The influence of diol chain extender on morphology and properties of thermally-triggered UV-stable self-healing polyurethane coatings

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ABSTRACT

Two sets of waterborne polyurethane dispersions were synthesised from polycarbonate polyol with molecular mass of 500 Da and hexamethylene diisocyanate or isophorone diisocyanate. Formulations were prepared without a chain extender, with aliphatic diol with two to five carbon atoms or with diethylene glycol. Coatings were prepared on cellulose triacetate sheets, damaged by a steel-wool scratch instrument and left to heal at room temperature and at 60 °C. Self-healing efficiency was examined by comparison of haze before damage and at intervals after damage. Samples were analysed using Differential Scanning Calorimetry, Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy and Scanning Electron Microscopy. The tests were repeated after 12 weeks to investigate ageing of the polymers. Samples were also tested for their stability to weathering.

Optimally designed coatings obtained up to 100% recovery within 10 min at 60 °C and partial recovery at room temperature. The self-healing properties of coatings were found to be linked to macro-organisation of polymer chains caused by interactions between hard segments and soft segments of the polyurethane moiety, leading to phase-mixing, promoted by bulky, non-symmetrical isophorone diisocyanate, or phase-separation, promoted by linear, symmetrical hexamethylene diisocyanate. The length of chain extender was found to have large influence on formulations prepared with hexamethylene diisocyanate, increasing phase-separation and haze with the increase of chain length. Diethylene glycol was found to improve phase-mixing and self-healing properties of hexamethylene diisocyanate based materials. The influence of chain extenders was found to be minimal for isophorone diisocyanate based materials.

1. Introduction

The development of hard and efficiently self-healing (SH) transparent coatings has been a research goal of many scientists [1]. The use of such materials in electronic devices with touch screens or other surfaces sensitive to damage could improve the service life of such items and improve customer satisfaction.

Polyurethanes (PU) are one of the most attractive materials with potential for use as SH coatings. These polymers show unique physical and mechanical properties and are already being widely used as protective coatings, lacquers and varnishes [2]. Due to their internal structure, two phases can be distinguished – rigid, polar hard segments (HS), formed by isocyanate and chain extenders (CE), and flexible, non-polar soft segments (SS) formed by long chain polyols [3]. As the result of their polar nature, HS tend to attract each other, aggregate and form hydrogen-bonded blocks [4]. The resulting copolymer can be considered as composed of islands of HS with higher glass transition temperatures (T_g) dispersed in SS of lower T_g, acting as physical cross-links providing toughness and elasticity [5]. Phase-separation facilitates packing of polymer chains within each phase, leading to highly organised structures, increased crystallinity in both phases where appropriate, and consequently higher haze in coatings as light scatters from the HS domains and/or crystallites. On the other hand, favourable interactions between HS and SS will lead to phase-mixing of the polyurethane matrix (Fig. 1). Phase-mixed systems tend to be more amorphous with smaller domain sizes and lower crystallinity and thus lower haze [6,7].

The presence of non-covalent supramolecular interactions, such as H-bonds creating the secondary structure of PU, is known to enable self-repair properties of a damaged polymer matrix [8]. Cordier et al. designed and synthesised highly crosslinked (*via* H-bonding) materials that repeatedly healed, bringing together broken surfaces at room temperature [9]. The healing model was further studied and explained using computer simulations [10]. Clustering of H-bonded supramolecular rubber was investigated by Herbst et al. [11]. They suggested that the SH of fractures was explained by a dynamic behaviour of the
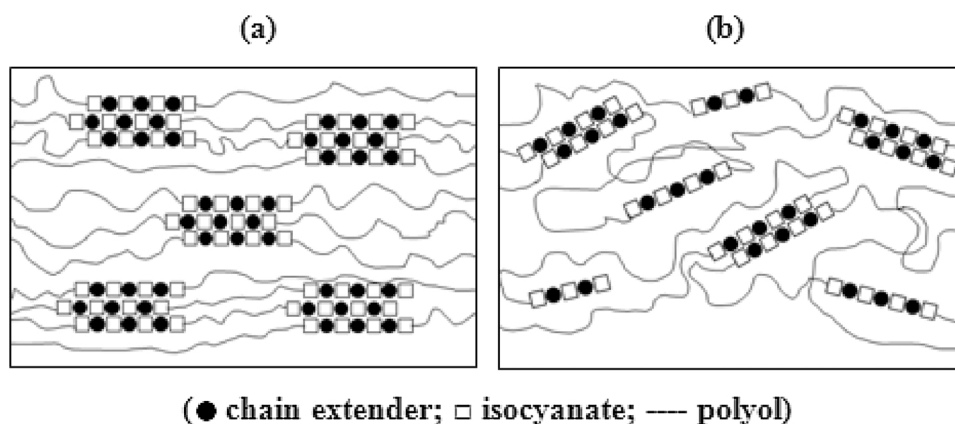
Fig. 1. Morphology of polyurethane matrix: (a) phase-separation and (b) phase-mixing.

network and thermoreversible aggregation and de-aggregation of supramolecular clusters. Moreover, Chen et al. reported that microphase separation of supramolecular moieties, obtained *via* supramolecular block copolymer architectures, induced SH behaviour [12]. In the novel, thermoresponsive material presented by Burattini et al. π-π stacking interactions, rather than H-bonding, led to formation of reversible network responsible for healable characteristics [13]. The thermal healability was further improved by combining π-π stacking interactions and interpolymer hydrogen bonding [14]. Later, Burnworth et al. presented rubbery metallosupramolecular polymers with non-covalent metal-ligand motifs converting a UV light energy into heat to quickly and efficiently dissociate and heal the defects [15]. Ghosh et al. observed lowering of T_g inside the scratch of damaged polymers, explained by a damage-induced chain scission and recombination reactions [16] and supported using molecular dynamics simulations [17]. Furthermore, rheological studies of supramolecular healing supported with reversible chemical disulphide bonds were reported by Grande et al. [18].

The phase-separation of PU [19] is dependent on the extent of H-bonds between the segments, as well as synthetic pathway and reaction conditions [20]. However, the key factor that influences the morphology of PU is the choice of molecular building blocks [6]. Phase-mixing was found to increase with a decrease of molecular mass of polyols by Eceiza et al. [21]. Garcia-Pacios et al. reported that lowering of the molecular mass of polyol led to an increase of coatings hardness and decrease of elastic modulus, T_g, gloss and yellowing index [22], while Lee et al. showed an increase of solvent swelling, emulsion viscosity and decrease of elongation at break [23]. Selim et al. and Gomez et al. reported that symmetric and linear diisocyanates, such as hexamethylene diisocyanate (HDI), promote crystallinity and phase-separation *via* long-range ordering of hydrogen bonds, while asymmetrical and bulky isophorone diisocyanate (IPDI) promotes phase-mixing [24,25]. In other studies it was observed that CE with even number of carbon atoms, with the exception of ethylene glycol, promote crystallinity and packing [26–28].

The relationship between morphology of PU and efficiency of SH was also studied in recent years. Ardjmand and Rad showed the influence of CE and isocyanate to polyol ratio on healing of automotive PU coatings [5]. The effect of molecular weight of PU and the amount of crosslinking on SH properties was explored by Kim et al. [29]. Gonzalez-Garcia et al. monitored thermal relaxation of SS during healing of damaged shape-memory PU coatings [30]. Additionally, a number of studies focused on improvement of supramolecular healing by introduction of reversible Diels-Alder crosslinks [31,32].

Despite all this previous research, there remains a gap in the understanding of the morphology and healing efficiency of protective coatings for optical applications. For such systems, there is clearly a need to also optimise clarity, bringing with it the need to further control the morphology. To the best of our knowledge, there are no studies reporting the influence of aliphatic diol CE on SH properties of polycarbonate-based transparent PU coatings. This article, therefore, reports syntheses of two sets of polyurethane dispersions (PUDs) prepared from copolycarbonate diol with HDI or IDPI. Coatings prepared without chain extender, with aliphatic diols with two to five carbon atoms or with diethylene glycol were investigated to evaluate their SH properties, pencil hardness and cross-cut adhesion. Additionally, polymer morphology analyses were performed using Differential Scanning Calorimetry (DSC), Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR FT-IR) and Scanning Electron Microscope (SEM), focusing on identification of the relationship between the diisocyanate, CE and SH performance.

2. Materials and methods

2.1. Materials

PH50, a copolycarbonate of pentanediol and hexanediol with MW of 500 Da (generously donated by UBS Industries), dried overnight in a vacuum oven at 80 °C, was used as the polyol. Hexamethylene diisocyanate (HDI, > 98%), isophorone diisocyanate (IPDI, > 98%), ethylene glycol (1,2-EG, 99%), 1,3-propanediol (1,3-PrD, 99%), 1,4-butanediol (1,4-BD, 99%), 1,5-pentanediol (1,5-PeD, 99%), diethylene glycol (DEG, 99%), dimethylol propionic acid (DMPA, 98%), dibutyltin dilaurate (DBTDL, 95%), and triethylamine (TEA, 99.5%) were purchased from Sigma Aldrich and used without further purification. Acetone (99%), distilled before use, was purchased from Sigma Aldrich. Additionally, deionised water was used as a dispersing phase.

2.2. Synthesis of the polyurethane dispersions

PUDs were prepared using the so-called *acetone process* [33]. Dry polyol (10 g, 20 mmol), DMPA (0.67 g, 5 mmol) and DBTDL (0.2 mL, 0.03 mmol) were placed in an oven-dried reaction vessel. 20 mL of anhydrous acetone and TEA (0.67 g, 7 mmol) were subsequently added. The mixture was stirred under nitrogen at 200 rpm for 30 min at 50 °C, after which the isocyanate (40 mmol for formulations with CE, 25 mmol for formulations without CE) was added drop-wise. Optionally, after 2–4 h CE (15 mmol) was added. The progress of the reaction was monitored by ATR FT-IR spectroscopy until a complete disappearance of NCO peak was observed. Subsequently, the mixture was cooled down to room temperature (RT), 30–50 mL of water was added and the solution was stirred at 600 rpm for 30 min to create polyurethane dispersion. Acetone was removed by rotary evaporation over 60 min at 50 °C and 300 mbar pressure.