Synthesis and Characterization of Novel UV-Curable PU-Si Hybrids: Influence of Silica on Thermal, Mechanical, and Water Sorption Properties of Polyurethane Acrylates

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Abstract: Organic-inorganic hybrid membranes (HM1-HM4) were synthesized by incorporating 3 wt% (HM1), 5 wt% (HM2), 10 wt% (HM3), and 20 wt% (HM4) of silica precursors into UV-curable polyurethane acrylate (PU) matrix using sol-gel technique. PU, which was prepared by reacting polycaprolactone triol (PCLT) and isophorone diisocyanate (IPDI), was used as the starting organic polymer whereas tetraethoxysilane (TEOS) was used as a precursor for the development of the inorganic phase. The completion of the polymerization reaction of PU and the synthesis of hybrid membranes were confirmed by Fourier transform infrared spectroscopy (FTIR) whereas the morphology was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The thermal, mechanical, and anti-water sorption properties of the hybrid membranes were examined by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), nanoindentator and thin film diffusion analysis, which revealed that HM2 has the highest thermal, mechanical, and anti-water sorption properties. TGA demonstrated that the thermal decomposition temperature $(T_{d10\%})$ of HM2 increased significantly, being 30 °C higher than that of pure PU, whereas DSC indicated that the introduction of 5 wt% of TEOS increased the glass transition temperature from 93.8 to 103 °C. Accordingly, the mechanical and water sorption properties were also enhanced greatly as evidenced by nanoindentation analysis and anti-water sorption data, in which HM2 shows the highest elastic modulus (8.354 GPa), hardness (0.262 GPa), and lowest water sorption capacity. These thermal, mechanical, and anti-water sorption improvements are important for the practical process and applications of PU.

Keywords: polyurethane, UV-curable, TEOS, hybrid membrane, sol-gel method, thermal property, mechanical property, water sorption property.

Introduction

In recent years, ultraviolet (UV) curing technologies have gained increasing interest due to their environmental safety, low energy consumption, high curing speed, cost efficient, low temperature and enhanced performance.¹ UV-radiation curable coatings represent a class of coatings with no or little volatile organic compounds (VOCs). In addition, the use of UV-radiation curable coatings offers many advantages such as instant drying, broad formulating range, reduced energy consumption, coating of heat sensitive substrate, and low space and capital requirement for curing equipment compared to thermally cured coatings.2

The increasing attention for UV coating and adhesive applications are due to the special molecular structures, such as a large number of end groups, compact molecular shape, decreasing chain entanglement, low melt, low viscosities and high functionalities.^{3,4} Added benefits of UVcurable materials such as fast curing speed, conservation of energy, high efficiency, and less pollution, have led to their increased uses in various industries such as paints, coating, adhesives, and inks.⁵⁻⁸ In the course of use, low viscosity and high curing speed are two important properties pursued for UV-curable oligomers.

Polyurethane acrylate is the most widely used UV-curable polymer as it has interesting physical and chemical proper-

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