bio-based products with particular chemical architectures succeed as a good alternative to conventional and fossil based chemical feedstock. For instance, triglyceride from seeds such as soybean or sunflower or the well-known castor oil [2,3] emerged as a good stand-in. Several fatty acid-based polymers with new macromolecular architectures such as thermoplastic polyamides and polyurethanes (TPUs) were recently synthesized [4–8].

TPUs are formed of hard segments (HS) linked together due to intermolecular hydrogen bonds which act as physical cross-linkage and of soft segments (SS) which are enabling an elastomeric behaviour. HS and SS are organised into microphases or domains. TPUs can be used in numerous fields such as automotive industry, construction engineering, consumer or domestic equipment, even in bio-medical field.

Recently, our group has shown that PA with a biobased content close to 100% can also be synthesized from fatty acids [9,10]. As some TPUs [4,11], PA can be synthesized from dimers obtained by dimerization according to a Diels Alder mechanism from different fatty acids. The corresponding dimer fatty acid polyamides (DAPA) display

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interesting properties [9,12,13]. For instance DAPA are more flexible than the conventional PA6-6 [14].

In order to increase the properties of TPUs [15] and the biobased content, TPU and DAPA can be mixed together. Since PA and TPU possess close hydrophobic/hydrophilic balances. Intermolecular interactions based on hydrogen bonds occur between the amide and urethane groups as shown by different studies on conventional fossil-based TPU/PA blends [16–20].

The aim of this study was to investigate the association of two renewable thermoplastics based on dimer fatty acids (DAPA and TPU). For this purpose different blends with a large variation of the composition were carried out by melting. The morphologies as well as the thermal, rheological and mechanical properties of the corresponding multiphase systems were fully investigated both, in solid and melt states, in order to better understand the behaviour and the "morphology-properties" relationship of these biobased multiphase systems.

2. Experimental section

2.1. Materials

2.1.1. Chemicals

The biobased polyester polyol used in this study was kindly supplied by Oleon (France). The polyol is based on dimeric fatty acids from rapeseed oil, with a purity higher than 98%, a weight average molar mass (M_w) around 3300 g mol^{-1} and a hydroxyl value of 33 mg (g KOH)$^{-1}$. DAPA has been kindly provided by Arkema (France), under the trade name of Platamid HX. 4,4′-Diphenylmethane diisocyanate (MDI) was supplied by Brenntag (France) and 1,4-butanediol (BDO) was purchased from Sigma Aldrich (France). Phenol, 1,2-diclorobenzene and dimethylformamide were used without any further purification.

2.1.1.1. TPU synthesis. TPU was prepared with a NCO/OH ratio equal to 1 and HS content of 17 wt%, by a two-step process as explained in Fig. 1. During the first step, a prepolymer is obtained. In a second step, the high molar mass TPU is elaborated with BDO, as a chain extender. The chemical synthesis was fully described in a previous publication [4]. After polymerisation, the system was cured overnight in an oven at 70 °C to ensure the complete reaction of NCO groups NCO content is evaluated in order to follow the reaction kinetics during the different steps.

2.1.1.2. Elaboration of the DAPA. DAPA used in this study has a biobased content close to 100%. It was obtained by a polycondensation reaction from a dimer fatty acid with a diamine. The synthesis was previously developed and reported in the literature [9]. The polyamide used in this study is industrially available under the trade name of Platamid® (Arkema-France). The chemical synthesis by the reaction of diamine with dimer acid, is given in Fig. 2.

2.1.2. Preparation of the blends

Before melt mixing, the TPU and DAPA pellets were dried at 60 °C in a vacuum oven overnight. The TPU/DAPA blends were carried out using an internal mixer (Counter-rotating mixer Rheomix 600p, Haake, USA) equipped with a pair of high-shear roller-type rotors, at 150 °C, with a speed of 80 rpm, during 8 min.

Based on a couette analogy, from Bousmina et al. [21] and Joubert et al. [22], we can show that during the process, the apparent shear rate $\dot{\gamma}$ can be calculated by Eq. (1):

$$\dot{\gamma}(s^{-1}) = 8.2\ 10^{-1} \times N \quad (1)$$

with N the rotor speed in rpm. In our case, the corresponding shear rate is 62.5 s^{-1}.

After melt processing, the blends were compression-moulded, to obtain films or plates, with a hot press at 160 °C applying 160 MPa pressure for 5 min and further quenched between two steel plates for 5 min.

The weight ratios (wt%/wt%) of the TPU/DAPA blends for this study were 80/20, 50/50 and 20/80, respectively. Neat polymers (100/0 and 0/100) were also analysed.

2.2. General methods

The number average molar mass (M_n), the weight average molar mass (M_w) and the polydispersity index (PDI or $Đ$) of the resulting samples were determined by Size Exclusion Chromatography (SEC), using Shimadzu liquid chromatograph (Japan). The columns used were PLGel

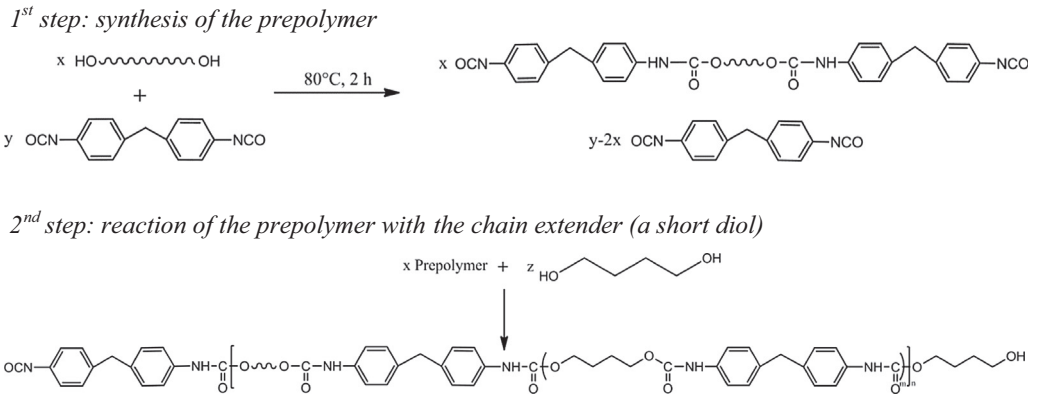

Fig. 1. TPU synthesis [11].