



Thermoplastic polyurethane coatings made with mixtures of polyethers of different molecular weights with pressure sensitive adhesion property

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ABSTRACT

Thermoplastic polyurethane (PU) coatings with pressure sensitive adhesion property were synthesized by reacting 4,4'-diphenylmethane diisocyanate (MDI) with 1,4-butanediol and mixtures of polypropylene glycols (PPGs) of different molecular weights (1000 and 2000 Da). Good tack at 10–37 °C was obtained in PU coatings prepared with PPG2000 + PPG1000 mixtures containing 50 wt% or more PPG2000. The pressure sensitive adhesion properties of the PU coatings were related to their minor content of bonded urethane groups and important degree of phase separation. Furthermore, these PU coatings followed Dahlquist criterion, they showed low glass transition temperatures, high tack, and low 180° peel strength. Therefore, the PU coatings had potential as pressure sensitive adhesives. Finally, PU coating made with PPG of molecular weight 1000 Da did not show pressure sensitive adhesion property.

1. Introduction

Pressure sensitive adhesives (PSAs) are commonly used in the manufacture of tapes and labels for several applications such as memory notes, patches, removable films, etc [1]. Several polymers are used for manufacturing PSAs such as synthetic rubbers, acrylics, silicones, polyesters and polyurethanes [2]. Because of environmental regulations, organic solvents must be removed from PSA formulations and, therefore, waterborne PSAs [3,4], hot-melt PSAs [5], ultraviolet curable PSAs [6] and electron beam curable PSAs [7] have been developed.

PSAs are characterized by forming immediate adhesion joints with several substrates under application of light pressure during short time. Because of the performance of PSAs is related to dual viscoelastic behavior, i.e. viscous component (to wet the substrate for good contact during bonding) and elastic component (to withstand shear stresses and peel forces during debonding), their viscoelastic properties must be carefully designed. Copolymers with segmented structure are commonly used for controlling the viscoelastic properties of PSAs because of the hard phase imparts the elastic properties and the soft phase imparts the viscous properties. In this sense, the thermoplastic polyurethanes can be good potential versatile polymers for manufacturing PSAs. On one side, the thermoplastic polyurethanes have tunable structure-property relationships which derive from the existence of thermodynamically incompatible hard and soft segments [8]. The soft “flexible” segments are constituted by high molecular weight polyols

providing flexibility to the polymer backbone, and the hard “rigid” segments due to the diisocyanate and low molecular weight diol or diamine (chain extender) are polar and impart the mechanical properties.

It is well known that the pressure sensitive adhesion property is not typical of the polyurethanes because of their low tack and low peel adhesive strength. Some previous patents [9,10] proposed the addition of tackifiers or the compounding with other polymers for adjusting the glass transition temperature and decreasing the elastic modulus at room temperature in polyurethanes intended for PSAs (PU PSAs). Unfortunately, these PU PSAs developed strong peel strength with the time causing damage of the substrate upon removal and, furthermore, the tackifier in the formulation migrates to the substrate surface [11,12]. In a different approach, Nakamura et al. [13] have recently demonstrated that the addition of crosslinking agent (trimethylolpropane/toluene-2,4-diisocyanate) increased the peel strength of polyurethane and exhibited frequency dependence of the storage modulus during dynamic viscoelastic measurements. Additionally, the rolling tack of the cross-linked PU PSAs did not depend on the rolling rate.

Grafting is another strategy used for obtaining PU PSAs with adequate performance. Baron et al. [14] reported the synthesis of graft polyurethanes by using the prepolymer method, and they found that the hard to soft segments ratio and the existence of crystallizable fragments could improve the adhesion properties of PU PSAs. On the other hand, polypropylene glycols (PPGs) with different molecular weights and hydroxyl-terminated polybutadiene (HTPB) polyols were reacted with

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aliphatic diisocyanates to obtain grafted PU PSAs [15]. It was found that the increase of the molecular weight of PPG, increased the storage modulus of the polyurethane, whereas the increase of the polybutadiene content increased the tack. Furthermore, high complex modulus was obtained anticipating high shear resistance.

Another recent strategy for obtaining PU PSAs is the use of waterborne hybrid polyurethanes for producing coatings with pressure sensitive adhesion property. Lopez et al. [16] used free radical mini-emulsion polymerization for the synthesis of acrylic/polyurethane hybrids which microstructure was modified by adding different diols as chain extenders. The use of bisphenol A as chain extender led to adhesives with greater shear resistance due to higher crosslinking density and acceptable viscoelasticity. In later publication, the same authors found that the increase of the chain transfer agent concentration increased the tack of the hybrid polyurethanes because of lower gel content and greater chain mobility [17]. A different research in mini-emulsion polymerization of polyurethane/acrylic hybrid polymers was carried out by Degrandi-Contraires et al. [18,19] in which grafted polyurethane prepolymer onto acrylic backbone through a reactive monomer was prepared.

In this study, different approach for preparing PU PSAs is proposed. Thermoplastic polyurethane (PU) coatings were synthesized by designing their structure in such a way that tack at room temperature can be obtained. Thermoplastic PU coatings were prepared by using the prepolymer method and the reactants were methylenediphenyl diisocyanate, 1,4-butanediol, and mixtures of polypropylene glycols of different molecular weights (1000 and 2000 Da). We propose that the pressure sensitive adhesion property of the thermoplastic PU coatings can be imparted by adequate design of the segmented structure of the polyurethane, i.e., the control of the degree of phase separation of the hard and soft segments.

2. Experimental

2.1. Materials

4,4'-Diphenylmethane diisocyanate (MDI) flakes – Desmodur® 44MC—supplied by Covestro (Leverkusen, Germany) was used as aromatic isocyanate. Polypropylene glycols with molecular weights of 2000 Da (PPG2000)—Alcupol® D2021 supplied by Repsol (Madrid, Spain)—and 1000 Da (PPG1000)—Alcupol® D1011 supplied by Repsol (Madrid, Spain)—were used as polyols. 1,4-butanediol (BD) supplied by Sigma Aldrich Co. LLC (St. Louis, MO, USA) was used as chain extender. Dibutyl tin dilaurate (DBTDL) supplied by Sigma Aldrich Co. LLC (St. Louis, MO, USA) was used as catalyst. Before use, the polyols were melted and dried at 80 °C under reduced pressure (300 mbar) for 2 h.

2.2. Synthesis of the thermoplastic polyurethanes

Thermoplastic polyurethanes were synthesized by using the prepolymer method. Polyurethane prepolymer was synthesized in 500 cm³ four-neck round-bottom glass reactor under nitrogen atmosphere by reacting melted MDI with dried PPG or mixtures of PPGs at 80 °C. The mixture was stirred with anchor shaped stirrer at 250 rpm and 80 °C during 30 min in Heidolph overhead stirrer RZR-2000 (Kelheim, Germany). Then, 0.04 mmol of catalyst (DBTDL) was added and the stirring was carried out at 80 °C and 80 rpm during 2 h. The amount of free NCO in the prepolymer was monitored by dibutylamine titration. Once the desired free NCO content was obtained, the chain extender (BD) was added and the mixture was stirred at 80 rpm and 80 °C during 5 min. The NCO/OH ratio used was 1.10. Fig. 1 shows the scheme of the synthesis of the thermoplastic polyurethanes.

The nomenclature and composition of PU PSAs are shown in Table 1. In general, the hard segment content of the polyurethanes was low and it was varied by changing the molecular weight of the PPG and the composition of the mixtures of PPGs. As expected, the higher hard

segment content corresponds to the polyurethane made with PPG1000 and the lowest one corresponds to the one made with PPG2000. Intermediate hard segment contents were obtained in the polyurethanes made with mixtures of PPGs.

2.3. Experimental techniques

2.3.1. Attenuated total reflection infrared spectroscopy (ATR-IR)

ATR-IR spectra of the polyols and thermoplastic polyurethanes were obtained in Tensor 27 FT-IR spectrometer (Bruker Optik GmbH, Erlanger, Germany) by using Golden Gate single reflection diamond ATR accessory at 25 °C. In absorbance mode, 64 scans were recorded and averaged with resolution of 4 cm⁻¹ in the wavenumber range of 4000–400 cm⁻¹.

2.3.2. Differential scanning calorimetry (DSC)

The structure and thermal properties of the polyols and the thermoplastic polyurethanes were determined in DSC Q100 calorimeter (TA Instruments, New Castle, DE, USA). Hermetically sealed aluminum pans containing 10 – 15 mg of sample were prepared. All samples were heated from –80 to 150 °C under nitrogen atmosphere (flow rate: 50 mL min⁻¹) by using a heating rate of 10 °C min⁻¹. The first DSC heating run was carried out to remove the thermal history of the polyurethanes and the glass transition temperature (T_g) was obtained from the second DSC heating run.

2.3.3. Thermal gravimetric analysis (TGA)

The thermal degradation of the thermoplastic polyurethanes was assessed in TGA Q500 equipment (TA Instruments, New Castle, USA) under nitrogen atmosphere (50 mL min⁻¹). 5 – 10 mg of thermoplastic polyurethanes were placed in platinum crucible and, then, heated from 50 to 800 °C by using a heating rate of 10 °C min⁻¹.

2.4. Plate-plate rheology

The rheological and viscoelastic properties of the thermoplastic polyurethanes were determined in DHR-2 rheometer (TA Instruments, New Castle, DE, USA) in parallel plate–plate geometry. The gap selected was 0.40 mm, and 20 mm diameter stainless steel parallel plates were used. The linear viscoelastic region (LVE) of the thermoplastic polyurethanes was established by stress amplitude sweep experiments at 25 °C and frequency of 1 Hz by using a range of shear strains from 0.01 to 100%. In the region of linear viscoelasticity, the storage (G') and loss (G'') moduli of PU PSAs were measured at 25 °C by frequency sweep mode experiments, a strain amplitude of 2.5% in the angular frequency range from 0.01 to 100 rad s⁻¹ was used.

Furthermore, the viscoelastic properties of PU PSAs were measured by temperature sweep mode experiments from –20 to 120 °C, a frequency of 1 Hz and a heating rate of 5 °C min⁻¹ were used.

2.5. Probe tack

The probe tack of the thermoplastic PU coatings was measured at 10, 25 and 37 °C in TA.XT2i Texture Analyzer (Stable Micro Systems, Surrey, UK). PU coatings of 40–80 μm thick were placed on rectangular stainless steel 304 plates of dimensions 7 × 7 × 0.01 cm. Flat end cylindrical stainless steel probe of 3 mm diameter was used. The probe was brought into contact with the PU coating for 1 s under a load of 5 N. Then, the probe was pulled out at a constant speed of 1 mm s⁻¹. For each PU coating, five replicates were carried out and averaged.

2.6. 180° peel strength

Adhesion properties of thermoplastic PU coatings were determined by 180° peel tests of aluminum 5754/PU coating/polyethylene terephthalate (PET) film joints. Around 80 μm thick PU coating was placed

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