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Preparation of a crosslinked coating containing fluorinated water-dispersible polyurethane particles

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ABSTRACT

The development of new polyurethane (PU) derivatives can readily enhance the properties of a diverse range of polymeric materials. Herein, we report a novel crosslinked coating matrix, which contains uniformly distributed fluorinated water-dispersible PU particles both on its surface and interspersed throughout its matrix. The desirable distribution of the functional particles results in a coating with outstanding transparency, liquid repellency, and adherence to various substrates. In addition, the coating provides the substrates with excellent corrosion resistance as well as a high degree of glossiness. The developed structural design is anticipated to give an inspiration for the functionalization of PU-based materials with applications in various fields.

1. Introduction

Polyurethane (PU) is one of the most versatile polymers with easily tailored properties such as elasticity and mechanical strength that can be readily altered by changing the polyol and isocyanate precursors [1–3]. These properties make PU a good candidate for coating materials, and thus many attempts have been made towards the structural modification of PU in order to fabricate desirable coatings for various applications [4–12]. In terms of the composition of previously reported PU-based coatings, ionic groups have been incorporated to provide environmentally-friendly water-dispersible PU (WPU) precursors [4,5], while silicone [6,7] or fluorine [8,9] units have been used to provide functionalized PU derivatives with a lower surface energy. Additionally, polyacrylate-based polymers (PA) have been chosen as combined components to yield hybrid coatings [10–12] exhibiting enhanced glossiness, as well as water and weathering resistance.

Although the PU-based coatings have been modified and progressively improved in recent years, there are still challenges that need to be addressed in order for the widespread use of these coatings to become a reality. For example, dried films prepared from WPU are generally water sensitive because they contain ionic groups [13,14]. In addition, the use of water as a solvent is known to weaken the adhesion of a coating to its substrate due to dewetting effects encountered during drying [15,16]. Due to the limited miscibility between PU and PA and the large degree of phase separation that occurs between the two polymers, the direct blending of PU with PA results in a less desirable product than would be predicted by the "rule of mixtures" [17–19].

In order to provide a possible strategy to overcome the issues described above, such as water sensitivity, weakened adhesion, and limited miscibility encountered with these modified coatings, a novel and highly practical heavily crosslinked fluorinated WPU matrix (CFWPU) was designed and is reported herein. The CFWPU was designed to contain uniformly distributed fluorinated WPU (FWPU) particles both on its surface and interspersed throughout its matrix, and the chemical bonding between the PU and PA components of the FWPU particles would significantly improve their miscibility. The incorporation of crosslinking chemistry is a well-recognized strategy to provide a particularly effective means of enhancing the water resistance and adhesion of water-borne coatings [20,21]. In addition, In addition, the crosslinked structure of the matrix could prevent any undesirable subsequent interactions from taking place and help to preserve the structural integrity of the nanostructures. To the best of our knowledge, there have been very

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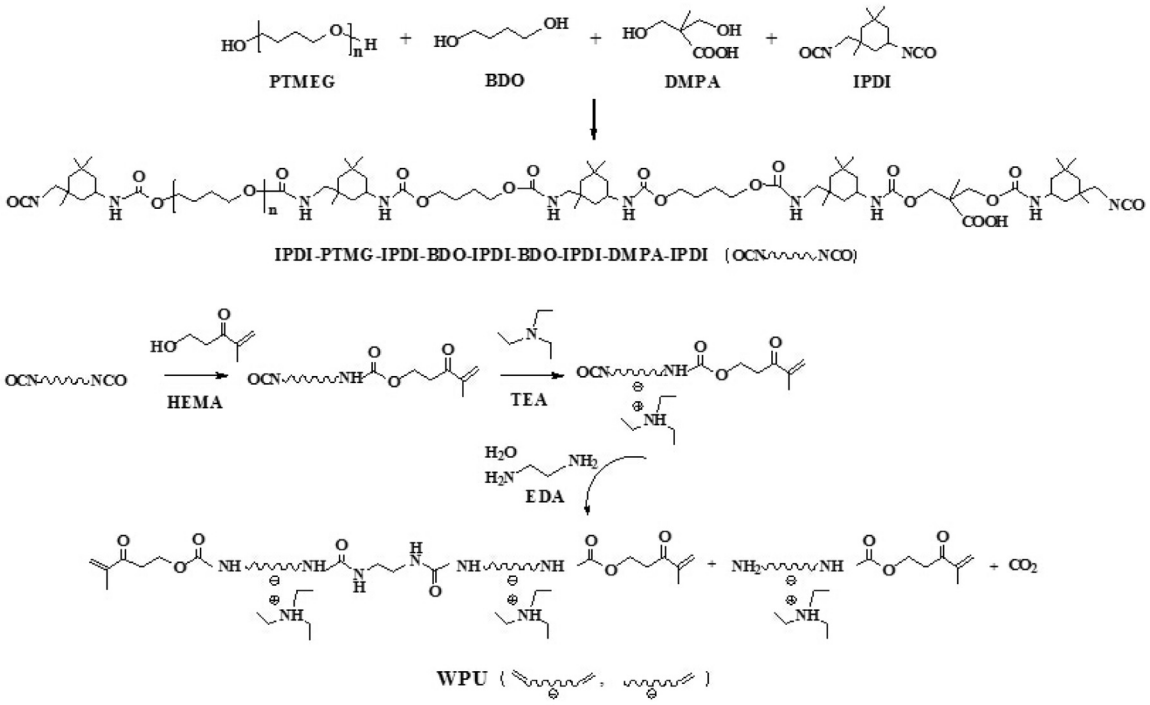
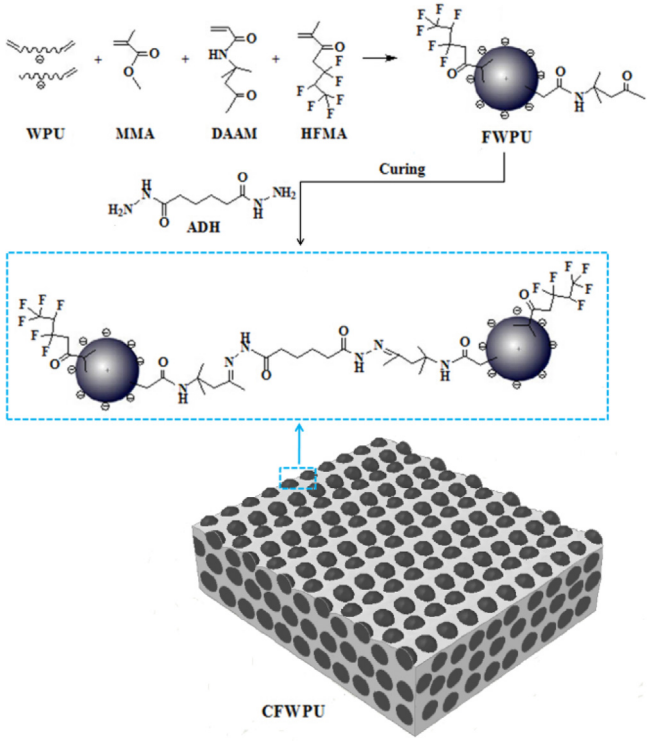


Scheme 1. Preparation of the WPU bearing vinyl groups.

few reports in the literature of the chemical bonding of acrylate-based monomers and low surface energy moieties to PU [22–25], and there have been no reports of heavily crosslinked PU coating matrices prepared from water-dispersible fluorinated precursors.

In the case of our WPU structure, Polytetramethylene ether glycol (PTMEG), 1,4-butanediol (BDO), dimethylol propionic acid (DMPA), and 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI) were used at the molar ratios of 1:2:1:5 in order to statistically obtain the IPDI-PTMG-IPDI-BDO-IPDI-BDO-IPDI-DMPA-IPDI precursor (Scheme 1). The double bond was incorporated by reacting this precursor with HEMA at a 1:1 molar ratio, in order to introduce vinyl groups at one end of the precursor. After the neutralization, half of the precursor chains were reacted with ethylene diamine (EDA) to fabricate an extended component bearing bifunctional vinyl groups at both ends, and the −NCO groups of the other half of the precursors bearing one vinyl group were also consumed by EDA. The bifunctional components allowed the linear polymer chains to branch, thus yielding a more rigid polymer network. For the preparation of FWPU, this rigidity hinders a healthy growth of the polymer particles, and the polymerization may fail when the bifunctional monomers are present or if they exceed a specific concentration [26,27]. Based on our experiments, the excess amount of the components bearing bifunctional vinyl groups (over 50 mol% with respect to WPU) would lead to an undesirable phase separation during the polymerization with the monomers of MMA, DAAM, and HFMA.

The synthetic pathway for the preparation of the FWPU and CFWPU is illustrated in Scheme 2. The moieties of the FWPU were selected for various reasons. For example, the poly(methyl methacrylate) (PMMA) components were incorporated to enhance the coating's transparency, since PMMA is a transparent polymer that is widely used in optical devices [28,29]. Dimethylol propionic acid (DMPA) was incorporated into PU to provide water-solubility and at the same time it allowed us to prepare the fluorinated WPU (FWPU) via surfactant-free emulsion copolymerization. Meanwhile, 2-hydroxyethyl methacrylate (HEMA) was chosen for its double bond that enabled the WPU to react with the other functional monomers. 2,2,3,4,4,4-Hexafluorobutyl methacrylate (HFMA) was selected as an environmentally friendly component with a low surface tension, and because of its ability to enrich the surface of the coating due to its low surface engergy [30,31]. Moreover, since the neighbouring particles should remain relatively free of crosslinks prior to their coalescence in order to achieve a thorough interdiffusion [32], diacetone acrylamide (DAAM) was chosen



Scheme 2. Preparation of the FWPU and the CFWPU.