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Mónica Fuensanta, José Antonio Jofre-Reche, Francisco Rodríguez-Llansola, Víctor Costa, José Miguel Martín-Martínez

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STRUCTURE AND ADHESION PROPERTIES BEFORE AND AFTER HYDROLYTIC AGEING OF POLYURETHANE UREA ADHESIVES MADE WITH MIXTURES OF WATERBORNE POLYURETHANE DISPERSIONS

Mónica Fuensanta[1], José Antonio Jofre-Reche[1], Francisco Rodríguez-Llansola[2], Víctor Costa[2], José Miguel Martín-Martínez[1,*]

[1]Adhesion and Adhesives Laboratory. Department of Inorganic Chemistry. University of Alicante. 03080 Alicante (Spain).

[2]UBE Corporation Europe. Polígono El Serrallo. 12100 Grao, Castellón (Spain).

Corresponding author: Prof. José Miguel Martín-Martínez. E-mail: jm.martin@ua.es; Phone no. +34 965903977; Fax no. +34 965900416

ABSTRACT

Several waterborne polyurethane urea dispersions (WPUUs) were prepared by mixing different amounts of two waterborne polyurethane urea dispersions made with polyester (WPUU-Polyester) and polycarbonate diol (WPUU-PCD). Their crystallinity, thermal, rheological, viscoelastic and adhesion properties depended on the segmented structure and degree of phase separation which were determined by the different content of the parent dispersions. The PUU films made with WPUU-Polyester+WPUU-PCD mixtures containing more than 50 wt% of WPUU-PCD showed higher hard segments content and lower degree of phase separation, and the addition of 25 wt% of WPUU-Polyester imparted crystallinity to the polyurethane urea due to the interactions between the carbonate groups in the soft segments. The differences in the degree of phase separation and crystallinity of the PUU films made with WPUU-Polyester+WPUU-PCD mixtures were evidenced by the increase in the glass transition temperature associated to the alpha relaxation of the soft segments, and the higher modulus at the cross-over between the storage and loss moduli. Excellent adhesion

was obtained in plasticized PVC/WPUU/plasticized PVC joints, and a cohesive failure of PVC was always obtained, irrespective of the composition of WPUU-Polyester+WPUU-PCD mixtures. Furthermore, the adhesion of surface-chlorinated vulcanized styrene-butadiene (SBR) rubber/WPUU+5 wt% hardener/roughened leather joints were high and similar in all joints and a dominant cohesive failure in the rubber substrate was produced. The accelerated ageing by immersion in water at 70 ºC during different times showed that the polyurethane urea film and the surface-chlorinated vulcanized SBR rubber/WPUU+5 wt% hardener/roughened leather joint made with WPUU-PCD dispersion were not affected, but noticeable hydrolytic degradation of the ester units in the soft segments was produced in PUU-Polyester and, to a less extent, in PUU-50Polyester/50PCD films and adhesive joints.

Keywords: A. Water based; A. Polyurethane; C. Peel; D. Aging

1. INTRODUCTION

Polyurethane adhesives are prepared by step-growth polymerization between isocyanate, polyol and chain extender. Environmental demands push the need for developing adhesives with low VOCs, and waterborne polyurethane urea (WPUUs) adhesives are one of the most common alternatives. WPUU dispersions are commonly synthesized by dispersing aqueous isocyanate-terminated polyurethane prepolymer in water in presence of diamine chain extender [1]. The structure of WPUUs consists of alternating soft and hard segments in separated microphases that under appropriate conditions form hard and soft domains. The soft segments are commonly made of polyol (polyether, polyester, polycaprolactone, polycarbonate diol), and the hard segments are obtained by reacting diisocyanate and low molecular weight diamine or diol chain extender. The physicochemical and adhesion properties of WPPUs can be designed by changing their chemical composition, the molecular weight of the raw materials, and the hard to soft segments ratio (NCO/OH ratio), among other parameters [2-19].

Few studies have been devoted to the use of polyol mixtures for improving the properties of WPUUs [20-26]. Recently, the synthesis and characterization of WPUUs made with mixtures of polyester polyol and polycarbonate diol (PCD) were carried out [27], and they showed particular features in terms of structure and degree of phase separation when the mixture of polyols contained more than 50 wt% of polycarbonate

diol (PCD). Furthermore, the increase of the PCD content in the WPUU adhesive improved the resistance to hydrolysis of the adhesive joints.

An alternative approach to the synthesis of WPUUs with mixtures of polyols of different nature is the mixing of different WPUUs. There are few investigations, mainly patents, on the use of mixtures of polyurethane dispersions intended for producing coatings with improved properties on wood, metal, fabrics and plastics [28,29]. More recently, Chai et al. [30] have proposed the so-called "special physical blending" method for obtaining waterborne polyurethane dispersions with high solids content (up to 66 wt%) that involved the addition of one waterborne polyurethane dispersion over another one during the acetone dispersion step, both having very different particle sizes. However, in that study the adhesion properties of the dispersions have not been considered. To the best of our knowledge the use of mixtures of different WPUU dispersions as adhesives has not been studied yet.

Upon water removal, a mixture of two waterborne polymer dispersions will yield a solid film composed of different phases of each polymer in which the structure will depend on their colloidal stability during the film formation process. Thus, the partial micelle flocculation during film formation will result in the formation of regions of one polymer component into the other [31]. In this study, the structure of different polyurethane urea (PUU) films prepared from mixtures containing different amounts of waterborne dispersion made with polyester polyol - WPUU-Polyester - and waterborne dispersion made with polycarbonate diol - WPUU-PCD – were studied. Figure 1 shows a scheme of the steps in the film formation process of PUU film prepared with mixtures of WPUU-Polyester and WPUU-PCD mixtures [PUU-xxPolyester/yyPCD] as compared to the one of PUU film prepared from one WPUU made with mixtures of polyester polyol and polycarbonate diol [WPUU-(xxPolyester/yyPCD)]. When the micelles of the WPUUs come into contact, their surfaces deform to yield a close-packed arrangement in which the structure is determined by the different distribution of hard and soft segments of the parent WPUUs. Therefore, the structure of the PUU films will differ depending on their content of WPUU-Polyester and WPUU-PCD dispersions, and their adhesion and resistance to ageing are expected to be different.

Figure 1. Scheme of the micelles aggregation during water evaporation in **(a)** WPUU made with mixture of polyester polyol and polycarbonate diol, and **(b)** mixtures of WPUU-Polyester and WPUU-PCD.

2. EXPERIMENTAL

2.1. Materials

Two polyols of different nature with molecular weight of 2000 g/mol, polycarbonate of 1,6-hexanediol (PCD) supplied by UBE Corporation Europe (Castellón, Spain), and polyadipate of 1,4-butanediol (Polyester) supplied by Synthesia Española S.A. (Barcelona, Spain) were used. Before use, the residual moisture of the polyols was removed by heating at 80 ºC under reduced pressure (300 mbar) for 2 hours.

The diisocyanate employed for WPUU synthesis was isophorone diisocyanate (IPDI, 98 wt% purity). 2,2-bis(hydroxymethyl) propionic acid (DMPA, 98 wt% purity) was used as internal emulsifier. Triethylamine (TEA, 99 wt% purity), monohydrated hydrazine (HZ, 60 wt % purity) and dibutyltin dilaurate (DBTDL, 95 wt % purity) were used as neutralization agent, chain extender and catalyst, respectively. All these reactants were used without further purification and were supplied by Aldrich (Sigma Aldrich Co. LLC, St. Louis, MO, USA). Deionized water was used as dispersed phase, and high purity acetone (99.5 wt% purity) supplied by Aldrich (Sigma Aldrich Co. LLC, St. Louis, MO, USA) was also employed.

2.2. Synthesis of polyurethane urea dispersions (WPUUs)

Waterborne polyurethane urea (WPUU) dispersions were prepared by using the acetone method. Polyurethane prepolymer was synthesized in a 500 cm^3 four-neck round-bottom glass reactor under a nitrogen atmosphere. The polyol (polyester or polycarbonate diol), DMPA and IPDI were added into the glass reactor heated at 80 ºC and stirred at 450 rpm. A NCO/OH ratio of 1.5 was used, 5 wt% DMPA was employed, and the targeted solids content was 40 wt%. 0.028 g of catalyst (DBTDL) was added 30 minutes after starting the prepolymer reaction. After 3 hours, the amount of residual NCO content was checked by *n*-dibutylamine back titration. Afterwards, the temperature was lowered to 40–45 ºC and TEA was added to neutralize the –COOH groups in the prepolymer followed by stirring at 450 rpm for 30 minutes; then, 2.7 g chain extender (hydrazine, HZ) was added and stirred at 450 rpm for 30 minutes. Deionized water was added into the reactor under high stirring (1050 rpm) during 10–30 minutes until a homogeneous mixture was obtained. Finally, the residual acetone was evaporated in a rotavapor unit at 50 ºC and 300 mbar over a period of 30 minutes. The composition of the WPUU-Polyester and WPUU-PCD dispersions are given in Table 1. Both WPPUs have a similar hard segment content (34.1-34.3 wt%) and therefore their properties will derive from the nature of the polyol mainly.

The mixtures of WPUU-Polyester and WPUU-PCD dispersions were prepared in a polypropylene container by mild manual stirring for 30 seconds (Figure 2). The nomenclature of the mixtures of WPUUs consists in the capital letter WPUU or PUU followed by "-" and the amount of WPUU-Polyester dispersion in wt%, then "/" and the amount of WPUU-PCD dispersion in wt%. For example, WPUU-75Polyester/25PCD corresponds to the WPUU obtained by mixing 75 wt% WPUU-Polyester and 25 wt% WPUU-PCD, and PUU-75Polyester/25PCD corresponds to the solid polyurethane urea film obtained by removal of the water in WPUU-75Polyester/25PCD dispersion.

Figure 2. Scheme of the mixing of WPUU-Polyester and WPUU-PCD dispersions.

2.3. Characterization of the polyurethane urea dispersions and films

Some properties of the polyurethane ureas were obtained from solid films that were obtained by placing 60 cm^3 of WPUUs in a rectangular silicone mould of dimensions 10 x 10 cm^2. The water was removed at room temperature for 72 hours followed by heating at 40 ºC for 8 hours to complete water removal in the solid polyurethane film.

Attenuated total reflectance (ATR) Fourier transform infrared spectroscopy (ATR-IR).

The ATR-IR spectra of PUU films before and after ageing were obtained in a Tensor 27 FT-IR spectrometer (Bruker Optik GmbH, Ettlinger, Germany) by using a Golden Gate single reflection diamond ATR accessory. 64 scans were recorded with a resolution of 4 cm^{-1} and averaged in the wavenumber range of 400–4000 cm^{-1}. The incidence angle of the IR beam was 45º.

Thermal gravimetric analysis (TGA).

The thermal stability and structure of the PUU films before and after ageing were studied in TGA Q500 equipment (TA Instruments, New Castle, DE, USA) under a nitrogen atmosphere (flow rate: 50 mL min^{-1}). 10–15 mg of polyurethane urea film was placed in a platinum crucible and heated from 80 to 800 ºC at a heating rate of 10 ºC min^{-1}.

Differential scanning calorimetry (DSC).

The glass transition temperature (T_g) of the PUU films was determined by differential scanning calorimetry in a DSC Q100 instrument (TA Instruments, New Castle, USA). 10 mg of PUU films were placed in an aluminum pan hermetically closed and were

heated from −80 to 100 ºC at a heating rate of 10 ºC min^{-1} under a nitrogen atmosphere (flow rate: 50 mL min^{-1}). Then, the PUU films were cooled to −80 ºC and a second heating run from −80 to 150 ºC at a heating rate of 10 ºC min^{-1} under nitrogen atmosphere (flow rate: 50 mL min^{-1}) was carried out. The glass transition temperature (T_g) was obtained from the DSC thermogram of the second heating run.

X-ray diffraction (XRD).

The crystallinity of the polyurethane ureas was determined in a Bruker D8-Advance diffractometer (Bruker, Ettlingen, Germany). The wavelength of copper Kα radiation (1.540598 A), copper cathode, and nickel filter with Göbel mirror were used. A scanning of 2Θ angles between 5º and 90º in 0.05º steps acquired at 3 s $step^{-1}$ was carried out.

Plate-plate rheology.

The rheological properties of the PUU films were measured in a DHR-2 rheometer (TA Instruments, New Castle, DE, USA) using parallel plates (upper plate diameter = 20 mm). One piece of PUU film was placed on the bottom plate heated at 150 ºC and, once melted, the upper plate was lowered onto the bottom plate with a gap of 1 mm. Then, the temperature was increased to 200 ºC and the excess dough was carefully trimmed off by using a spatula. Experiments were performed in the region of linear viscoelasticity by decreasing the temperature from 200 to 30 ºC in a Peltier system by using a cooling rate of 5 ºC min^{-1}. A frequency of 1 Hz and a strain amplitude of 0.05 % were used.

Dynamic mechanical thermal analysis (DMTA).

The viscoelastic properties of the PUU films were measured in a DMA-Q800 equipment (TA Instruments, New Castle, DE, USA) using the single cantilever mode. PUU films with dimensions of 18 mm x 13 mm x 2 mm were used which were heated from −100 to 70 ºC under a nitrogen atmosphere (flow rate: 100 mL min^{-1}) at a heating rate of 5 ºC min^{-1}. All experiments were carried out at a frequency of 1 Hz, and an amplitude of 20 µm and strain of 0.5%.

2.4. Adhesion properties of waterborne polyurethane urea dispersions

Adhesive strengths (under peeling stresses) of the WPUUs were obtained from T-peel tests of solvent-wiped plasticized PVC/WPUU dispersion/solvent-wiped plasticized PVC joints. The plasticized PVC test samples used had dimensions of 30 mm × 150

mm × 5 mm. Before applying the WPUU, the PVC surface was methyl ethyl ketone wiped for plasticizer removal allowing the solvent to evaporate for 30 minutes under open air. Then, 0.90 g WPUU solution was applied by brush to each PVC strip to be joined. After water evaporation at 25 ºC (it took about 90 min) the adhesive film was heated suddenly at 80 °C for 10 seconds under infrared radiation (reactivation process). The PVC strips were immediately placed in contact and a pressure of 0.8 MPa was applied for 10 seconds to achieve a suitable joint. The T-peel strength was measured 72 hours after joint formation in an Instron 4411 universal testing machine (Instron Ltd., Buckinghamshire, UK) by using a cross-head speed of 100 mm min^{-1}. The values obtained were the average of five replicates.

2.5. Ageing by immersion in water at 70 ºC of polyurethane urea films and adhesive joints

PUU films for ageing test were prepared by mixing 30 g WPUU dispersion with waterborne aliphatic isocyanate crosslinker (Desmodur DN - Covestro, Leverkusen, Germany) for increasing ageing resistance. The mixture was placed in a silicone mold and the water was evaporated at room temperature for 3 days, followed by drying in an oven at 40 °C overnight. Accelerated ageing test was carried out by immersion of 0.25 g of PUU films in 10 mL of deionized water inside sealed laboratory bottles that were placed in an air convection oven at 70 ºC for 72 hours. Afterwards, the water was removed and the aged PUU films were dried at room temperature and under open air for 24 hours followed by heating in an oven at 40 ºC overnight. The structural changes in the aged PUU films were assessed by ATR-IR spectroscopy and TGA measurements, the experiments were performed under the same experimental conditions described above.

The influence of ageing on the adhesion of WPUUs was determined from T-peel tests of chlorinated vulcanized styrene-butadiene (SBR) rubber/WPUU dispersion/roughened leather joints. The test samples used had dimensions of 30 mm × 150 mm × 5 mm. Before applying the adhesive, the vulcanized SBR rubber surface was methyl ethyl ketone wiped allowing the solvent to evaporate for 30 minutes under open air. Afterwards, the surface of the SBR rubber was chemically treated with solution in MEK of 3 wt% trichloroisocyanuric acid. On the other hand, the leather was roughened by using a scouring machine for exposing the corium to the surface. Before joint formation, 5 wt% of waterborne aliphatic isocyanate cross-linker (Desmodur DN - Covestro, Leverkusen, Germany) was added to the WPUU dispersion. Then, 0.90 g of

adhesive solution was applied by brush to each substrate to be joined. After water evaporation, the adhesive film was heated suddenly at 80 ºC for 10 seconds under infrared radiation (reactivation process). Immediately the rubber and leather strips were placed in contact and a pressure of 0.8 MPa was applied for 10 seconds to achieve a suitable joint. The T-peel strength was measured 72 hours after joint formation in an Instron 4411 universal testing machine (Instron Ltd., Buckinghamshire, UK) using a cross-head speed of 100 mm min^{-1}. The values obtained were the average of five replicates.

The just-prepared adhesive joints were aged by immersion in deionized water at 70 ºC for up to 5 days. Afterwards, the aged joints were conditioned at room temperature for 24 hours and, then, the adhesion properties were examined by means of T-peel tests according to ASTM D1876-01 standard. T-peel tests were carried out in Instron 4411 universal testing machine (Instron Ltd., Buckinghamshire, UK) using a crosshead speed of 100 mm min^{-1}.

3. RESULTS AND DISCUSSION

3.1. Characterization of polyurethane urea films obtained from WPUU-Polyester+WPUU-PCD mixtures.

Extensive characterization of WPUU-Polyester and WPUU-PCD dispersions and their corresponding PUU films has been published elsewhere [27]. The chemical characterization of PUU-Polyester, PUU-PCD and PUU films obtained from WPUU-Polyester+WPUU-PCD mixtures have been analyzed by ATR-IR spectroscopy. Figure 3a shows the ATR-IR spectra of the PUU films. The broad absorption band at 3374-3342 cm^{-1} corresponds to N-H stretching, and the asymmetric and symmetric C-H stretching bands appear at 2952-2939 cm^{-1} and 2872-2962 cm^{-1} respectively. The stretching absorption band of C=O appears in the range of 1738-1662 cm^{-1}, and the absorption band at 1537-1531 cm^{-1} is attributed to C-N and N-H groups. On the other hand, the ATR-IR spectra shows the characteristic C-O-C stretching absorption bands of the polyols (1240 cm^{-1} for polycarbonate diol and 1258, 1162 – the most intense - and 958 cm^{-1} for polyester polyol) [27]. These bands overlap with the asymmetric and symmetric NCO-O stretching in urethane at 1256-1242 cm^{-1} and 1041-1034 cm^{-1} respectively. The main differences between the PUUs can be observed in the C-O-C and C=O bands.

Figure 3 a. ATR-IR spectra of PUU-Polyester, PUU-PCD and PUUs made from WPUU-Polyester+WPUU-PCD mixtures, **b.** Curve fitting of the carbonyl region (1800-1600 cm^{-1}) of the ATR-IR spectrum of PUU-75Polyester/25PCD.

The formation of urea and urethane groups in PUUs is determined by the different reactivity of the amine and hydroxyl groups (amine has major nucleophilic character), and these differences affect their hydrogen bonding capacities having a notorious influence on the morphology and properties. Furthermore, the different polarity of the urethane and urea groups plays an important role in the degree of phase separation in the PUUs. It can be assumed that the structure of the PUUs involves two types of totally separated hard segments, IPDI-DMPA/TEA-IPDI and IPDI-HZ-IPDI, and two types of totally separated soft segments too, IPDI-Polyester-IPDI and IPDI-PDC-IPDI. The existence of these different structures can be assessed by curve fitting of the carbonyl region of the ATR-IR spectra of the PUUs. For curve fitting of the carbonyl region, it was assumed that the free urethane appears at 1738-1728 cm^{-1}, the H-bonded urethane appears at 1718-1707 cm^{-1}, the free urea is assigned at 1701-1695 cm^{-1}, and the H-bonded urea appears at 1662 cm^{-1}.

Figure 3b shows a typical example of the curve fitting of the carbonyl region (1800-1600 cm^{-1}) of the ATR-IR spectrum of PUU-75Polyester/25PCD in which the contributions to free and H-bonded urethane and urea groups can be distinguished. The relative contributions of urethane and urea groups of the PUUs are given in Table 2. PUU-Polyester has a lower free urethane content and a higher bonded urea content than PUU-PCD. PUU-75Polyester/25PCD and PUU-50Polyester/50PCD have higher free urethane contributions than PUU-Polyester and PUU-25Polyester/75PCD, whereas the contribution of free urea is more important in PUU-25Polyester/75PCD. Therefore, the structure and degree of phase separation in PUUs is different depending on the amounts of WPUU-Polyester and WPUU-PCD dispersions from which they are obtained. The degree of phase separation in the PUUs can be estimated from the occurrence of H-bonded groups in the hard phase. Thus, higher degree of phase separation corresponds to PUU-PCD, PUU-75Polyester/25PCD and PUU-50Polyester/50PCD because of their minor H-bonded urethane and urea contents. Interestingly, the H-bonded urethane content in PUU-25Polyester/75PCD is higher and the free urethane is lower than expected, suggesting a lower degree of phase separation.

Thermal gravimetric analysis has been employed to analyze the structure and thermal degradation of the PUUs. TGA thermograms of the PUU films are given in Figure 4a. In agreement with previous studies [27,32], PUU-Polyester is more thermally stable than PUU-PCD, and consequently the increase of the WPUU-PCD content in the WPUUs mixture produces less thermally stable PUUs with respect to PUU-Polyester, as evidenced by the lower temperatures corresponding to 50 wt% loss ($T_{50\%}$) and temperatures of maximum decomposition (T_{max}) (Table 3a). However, the thermal stability of PUU-25Polyester/75PCD is higher than expected because of its higher T_{max}.

It is well documented that the mechanism of thermal decomposition of PUUs is very complex due to the degradation of the secondary products formed during the TGA experiment [32]. The thermal degradation of the PUUs are evidenced better in the derivative of the TGA thermograms which are shown in Figure 4b. The first thermal degradation at 170-180 ºC corresponds to removal of residual water retained in the PUU network. The thermal decomposition of the urea hard domains is observed at 261–266 ºC and decomposition of the urethane hard domains appears at 318–320 ºC. The decomposition of the soft domains occurs at 344–377 ºC and the thermal degradation at higher temperature corresponding to secondary by-products produced during the TGA experiment occurs at 483–505 ºC. Table 3b shows the thermal decomposition temperatures and mass losses due to the hard and soft domains in the PUU films. DTGA thermograms of PUU-Polyester and PUU-PCD show more defined peaks than the PUUs made from WPUU-Polyester+WPUU-PCD mixtures indicating more complex structures. Similar thermal decomposition behavior is observed for PUU-75Polyester/25PCD and PUU-50Polyester/50PCD in agreement with the ATR-IR spectra, and PUU-25Polyester/75PCD shows less content of hard domains and higher content of soft domains likely due to lower degree of phase separation. Furthermore, the intensities of the thermal degradation peaks depend on the chemical nature of the polyol in the soft segments and they are indicative of the differences in the degree of phase separation [23,32].

Figure 4. Variation of **(a)** the weight and **(b)** the derivative of the weight as a function of the temperature for PUU-Polyester, PUU-PCD and PUUs made from WPUU-Polyester+WPUU-PCD mixtures. TGA experiments.

DSC thermograms of the PUUs show one glass transition temperature only (figure not shown here) corresponding to the soft segments. The glass transition temperature (T_g) of PUU-Polyester appears at −51 ºC and that of PUU-PCD is located at −34 ºC (Figure 5). The values of the T_gs of the PUUs made from WPUU-Polyester+WPUU-PCD mixtures are intermediate, and they increase by increasing their content in WPUU-PCD.

Figure 5. Variation of the glass transition temperatures of the PUUs as a function of their WPUU-PCD content. DSC experiments.

The crystallinity of the PUU films was analyzed by X-ray diffraction and their X-ray diffractograms are shown in Figure 6. As reported in a previous study [27], PUU-Polyester is partially crystalline because of the presence of two narrow diffraction peaks at 2θ values of 21º and 22º due to the interactions between the ester groups in the soft segments, but PUU-PCD shows a broad diffraction peak characteristic of an amorphous structure. X-ray diffractograms of the PUU films made from WPUU-Polyester+WPUU-PCD mixtures show different diffraction peaks depending on their WPUU-PCD content (Figure 6). The X-ray diffractogram of PUU-75Polyester/25PCD is very similar to that of PUU-Polyester even when 25 wt% of WPUU-PCD is added, although the crystallinity decreases slightly (Table 4). Interestingly, the X-ray diffractogram of PUU-50Polyester/50PCD (Figure 6) shows the same diffraction peaks as PUU-Polyester at 2θ values of 21º and 22º due to the polyester soft segments but two additional diffraction peaks at 2θ values of 20º and 23º can be distinguished; these additional two diffraction peaks correspond to the polycarbonate diol [27] and they are not present in the X-ray diffractogram of PUU-PCD. Table 4 shows that the crystallinity of PUU-50Polyester/50PCD is lower than for PUU-75Polyester/25PCD. On the other hand, the X-ray diffractogram of PUU-25Polyester/75PCD shows the two diffraction peaks of the polycarbonate diol at 2θ values of 20º and 23º and only one of the polyester (Figure 6) indicating that the addition of 25 wt% PUU-Polyester favours the interactions between the polycarbonate diol soft segments, leading to an increase in crystallinity. Therefore, the use of WPUU-Polyester+WPUU-PCD mixtures imparts particular different structure to the PUUs leading to different degree of phase

separation than expected with respect to that of the PUUs made with the parent dispersions, this is more noticeable when more than 50 wt% PUU-PCD is added.

Figure 6. X-ray diffractograms of the PUUs.

The viscoelastic properties of the PUUs were evaluated by plate-plate rheology. Figure 7a shows the variation of storage modulus (G') as a function of temperature for the PUUs films. The rheological curves are almost parallel in all PUUs except in PUU-25Polyester/75PCD, likely due to its lower degree of phase separation and the interactions of the polycarbonate diol soft segments. In general, an increase in WPUU-PCD content produces an increase in the storage moduli of the PUUs.

The variation of storage (G´) and loss (G´´) moduli as a function of temperature for PUU-50Polyester/50PCD is shown as a typical example in Figure 7b. There is a cross-over between the storage and loss (G'') moduli at 94 ºC. At temperatures below 94 ºC, PUU-50Polyester/50PCD is mainly elastic but at higher temperature, the viscous rheological regime is dominant.

Figure 7 a. Variation of the storage modulus (G´) as a function of the temperature for PUUs. Plate-plate rheology experiments, **b.** Variation of the storage (G´) and loss (G´´) moduli as a function of the temperature for PUU-50Polyester/50PCD. Plate-plate rheology experiments.

The viscous behavior of the PUUs is mainly determined by their soft segments and degree of phase separation, and, therefore, their structures will determine the values of temperature and modulus at the cross-over between the storage and loss moduli. The values of temperature and modulus at the cross-over of the storage and loss moduli of the PUUs are given in Table 5. PUU-Polyester has a lower temperature and higher modulus at the cross-over than PUU-PCD, likely due to the mixing of soft and hard phases in PUU-PCD. Furthermore, the moduli at the cross-over of the PUUs made from WPUU-Polyester+WPUU-PCD mixtures are higher, indicating the existence of stronger interactions between the hard and soft domains which lead to a lower degree of phase separation. On the other hand, the temperature at the cross-over of the PUUs made from WPUU-Polyester+WPUU-PCD mixtures are intermediate between the ones of PUU-Polyester and PUU-PCD, except for PUU-25Polyester/75PCD that has a much

higher cross-over temperature likely due to the contribution of the crystallinity of the polycarbonate diol soft domains, in agreement with X-ray diffraction results.

Figure 8a shows the variation of storage modulus (E´) as a function of temperature for the PUUs. In the glassy region, below -20 ºC, the storage moduli of all PUUs does not vary with temperature, and the storage moduli of PUU-75Polyester/25PCD and PUU-50Polyester/50PCD are higher than for PUU-Polyester, likely due to higher degree of phase separation. Whereas the glass transition region is poorly marked in PUU-Polyester, an important decrease of the storage modulus in that region is produced in PUU-PCD; consequently, the rubbery plateau is more extended in PUU-Polyester. Once the glass transition is reached there is an important decrease in the storage moduli of PUU-PCD and PUU-25Polyester/75PCD, but somewhat similar values of the storage moduli are obtained in all PPUs made with 50 wt% or less WPUU-PCD. On the other hand, the melting of the PUUs starts at lower temperature when their WPUU-PCD content increases, in agreement with TGA experiments.

The maximum of the structural α relaxation in the tan delta curves (Figure 8b) can be associated with the glass transition temperature of the PUUs. The temperature of the maximum in the α relaxation can be associated with the glass transition temperature (T_g), and the value of T_g of PUU-Polyester is lower than for PUU-PCD; the T_gs of the PUUs made from WPUU-Polyester+WPUU-PCD mixtures are intermediate (Table 6) and they decrease with increasing WPUU-PCD content; however, the T_g value of PUU-25Polyester/75PCD is similar to that of PUU-PCD but the maximum in tan delta is much lower, because of the stronger interactions between the polycarbonate diol soft segments. On the other hand, the maximum in tan delta is much higher in PUU-PCD than in the other PUUs indicating lower interactions between the polymeric chains due to the absence of crystallinity. The addition of 25 wt% WPUU-Polyester only decreases noticeably the maximum of tan delta because of its higher crystallinity due to the interactions between the carbonate groups in the soft domains. On the other hand, smaller differences are produced by increasing the amount of WPUU-Polyester in the mixtures. The trends in the values of Tg and the maximum of tan delta can be related to the variation of the crystallinity and the degree of phase separation in the PUUs.

Figure 8. Variation of **(a)** the storage (E´) and **(b)** tan δ as a function of the temperature for the PUUs. DMTA experiments.

The adhesion of the WPUUs was obtained from T-peel tests of plasticized PVC/WPUU/plasticized PVC joints. Figure 9 shows that all joints show similar T-peel strength values and the failure is produced cohesively in the PVC substrate in the joints made with WPUU-Polyester and WPUU-PCD; however, mixed loci of failure (cohesive failure of the adhesive + cohesive failure of the PVC - the main kind of failure) are obtained in the joints made with WPUU-Polyester+WPUU-PCD mixtures. Therefore, the adhesion is good in all joints and no significant differences are obtained between the joints made with parent and WPUUs mixtures.

Figure 9. Variation of the T-peel strength of plasticized PVC/WPUU/plasticized PVC joints as a function of their WPUU-PCD content. Locus of failure : CA :Cohesive failure of the adhesive; CS : Cohesive failure of PVC.

3.2. Ageing of PUU films and adhesive joints

One of the drawbacks of the adhesive joints made with waterborne polyurethane adhesives is their limited ageing resistance derived from the existence of residual moisture in the solid polyurethane films. For improving the ageing resistance, isocyanate cross-linker is commonly added to the waterborne adhesive before joint formation. In this study, severe ageing by immersion in water at 70 ºC during several days was chosen for the joints made with WPUUs+5 wt% isocyanate hardener.

The T-peel strength values of surface-chlorinated vulcanized SBR rubber/WPUU+5 wt% hardener/roughened leather joints before and after ageing by immersion in deionized water at 70 ºC during different times are given in Figure 10. Before ageing, T-peel strength values higher than 10 kN/m are obtained, irrespective of the adhesive composition, and always a cohesive failure in the rubber substrate is produced. After one day of ageing, the T-peel strength of the joint made with WPUU-Polyester decreases dramatically and the failure is produced cohesively in the adhesive, whereas the ones made with WPUU-50Polyester/50PCD and WPUU-PCD show high adhesion and they fail cohesively in the rubber substrate. After 3 days of ageing, the joint made with WPUU-PCD maintains high adhesion and a failure in the rubber substrate is obtained, but the adhesion of the joints made with WPUU-Polyester and WPUU-50Polyester/50PCD decreases noticeably and they show a cohesive failure in the adhesive. The loss of adhesion in the joints made with WPUU-Polyester and WPUU-50Polyester/50PCD can be ascribed to hydrolytic degradation of the polyester soft

segments in the adhesive [27], and the hydrolysis process is delayed when the PUU contains soft segments of polycarbonate diol.

Figure 10. Variation of the T-peel strength of surface-chlorinated vulcanized SBR rubber/WPUU+5 wt% hardener/roughened leather joints as a function of the ageing time in water at 70 ºC. Locus of failure : CA :Cohesive failure of the adhesive; CS : Cohesive failure of the PVC.

For determining the causes of loss of adhesion after ageing in the joints made with WPUU-Polyester and WPUU-50Polyester/50PCD, PUU films obtained from WPUU+5 wt% isocyanate hardener were immersed in deionized water at 70 ºC for 3 days. After 3 days of ageing, the PUU-PCD film shows some swelling (Figure 11), but PUU-Polyester and PUU-50Polyester/50PCD films are noticeably degraded, particularly PUU-Polyester film. Therefore, the ageing resistance of the PUUs is improved but not inhibited, when they contain important amounts of soft segments of polycarbonate diol.

Figure 11. Photos of PUU+5 wt% hardener films after immersion in water at 70 ºC during 3 days.

The chemical and structural changes in the PUU films before and after ageing were assessed by ATR-IR spectroscopy. The ATR-IR spectra of PUU-Polyester+5 wt% hardener film before and after ageing show significant chemical changes (Figure 12a), and the ATR-IR spectra of PUU-50Polyester/50PCD+5 wt% hardener film too, although they are less marked (Figure 12b). However, the ATR-IR spectra of PUU-PCD+5 wt% hardener before and after ageing are similar, indicating that the ageing does not change its structure (Figure 12c). After ageing a new intense band at 1686 cm^{-1} appears in the ATR-IR spectrum of PUU-Polyester+5 wt% hardener film and an increase in the intensity of the band at 1460 cm^{-1} is noticed, both bands can be ascribed to the stretching of COO^- groups from carboxylic acid that have been formed by hydrolysis of the ester groups in the soft segments [33]. On the other hand, after ageing the intensities of the bands of the amide group at 1530 and 1256 cm^{-1} in the ATR-IR spectrum of PUU-Polyester decreases (Figure 12a), indicating the partial disruption of the urea groups [34], and, as a consequence, the N-H stretching band of the hard segments is displaced to 3356 cm^{-1} and becomes more intense than in the non-aged PUU-Polyester film. Additionally, after ageing, the stretching C-H bands at 2949-2872 cm^{-1} are more intense and a new band at 764 cm^{-1}, that can be ascribed to

the C-O group, appears. In summary, the ageing of PUU-Polyester film causes hydrolytic degradation of the ester groups in the soft segments that changes its degree of phase separation. The effect of ageing on the structure of PUU-50Polyester/50PCD+5 wt% hardener film is less marked (Figure 12b) than for PUU-Polyester as there is a slight decrease of the C=O band of urethane at 1728 cm^{-1} and an important increase of the band at 1168 cm^{-1}, indicating that the presence of soft segments of polycarbonate diol in PUU-50Polyester/50PCD inhibits partially its hydrolytic degradation.

Figure 12 a. ATR-IR spectra of PUU-Polyester+5 wt% hardener film before and after ageing by immersion in water at 70 ºC during 3 days, **b.** ATR-IR spectra of PUU-50Polyester/50PCD film+5 wt% hardener before and after ageing by immersion in water at 70 ºC during 3 days, **c.** ATR-IR spectra of PUU-PCD+5 wt% hardener film before and after ageing by immersion in water at 70 ºC during 3 days.

The structural changes of the PUU+5 wt% hardener films after ageing were also assessed by TGA. DTGA thermograms of the PPU+5 wt% hardener films before and after ageing are shown in Figure 13. Somewhat similar DTGA thermograms are obtained for PUU-PCD+5 wt% hardener film before and after ageing, although after ageing the weight losses of the thermal decompositions at 436 and 527 ºC are more important due to the formation of higher amounts of new structures by secondary reactions during the TGA experiments (Table 7). However, different DTGA thermograms are obtained before and after ageing in PUU-Polyester+5 wt% hardener and PUU-50Polyester/50PCD+5 wt% hardener films, the ageing produces more complex structures. Thus, after ageing the thermal decomposition at 177–180 ºC assigned to water retained in the PUU films disappears, indicating its removal during ageing at 70 ºC. Furthermore, for PUU-Polyester+5 wt% hardener and PUU-50Polyester/50PCD+5 wt% hardener films, the thermal decompositions of the urethane and urea hard domains at 265–266 °C and the thermal decomposition of the soft domains at 355–384 °C change noticeably after ageing: additionally, after ageing the thermal decomposition at 425–522 °C shifts to higher temperature (436–527ºC) in PUU-Polyester+5 wt% hardener and PUU-50Polyester/50PCD+5 wt% hardener films and the weight loss associated with decomposition also increases (4–13 wt%) (Table 7). On the other hand, the ageing of PUU-Polyester+5 wt% hardener produces the splitting of the degradation peak of the soft domains at 384 ºC (70 wt% loss) into two

degradation peaks at 352 ºC (32 wt% loss) and 438 ºC (50 wt% loss) (Table 7), this is an indication of the hydrolytic degradation of urethane and urea groups, which hydrolyze faster than the urethane groups [35]. Similar features are observed for PUU-50Polyester/50PCD+5 wt% hardener film in which, after ageing, the peak at 355 ºC (67 wt% loss) splits into two main degradation peaks at 337 ºC (46 wt% loss) and 442 ºC (36 wt% loss) (Figure 13).

Figure 13. Variation of the derivative of the weight as a function of the temperature for the PUU+5 wt% hardener films before and after ageing by immersion in water at 70 ºC during 3 days.

4. CONCLUSIONS

WPUUs prepared by mixing different amounts of WPUU-Polyester and WPUU-PCD dispersions showed particular structures and differences in the degree of phase separation which affect their properties. The PUU films made with WPUU-Polyester+WPUU-PCD mixtures containing more than 50 wt% of WPUU-PCD showed higher hard segment contents and lower degrees of phase separation due to the complex interactions between the two types of totally separated hard segments [i.e., -(IPDI-DMPA/TEA-IPDI)- and -(IPDI-HZ-IPDI)-] and the two types of totally separated soft segments [i.e., -(IPDI-PCD-IPDI)- and -(IPDI-PE-IPDI)-]. Furthermore, the addition of 25 wt% of WPUU-Polyester imparted crystallinity to the polyurethane urea due to the interactions between the carbonate groups in the soft segments. The differences in the degree of phase separation and crystallinity of PUU films made from WPUU-Polyester+WPUU-PCD mixtures were evidenced by the increase in the glass transition temperature associated with the alpha relaxation of the soft segments, and the higher modulus at the cross-over between the storage and loss moduli. The adhesion of plasticized PVC/WPUU/plasticized PVC and surface-chlorinated vulcanized SBR rubber/WPUU+5 wt% hardener/roughened leather joints were high and similar in all joints, a dominant cohesive failure in the polymeric substrate was produced. On the other hand, accelerated ageing by immersion in water at 70 ºC during different times showed that the polyurethane urea film and the joint made with WPUU-PCD were not affected, but noticeable hydrolytic degradation of the ester units in the soft segments occurred in PUU-Polyester and, to a less extent, in PUU-50Polyester/50PCD films and joints. The co-existence of soft segments of polycarbonate diol and polyester delayed

but did not inhibit the hydrolytic degradation of the ester groups in the polyurethane urea film.

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References

[1] Jhon YK, Cheong IW, Kim JH. Chain extension study of aqueous polyurethane dispersions. Colloids Surf A: Physicochem Eng Aspects 2001;179:71-8.

[2] Jang JY, Jhon YK, Cheong IC, Kim JH. Effect of process variables on molecular weight and mechanical properties of water based polyurethane dispersion. Colloids Surf A: Physicochem Eng Aspects 2002;196:135-43.

[3] Nanda AK, Wicks DA. The influence of the ionic concentration, concentration of the polymer, degree of neutralization and chain extension on aqueous polyurethane dispersions prepared by the acetone process. Polymer 2006;47:1805-11.

[4] Sardon H, Irusta L, Fernández-Berridi MJ, Luna J, Lansalot M, Bourgeat-Lami E. Waterborne polyurethane dispersions obtained by the acetone process: A study of colloidal features. J Appl Polym Sci 2011;120:2054-62.

[5] Barikani M, Valipour Ebrahimi M, Seyed Mohaghegh SM. Preparation and characterization of aqueous polyurethane dispersions containing ionic centers. J Appl Polym Sci 2007;104:3931-7.

[6] García-Pacios V, Costa V, Colera M, Martín-Martínez JM. Influence of the solids content on the properties of waterborne polyurethane dispersions obtained with polycarbonate of hexanediol. Int J Adhes Adhes 2011;31:787-94.

[7] Peng S, Jin Y, Sun T, Qi R, Fan B, Cheng X, Synthesis of high solid content waterborne polyurethanes with controllable bimodal particle size distribution. J Appl Polym Sci 2014;131:40420-9.

[8] Sakurai S, Okamoto Y, Sakaue H, Nakamura T, Banda L, Nomura S. Structure and properties of segmented poly(urethaneurea)s with relatively short hard segment chains. J Polym Sci Part B: Polym Phys 2000;38:1716-28.

[9] Cakic SM, Spirkova M, Ristic IS, B-Simendic JK, Cincovic MM, Poreba R. The waterborne polyurethane dispersions based on polycarbonate diol: Effect of ionic content. Mater Chem Phys 2013;138:277-85.

[10] García-Pacios V, Colera M, Iwata I, Martín-Martínez JM. Incidence of the polyol nature in waterborne polyurethane dispersions on their performance as coatings on stainless steel. Prog Org Coat 2013;76:1726-9.

[11] García-Pacios V, Jofre-Reche JA, Costa V, Colera M, Martín-Martínez JM. Coatings prepared from waterborne polyurethane dispersions obtained with polycarbonates of 1, 6-hexanediol of different molecular weights. Prog Org Coat 2013;76:1484-93.

[12] Wang H, Zhou Y, He M, Dai Z. Effects of soft segments on the waterproof of anionic waterborne polyurethane. Colloid Polym Sci 2015;293:875-81.

[13] Liu N, Zhao Y, Kang M, Wang X, Fenga Y, Yin N, Li Q. The effects of the molecular weight and structure of polycarbonate diols on the properties of waterborne polyurethanes. Prog Org Coat 2015;82:46-56.

[14] Jhon YK, Cheong IW, Kim JH. Chain extension study of aqueous polyurethane dispersions. Colloids Surf A: Physicochem Eng Aspects 2001;179:71-8.

[15] Lei L, Zhong L, Lin X, Li Y. Synthesis and characterization of waterborne polyurethane dispersions with different chain extenders for potential application in waterborne ink. Chem Eng J 2014;253:518-65.

[16] Peng X, Wang W, Ma N, Guo W, Yu X, Chen X. Research on the postchain extension of aqueous polyurethane dispersions. RSC Adv 2016;6:36510-5.

[17] Santamaria-Echart A, Fernandes I, Saralegi A, Costa MRPRN, Barreiro F, Corcuera MA, Eceiza A. Synthesis of waterborne polyurethane-urea dispersions with chain extension step in homogeneous and heterogeneous media. J Colloid Interf Sci 2016;476:184-92.

[18] García-Pacios V, Costa V, Colera M, Martín-Martínez JM. Affect of polydispersity on the properties of waterborne polyurethane dispersions based on polycarbonate polyol. Int J Adhes Adhes 2010;30:456-65.

[19] García-Pacios V, Costa V, Colera M, Martín-Martínez JM. Waterborne polyurethane dispersions obtained with polycarbonate of hexanediol intended for use as coatings. Prog Org Coat 2011;71:136-46.

[20] Gündüz G, Kisakürek. Kinetic aspects of chain extension reaction using water-soluble diamines in aqueous polyurethane dispersion. J Disper Sci Technol 2004;25:217-28.

[21] Kwak YS, Park SW, Lee YH, Kim HD. Preparation and properties of waterborne polyurethanes for water-vapor-permeable coating materials. J Appl Polym Sci 2003;89:123-9.

[22] Meng QB, Lee SI, Nah C, Lee YS. Preparation of waterborne polyurethanes using an amphiphilic diol for breathable waterproof textile coatings. Prog Org Coat 2009;66:382-6.

[23] Cakic SM, Ristic IS, Krakovsky I, Stojiljkovic DT, Belsky P, Kollova L. Crystallization and thermal properties in waterborne polyurethane elastomers: Influence of mixed soft segment block. Mater Chem Phys 2014;144:31-40.

[24] Cakic SM, Ristic IS, Marinovic-Cincovic M, Spirkova M, The effects of the structure and molecular weight of the macrodiol on the properties polyurethane anionic adhesives. Int. J Adhes Adhes 2013;41:132-9.

[25] Ou CW, Su CH, Jeng US, SHsu SH. Characterization of biodegradable polyurethane nanoparticles and thermally induced self-assembly in water dispersion. ACS Appl Mater.Interfaces 2014;6:5685-94.

[26] Lijie H, Yongtao D, Zhiliang Z, Zhongsheng S, Zhihua, S. Synergistic effect of anionic and nonionic monomers on the synthesis of high solid content waterborne polyurethane. Colloids Surf A: Physicochem Eng Aspects 2015;467:46-56.

[27] Fuensanta M, Jofre-Reche JA, Rodríguez-Llansola F, Costa V, Iglesia JI, Martín-Martínez JM. Structural characterization of polyurethane ureas and waterborne polyurethane urea dispersions made with mixtures of polyester polyol and polycarbonate diol. Prog Org Coat 2017;112:141-52.

[28] Schipper K, Verbiest R, Geurink PJA, inventors; Akzo Nobel N.V., assignee. Aqueous coating composition comprising a mixture of polyurethane dispersions. United States patent US6579932B1. 2003 June 17.

[29] Wenzel W, Schöer, Preuss H, Koch HJ, inventors; Bayer Aktiengesellschaft, assignee. Coating compositions based on a mixture of aqueous polyurethane dispersions. United States patent US4206255. 1980 June 3.

[30] Chai Ch-P, Ma Y-F, Li G-P, Ge Z, Ma S-Y, Luo Y-J. The preparation of high solid content waterborne polyurethane by special physical blending. Prog Org Coat 2018;115:79-85.

[31] Winnik MA. The formation and properties of latex films. In: Lovell PA, El-Aasser MS, editors. Emulsion Polymerization and Emulsion Polymers, Wiley, New York, 1997, pp. 46-515.

[32] Princi E, Vicini S, Castro K, Capitani D, Proietti N, Mannina N. On the microphase separation in water polyurethanes. Macromol Chem Physics 2009;210:879-89.

[33] Mondal S, Martin D. Hydrolytic degradation of segmented polyurethane copolymers for biomedical applications. Polym. Degrad. Stab. 2012;97:1553-61.

[34] Pretsch T, Jakob I, Müller W. Hydrolytic degradation and functional stability of a segmented shape memory poly(ester urethane). Polym. Degrad. Stab. 2009;94:61-73.

[35] Cauich-Rodríguez JV, Chan-Chan LH, Hernandez-Sánchez F, Cervantes-Uc JM. Degradation of polyurethanes for cardiovascular applications. In: Pignatello R, editor. Advances in biomaterials science and biomedical applications, Chapter 3, pp 51-82, DOI: 10.5772/53681.

TABLES

Table 1. Nomenclature and composition of the waterborne polyurethane urea (WPUU) dispersions made with polyester polyol or polycarbonate diol.

WPUU	IPDI (g)	Hydrazine (g)	DMPA (g)	Polyol (g)	TEA	HS (w%)[a]
WPUU-Polyester	25	2.7	5	70	2.8	34.3
WPUU-PCD	25	2.7	5	70	2.8	34.1

[a] Hard segment content (HS) was calculated as [Mass (IPDI + DMPA+ HZ+ TEA)/Mass (Polyol + DMPA+ IPDI + HZ+ TEA)] x 100.

Table 2. Relative contributions of free and H-bonded urethane and urea groups in the PUU films.

Wavenumber (cm^{-1})	Relative contribution of species (%)				
	PUU-Polyester	PUU-75Polyester/25PCD	PUU-50Polyester/50PCD	PUU-25Polyester/75PCD	PUU-PCD
1738-1728 (free urethane)	44	57	54	43	53
1718-1707 (H-bonded urethane)	5	6	4	10	4
1701-1695 (free urea)	19	13	15	17	16
1662 (H-bonded urea)	32	24	27	30	27

Table 3a. Temperatures at which 5 ($T_{5\%}$) and 50 wt% ($T_{50\%}$) are lost, and temperature of maximum decomposition (T_{max}) of the PUU films prepared from WPUU-Polyester+WPUU-PCD mixtures. TGA experiments.

PUU	$T_{5\%}$ (ºC)	$T_{50\%}$ (ºC)	T_{max} (ºC)
PUU-Polyester	227	352	377
PUU-75Polyester/25PCD	216	343	380
PUU-50Polyester/50PCD	228	337	356
PUU-25Polyester/75PCD	230	325	372
PUU-PCD	232	322	347

Table 3b. Main thermal decompositions in the derivative of TGA thermograms of the PUU films. TGA experiments.

PUU	Hard domain		Soft domain	
	T (ºC)	Weight loss (wt%)	T (ºC)	Weight loss (wt%)
PUU-Polyester	266, 320	33	377	51
PUU-75Polyester/25PCD	263	11	345, 372	75
PUU-50Polyester/50PCD	264	11	356	78

PUU-25Polyester/75PCD	261	9	344	81
PUU-PCD	258, 318	48	347	45

Table 4. Intensities of the diffraction peaks of the PUU films. X-ray diffraction experiments.

2θ (º)	Intensity (a.u.)				
	PUU-Polyester	PUU-75Polyester/25PCD	PUU-50Polyester/50PCD	PUU-25Polyester/75PCD	PUU-PCD
20	-	-	1714	2241	-
21	3826	3220	2258	1896	-
22	3161	2828	2244	-	-
23	-	-	1435	1614	-

Table 5. Values of temperature ($T_{cross\text{-}over}$) and modulus ($G_{cross\text{-}over}$) at the cross-over of the storage and loss moduli of the PUUs. Plate-plate rheology experiments.

PUU	$T_{cross\text{-}over}$ (ºC)	$G_{cross\text{-}over}$ (Pa)
PUU-Polyester	74	$1.1 \cdot 10^5$
PUU-75Polyester/25PCD	83	$1.5 \cdot 10^5$
PUU-50Polyester/50PCD	94	$1.2 \cdot 10^5$
PUU-25Polyester/75PCD	102	$1.3 \cdot 10^5$
PUU-PCD	111	$9.9 \cdot 10^4$

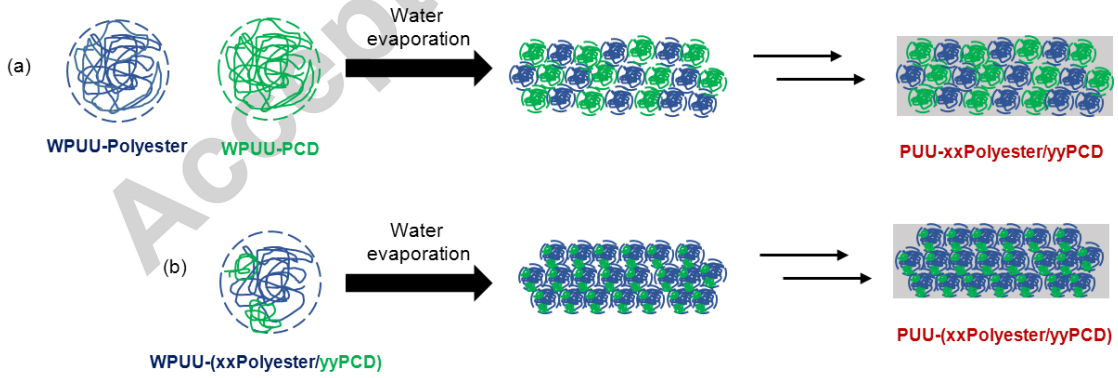
Table 6. Values of the glass transition temperature and the maximum of tan delta of the structural α relaxation of the PUUs. DMTA experiments.

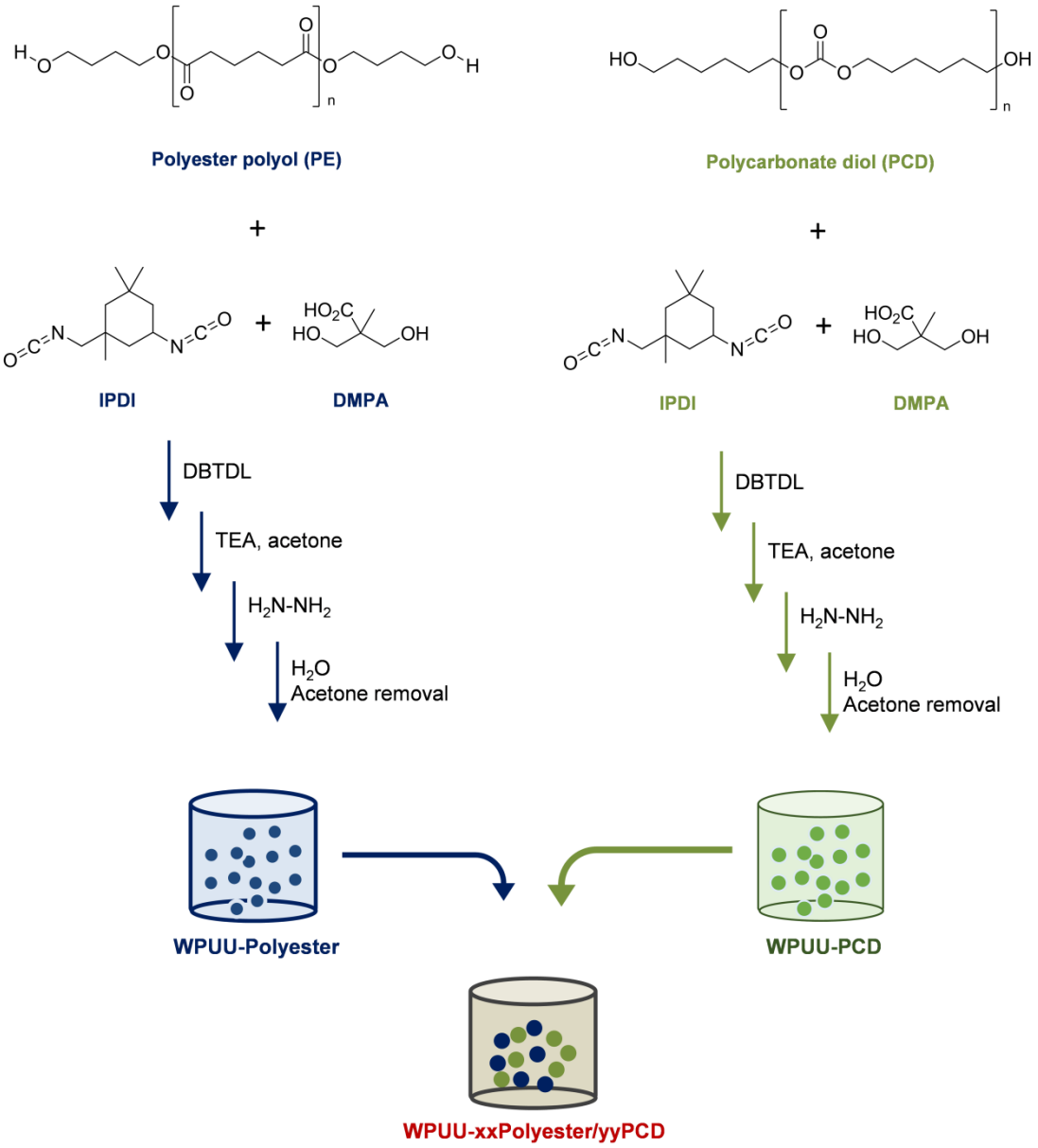
PUU	T_g (ºC)	Maximum of tan δ
PUU-Polyester	-19	0.04

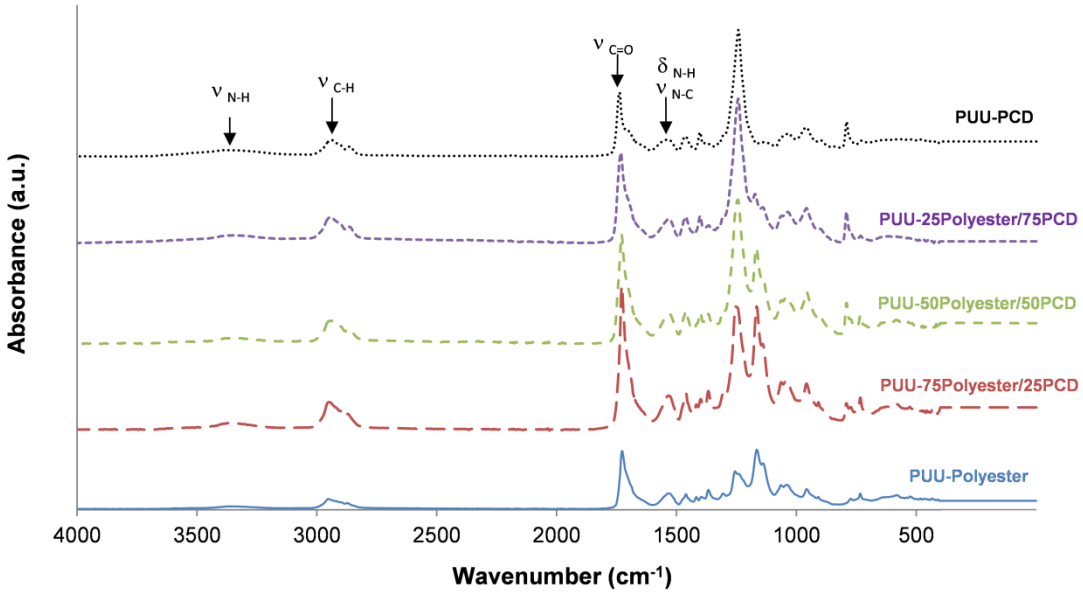
PUU-75Polyester/25PCD	-16	0.06
PUU-50Polyester/50PCD	-12	0.06
PUU-25Polyester/75PCD	-8	0.10
PUU-PCD	-9	0.25

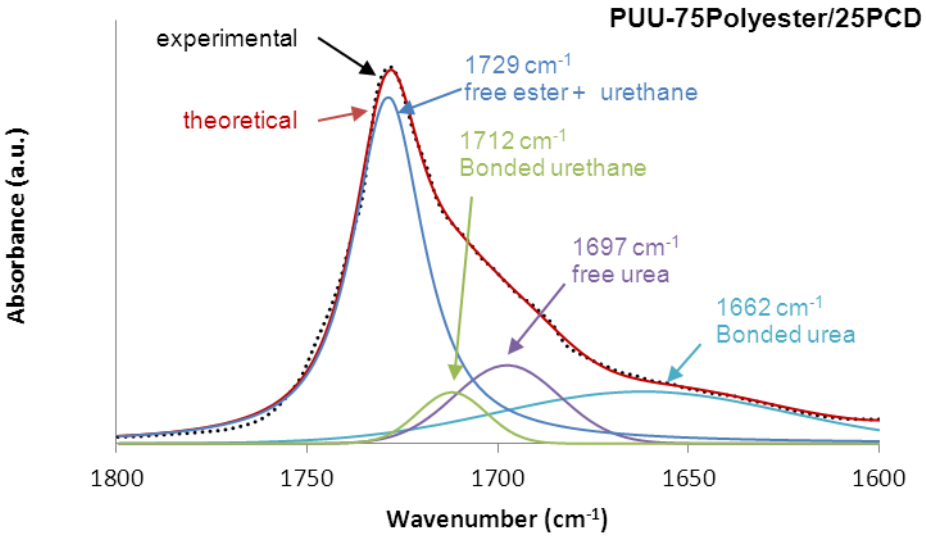
Table 7. Main thermal decompositions in the derivative of TGA thermograms of the PUU+5 wt% hardener films before and after ageing. TGA experiments.

PUU	T_1 (ºC)	Weight $loss_1$ (wt%)	T_2 (ºC)	Weight $loss_2$ (wt%)	T_3 (ºC)	Weight $loss_3$ (wt%)	T_4 (ºC)	Weight $loss_4$ (wt%)	T_5 (ºC)	Weight $loss_5$ (wt%)
PUU-Polyester Before ageing	180	3	266	11	384	70	434	4	503	12
PUU-Polyester After ageing	–	–	246	4	352	32	438	53	556	11
PUU-50Polyester/50PCD Before ageing	177	3	265	11	355	67	440	9	522	10
PUU-50Polyester/50PCD After ageing	–	–	256	5	337	47	452	36	545	12
PUU-PCD Before ageing	180	3	266	10	358	76	425	6	518	5
PUU-PCD After ageing	–	–	260	6	349	76	436	10	527	8

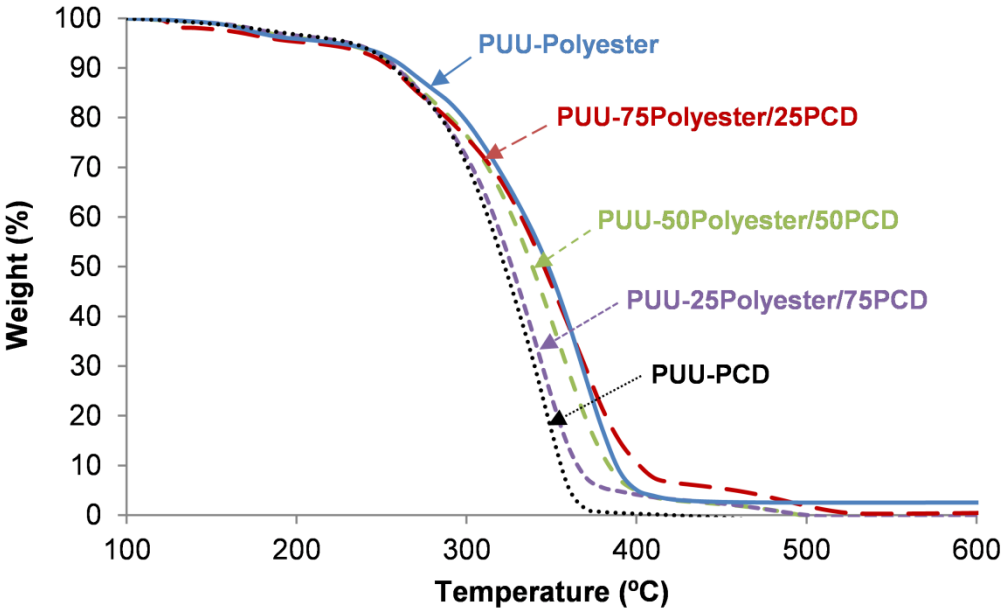



Polyester polyol (PE)
Polycarbonate diol (PCD)
IPDI
DMPA
IPDI
DMPA
DBTDL
TEA, acetone
H_2N-NH_2
H_2O
Acetone removal
DBTDL
TEA, acetone
H_2N-NH_2
H_2O
Acetone removal
WPUU-Polyester
WPUU-PCD
WPUU-xxPolyester/yyPCD

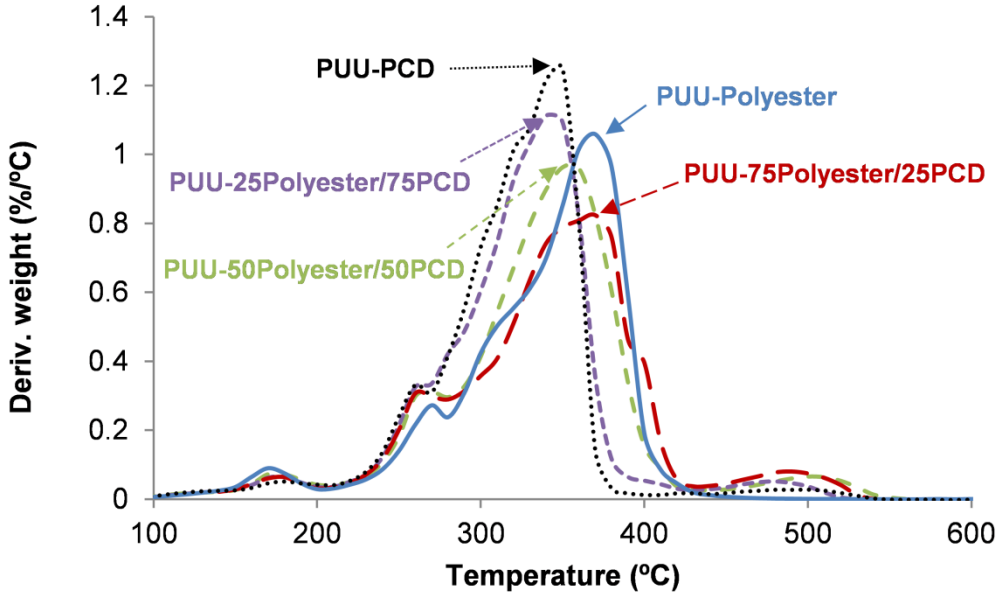

ν C=O
δ N-H
ν N-C
ν N-H
ν C-H
PUU-PCD
PUU-25Polyester/75PCD
PUU-50Polyester/50PCD
PUU-75Polyester/25PCD
PUU-Polyester
Absorbance (a.u.)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

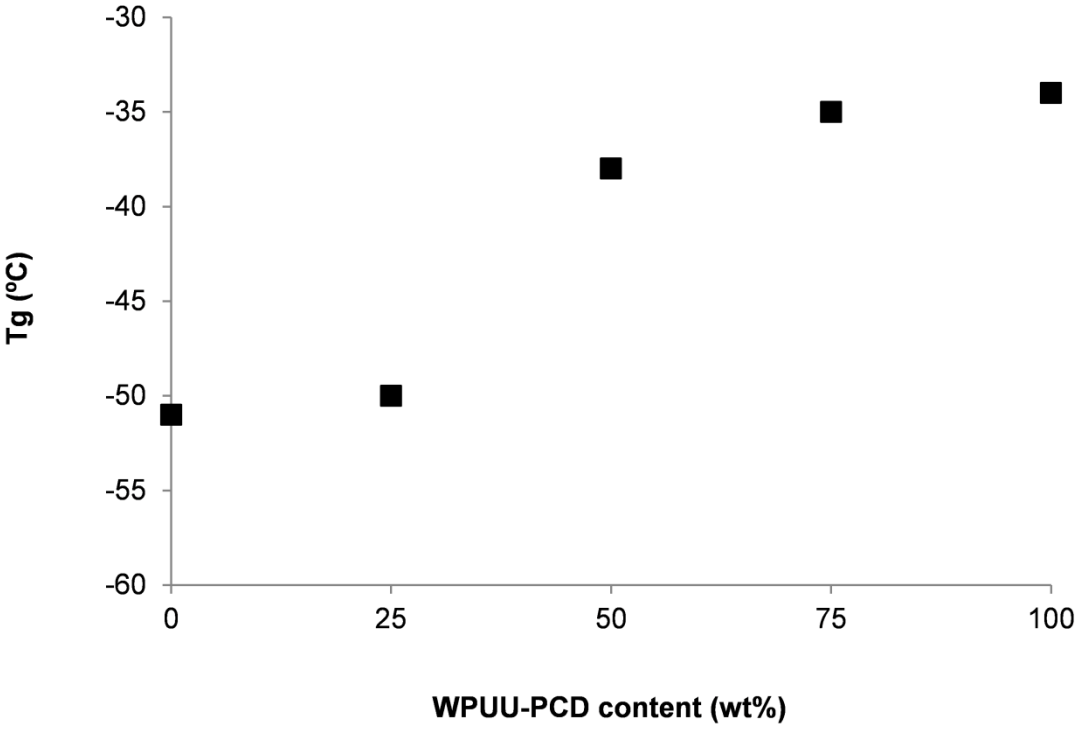

PUU-75Polyester/25PCD
experimental
theoretical
1729 cm-1
free ester + urethane
1712 cm-1
Bonded urethane
1697 cm-1
free urea
1662 cm-1
Bonded urea
Absorbance (a.u.)
1800
1750
1700
1650
1600
Wavenumber (cm-1)

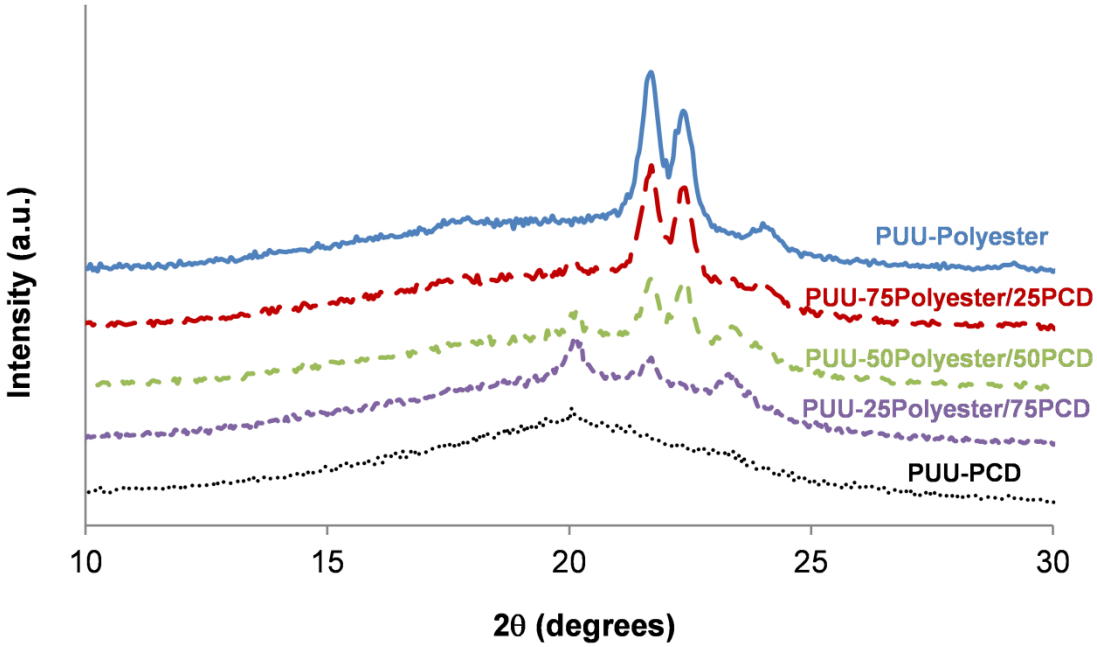
a)

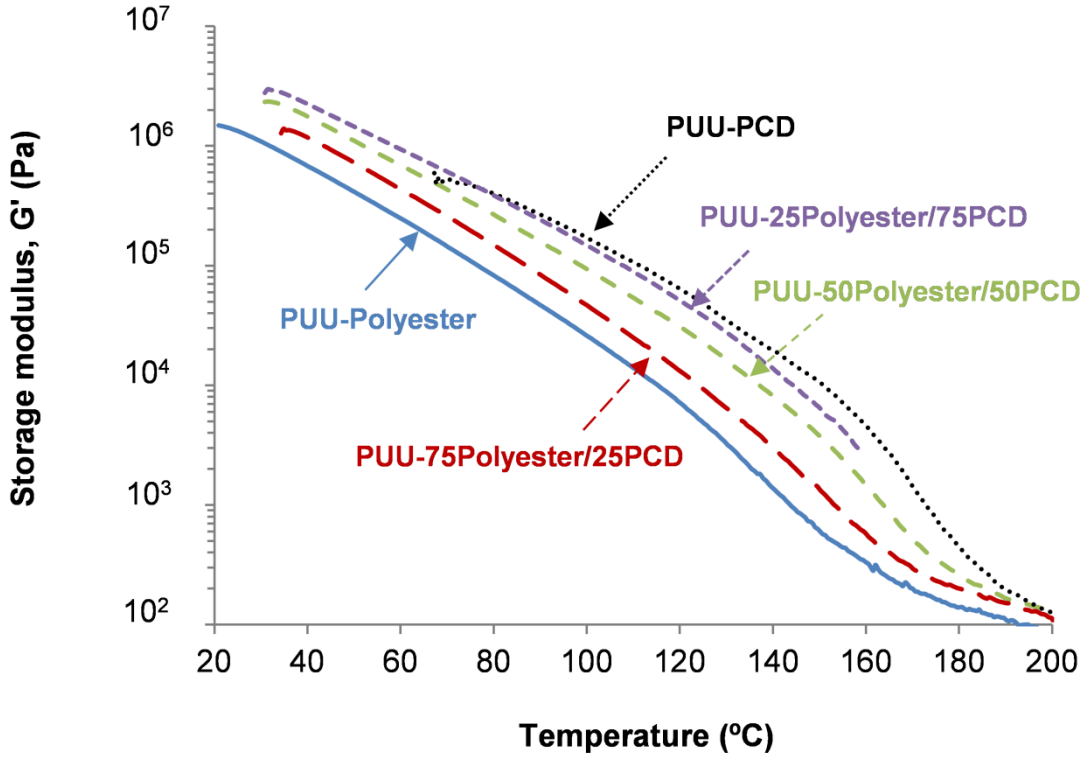

Weight (%)
100
90
80
70
60
50
40
30
20
10
0
100
200
300
400
500
600
Temperature (ºC)
PUU-Polyester
PUU-75Polyester/25PCD
PUU-50Polyester/50PCD
PUU-25Polyester/75PCD
PUU-PCD

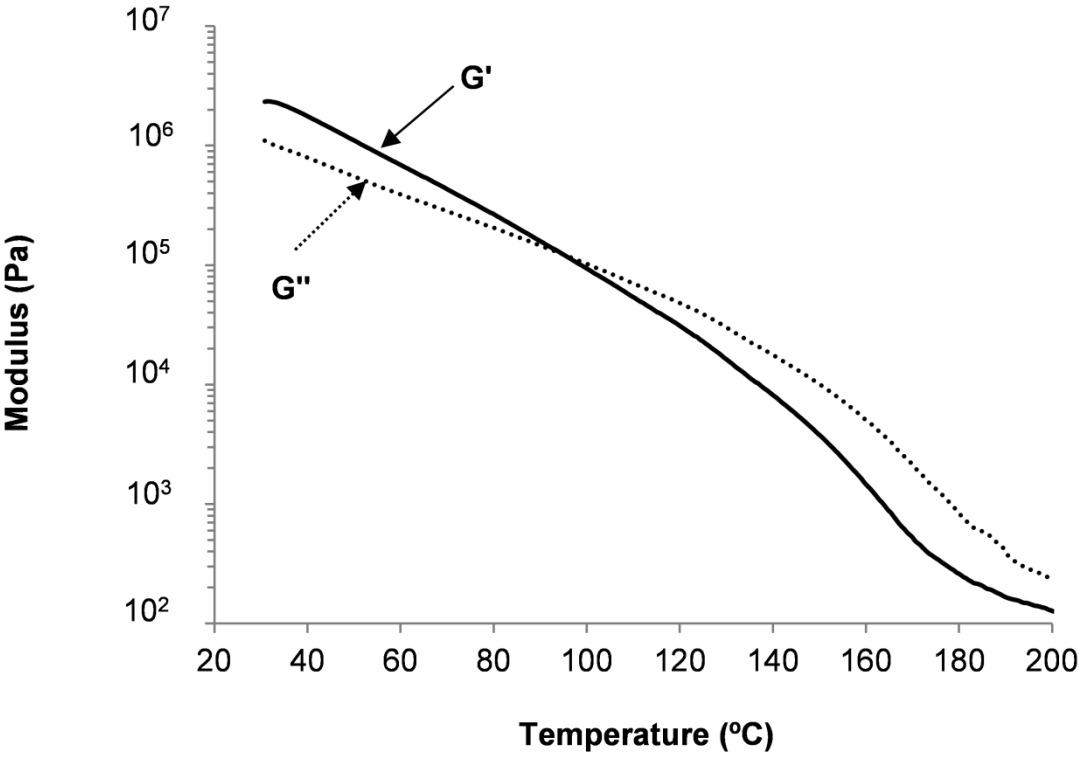
b)


Deriv. weight (%/ºC)
1.4
1.2
1
0.8
0.6
0.4
0.2
0
100
200
300
400
500
600
Temperature (ºC)
PUU-PCD
PUU-Polyester
PUU-75Polyester/25PCD
PUU-25Polyester/75PCD
PUU-50Polyester/50PCD

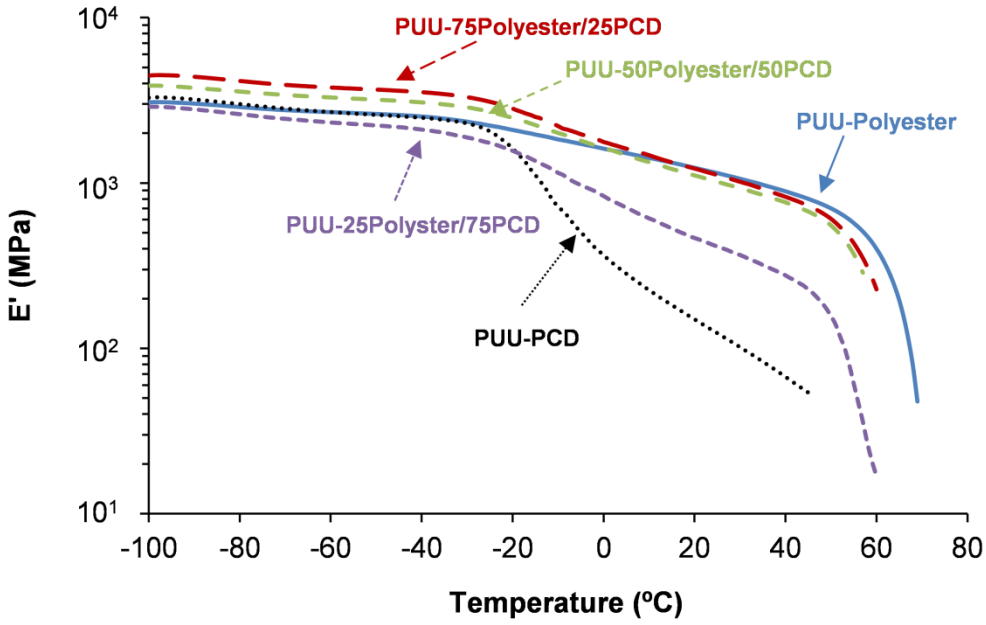

-30
-35
-40
-45
-50
-55
-60
Tg (ºC)
0
25
50
75
100
WPUU-PCD content (wt%)


Intensity (a.u.)
PUU-Polyester
PUU-75Polyester/25PCD
PUU-50Polyester/50PCD
PUU-25Polyester/75PCD
PUU-PCD
10
15
20
25
30
2θ (degrees)

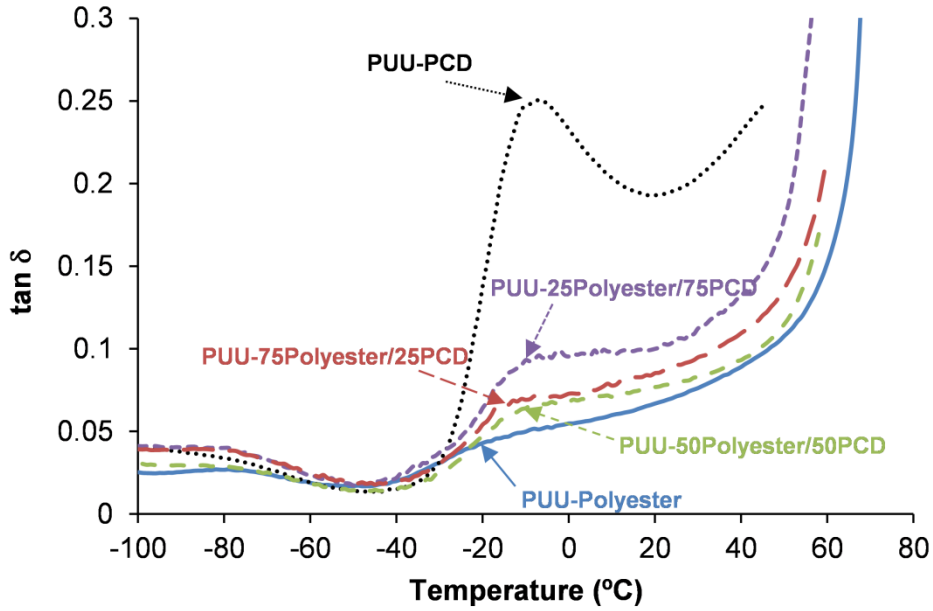

Storage modulus, G' (Pa)
10^7
10^6
10^5
10^4
10^3
10^2
PUU-PCD
PUU-25Polyester/75PCD
PUU-50Polyester/50PCD
PUU-Polyester
PUU-75Polyester/25PCD
20
40
60
80
100
120
140
160
180
200
Temperature (ºC)

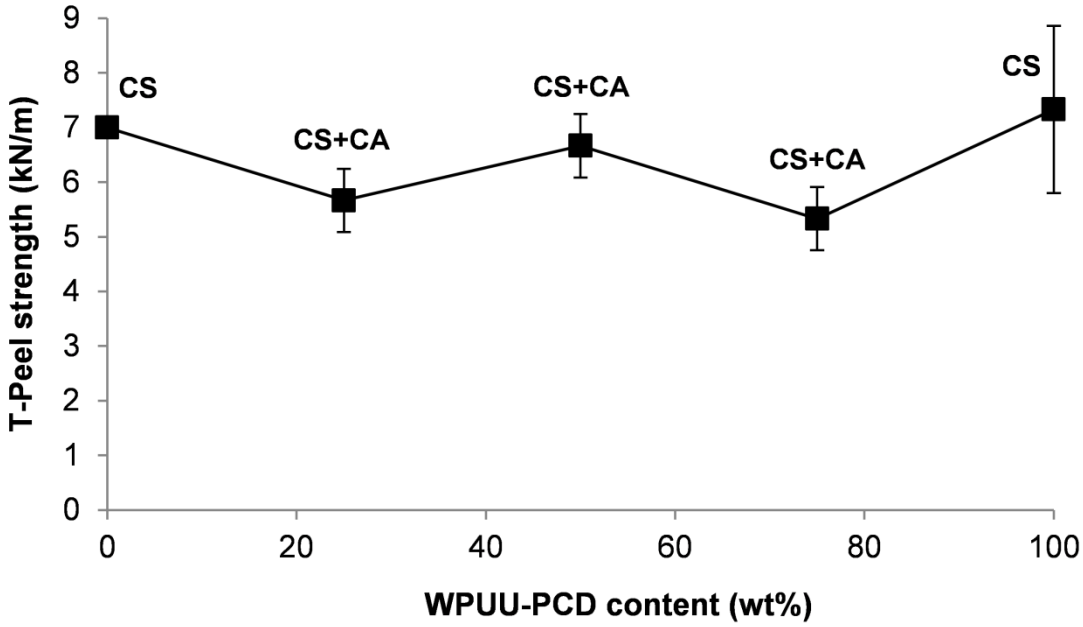

Modulus (Pa)
10^7
10^6
10^5
10^4
10^3
10^2
G'
G''
20
40
60
80
100
120
140
160
180
200
Temperature (ºC)

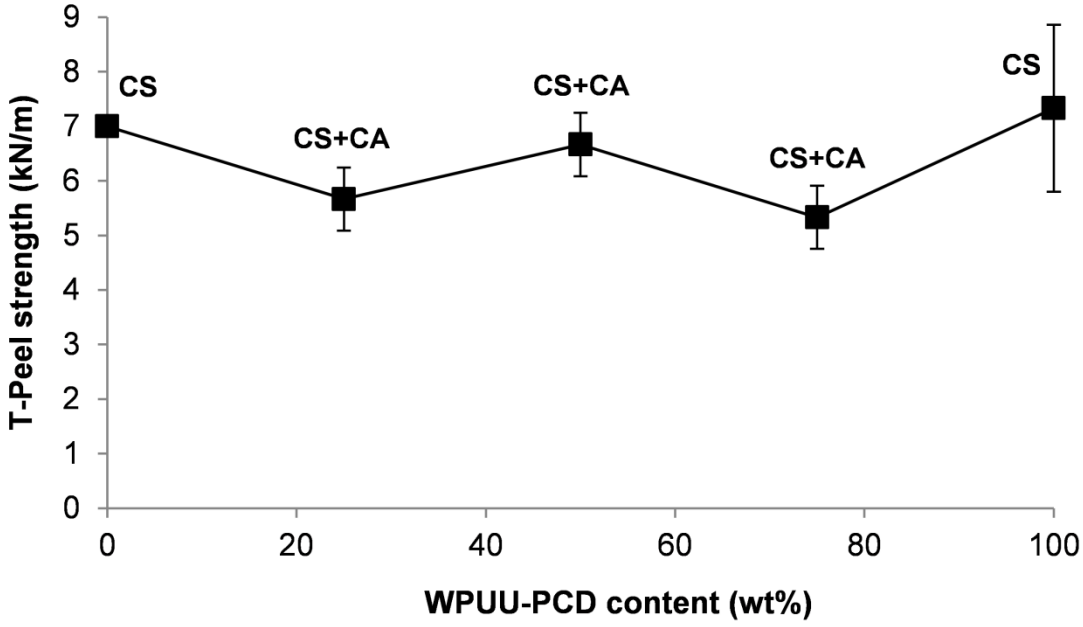
a)

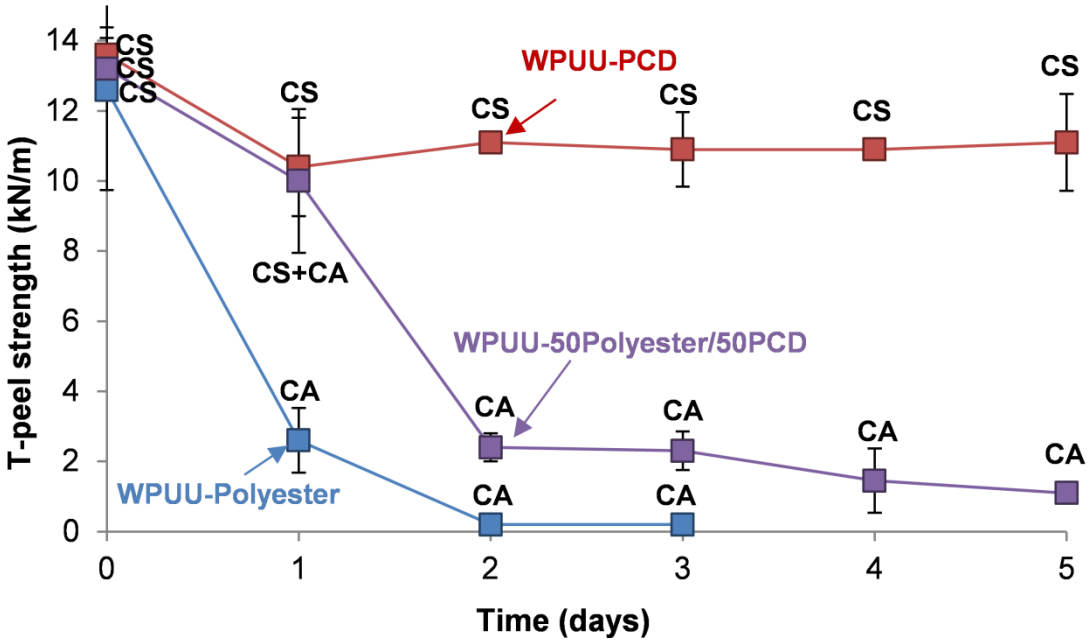

PUU-75Polyester/25PCD
PUU-50Polyester/50PCD
PUU-Polyester
PUU-25Polyster/75PCD
PUU-PCD
E' (MPa)
Temperature (ºC)

b)

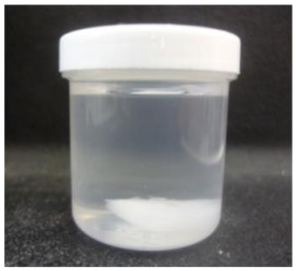

PUU-PCD
PUU-25Polyester/75PCD
PUU-75Polyester/25PCD
PUU-50Polyester/50PCD
PUU-Polyester
tan δ
Temperature (ºC)


T-Peel strength (kN/m)
WPUU-PCD content (wt%)
CS
CS+CA
CS+CA
CS+CA
CS
0
1
2
3
4
5
6
7
8
9
0
20
40
60
80
100


T-Peel strength (kN/m)
WPUU-PCD content (wt%)
CS
CS+CA
CS+CA
CS+CA
CS
0
1
2
3
4
5
6
7
8
9
0
20
40
60
80
100

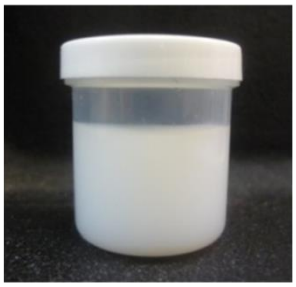


PUU-Polyester



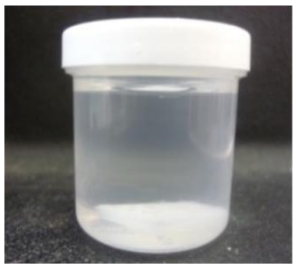
Before ageing

PUU-Polyester



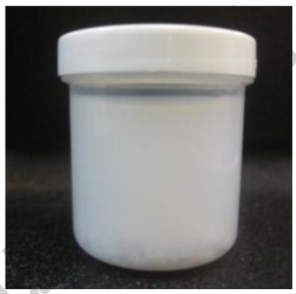
After ageing

PUU-50Polyester/50PCD



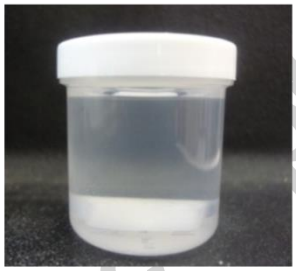
Before ageing

PUU-50Polyester/50PCD



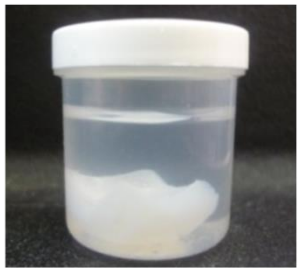
After ageing

PUU-PCD

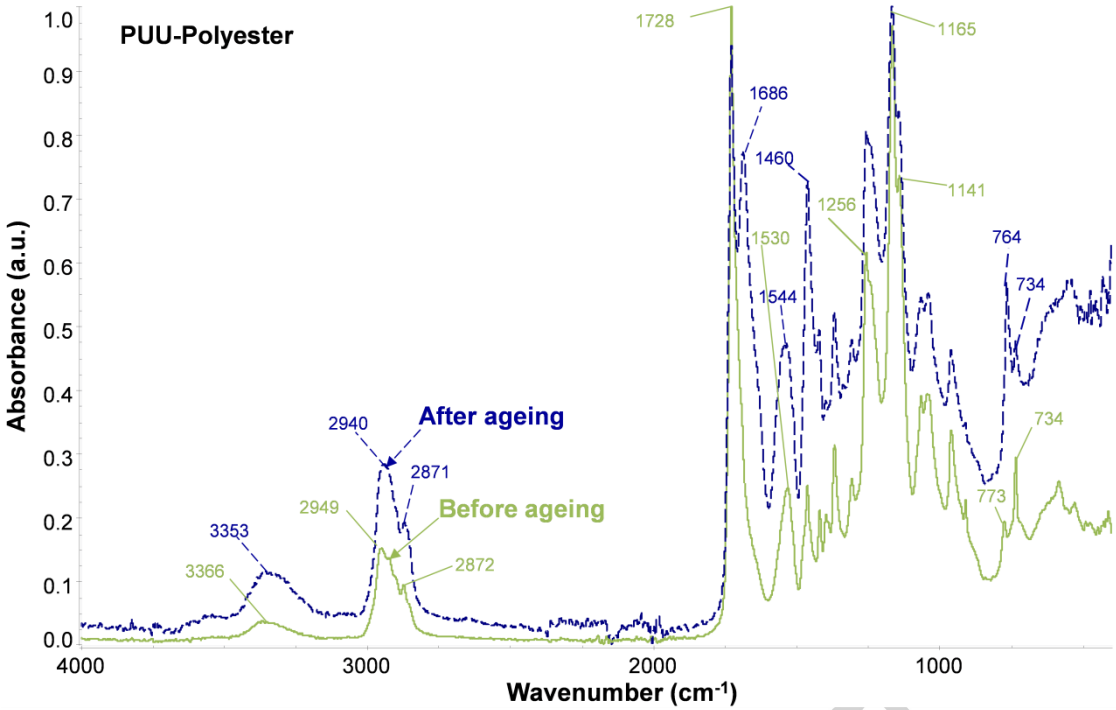


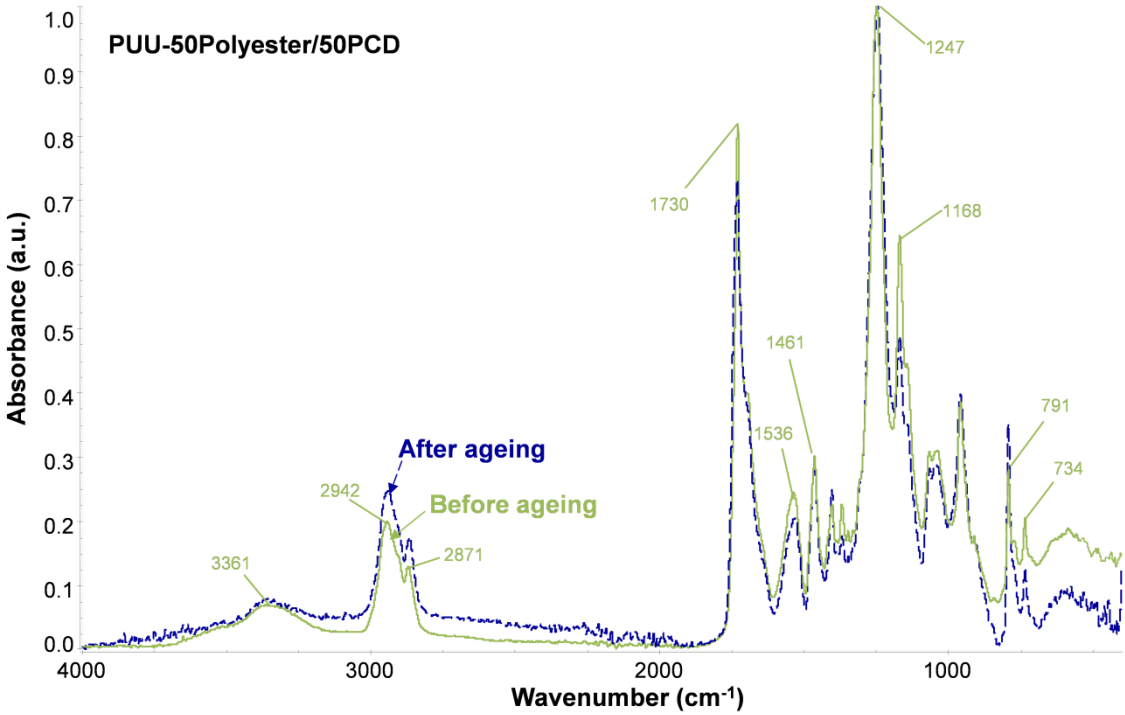
Before ageing

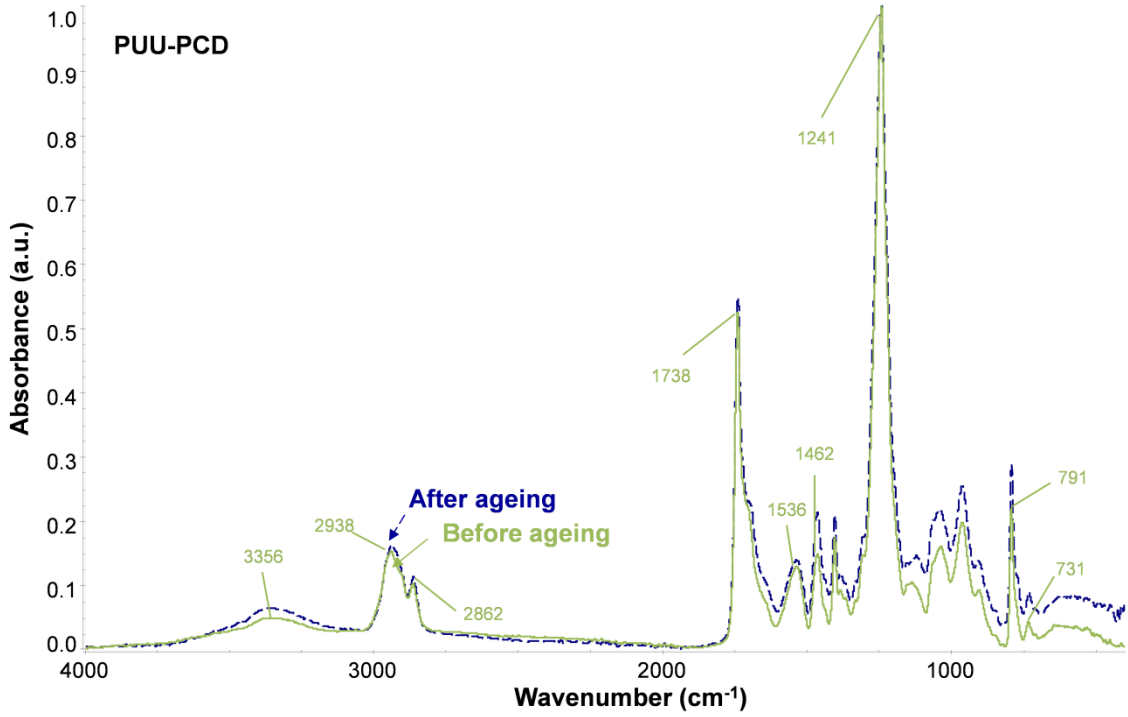
PUU-PCD

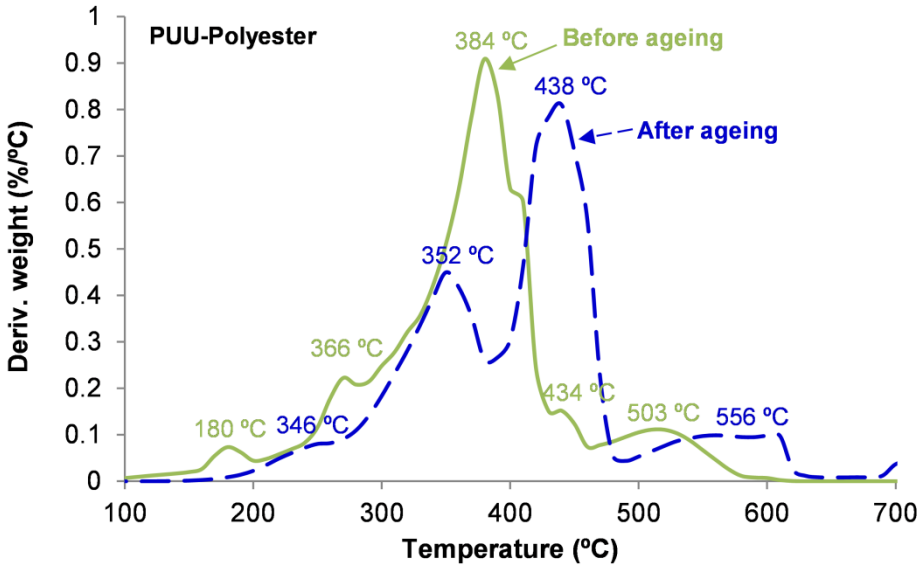


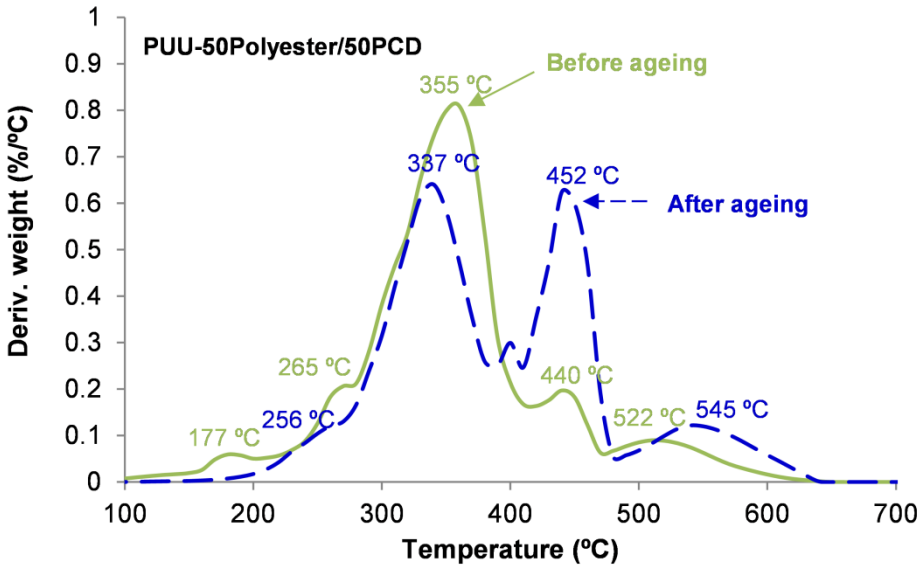
After ageing

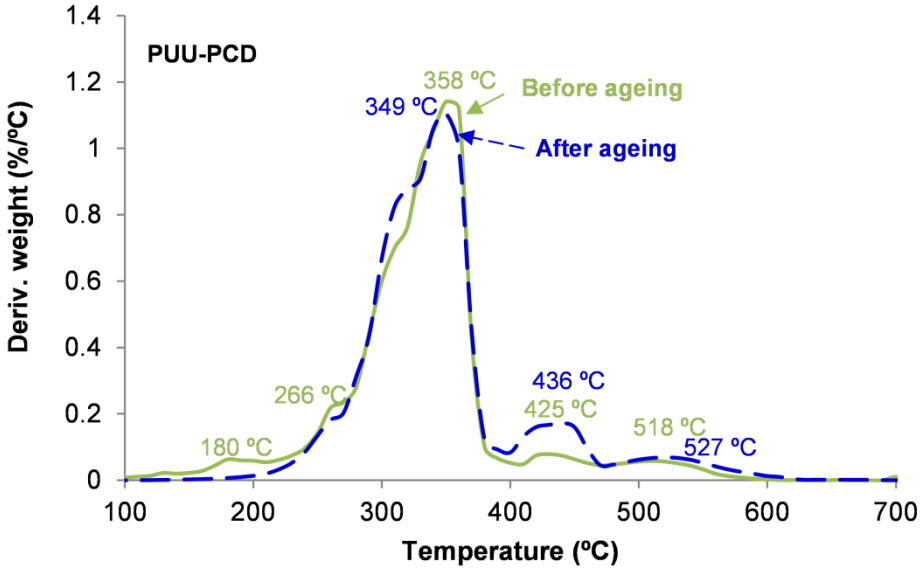







PUU-Polyester
Before ageing
After ageing
384 ºC
438 ºC
352 ºC
366 ºC
434 ºC
503 ºC
556 ºC
180 ºC
346 ºC
Deriv. weight (%/ºC)
Temperature (ºC)


PUU-50Polyester/50PCD
Before ageing
After ageing
355 ºC
337 ºC
452 ºC
265 ºC
440 ºC
522 ºC
545 ºC
177 ºC
256 ºC
Deriv. weight (%/ºC)
Temperature (ºC)


PUU-PCD
Before ageing
After ageing
358 ºC
349 ºC
436 ºC
425 ºC
266 ºC
518 ºC
527 ºC
180 ºC
Deriv. weight (%/ºC)
Temperature (ºC)