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The phase mixing of moisture cured polyurethane-urea during cure

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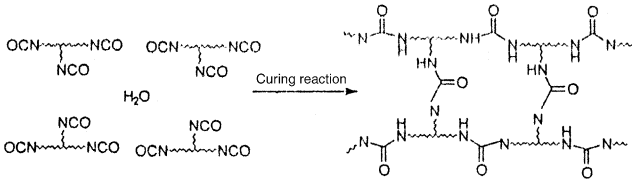
Abstract

Moisture cured polyurethane-ureas (MCPUs) is one of the industrially important polymer, which shows good thermal–mechanical and weathering properties and widely used in the reactive hot melt adhesives and coatings. In this study, chemically crosslinked MCPUs were prepared by reacting isophorone diisocyanate (IPDI) with polyethers like polytetramethyleneglycol (PTMG)-1000 and polyethyleneglycol (PEG)-1000, with NCO/OH ratio 1.6:1. Trimethylol propane (TMP) was used as a crosslinking agent during the prepolymer synthesis. The excess isocyanate of the prepolymers was cured with moisture at 25 °C and humidity of 40%. Fourier transform infrared spectroscopy (FTIR) and dynamic mechanical thermal analyzer (DMTA) measurements were used to monitor curing process of polyurethane-urea systems. Higher correlation coefficient (R^2) values were obtained for the second-order cure model compared to the first- and third-order for both the synthesized prepolymers.



The change in short range ordering associated with hydrogen bonding as well as decrease in crystallinity of soft segment during the phase mixing was observed from differential scanning calorimetry (DSC) measurements. The change in thermal stability was assessed by thermogravimetric (TG) analysis. Characterizations of the curing process provide an essential base to obtain best polymer.

The phase mixing phenomenon was confirmed from the angle resolved X-ray photoelectron spectroscopy (AR-XPS).

Keywords: Polyurethane prepolymer; Moisture cure; Soft segment; Phase mixing

1. Introduction

Moisture-curing technology is one of the viable alternatives in the use of low volatile organic component (VOC) in the coating industry. This type of coating is one of the finest one available that can be produced without the application of heat or other external energy source. The advantages of moisture-curing polyurethane/polyurea coatings have been summarized by Gardner [1]. First of all, they can be manufactured as a one-package system and their application is easier than the usual 2-K systems. Secondly, since the salient reactant is water, the formulations have less VOC than 2-K polyurethane coatings. In comparison of 2-K polyurethanes, the moisture-cured polyurethane/polyurea coatings have good adhesion, abrasion resistance, thermal stability, hardness, chemical and solvent resistance, and high humidity tolerance [2]. All of these properties are related and depend on the degree of cure. The excellent performance results primarily from the formation of crosslinks during cure. The process of curing defines the properties of the finished

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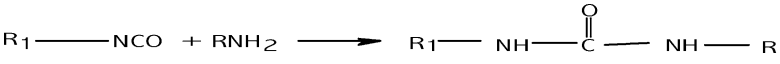
coating material. Temperature, humidity level and the state of cure are, therefore, key aspects for understanding and controlling the coating performance. Also the kinetics of cure allows one to develop a conversion profile at a particular temperature and relative humidity to assess the usefulness and relative importance of the different parameters leading to the final product.

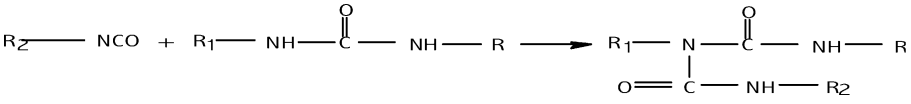
The MCPUs consist of isocyanate-capped low molecular weigh prepolymers prepared from polyester and or polyether glycols and diisocyanates. Water vapor from the atmosphere diffuses into the MCPU, and the nucleophilic attack of water on NCO-terminated prepolymer results in an irreversible reaction, which produces carbamic acid. The carbamic acid is unstable at room temperature and decomposes into carbon dioxide and a primary amine (1). The primary amine is reactive with the NCO-terminated prepolymer and produces urea (2). This reaction leads to the development of a three-dimensional network in the presence of a tri-functional monomer in the reactive prepolymers [3,4]:

$$R\text{–}NCO + H_2O \rightarrow R\text{–}NH_2 + CO_2\,(\uparrow) \quad (1)$$

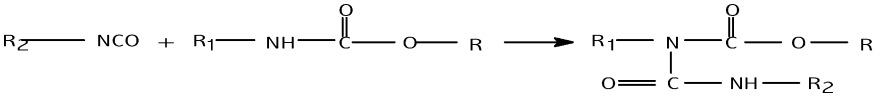


(2)

Crosslinking reaction are also possible between urea, urethane and residual isocyanates end groups that results in the formation of biuret (3) and allophanate (4) linkages.



(3)



(4)

However, Duff and Maciel [5] reported that, the predominant postcure process is due to the reaction of isocyanate group with atmospheric moisture to form an amine, which further condenses with an additional isocyanate group from the immediate vicinity to form a urea linkage. Cui et al. [6] reported that the presence of side products enhances adhesion. Biuret and allophanate are more thermally stable than the polyurethane/urea network as reported by Koscielecka [7] and Kordomenos et al. [8].

In moisture cured polyurethane, the chemical reactions that take place within the material occur much faster than the rate of water vapor diffusion. Thus, the material may quickly form skins after application and exposure to the air. This skin then acts as a barrier for the permeation of water into the remaining uncured material inside the bulk. Any water, which passes through the barrier layer quickly reacts with the uncured material and thickness of the barrier increases.

The kinetic investigation is probably the most active research because the rate and extent of crosslinking thoroughly affect the mechanical properties. As in the case of other thermosetting materials, the cure of NCO-terminated polyurethane prepolymer with moisture requires a careful control of processing conditions, in order to follow an adequate modulus and strength development, which are strictly dependent on parameters such as relative humidity, catalyst type and concentration, and excess isocyanate content in the prepolymer. So, the determination of cure conditions for such type of coating system is a prime prerequisite for developing custom tailored properties [9–14].

In the present study, the focus is on the cure behavior and modulus development of two-moisture cure formulations. Infrared spectroscopy was used for the quantitative evaluation of the extent of cure. Modulus measurements were carried out by DMTA. Thermal stability and calorimetric evaluation during cure was accomplished with TGA, and DSC instrument. The change in surface property during cure as well as with depth was evaluated through AR-XPS.

2. Experimental

2.1. Materials

Poly(tetramethylene glycol) [PTMG, M.W. = 1000], poly(ethylene glycol) [PEG, M.W. = 1000], trimethylol propane (TMP), isophorone diisocyanate (IPDI) and dibutyltin laurate (DBTL) from Aldrich (USA), 2-ethoxyethyl acetate, triethylamine and sulfur free toluene from S.D Fine chem. (Mumbai, India) were used. Solvents were stored over activated 3–4 Å molecular sieves.

2.2. Method

The resin kettle was equipped with a dropping funnel, stirrer, thermometer, reflux condenser and a nitrogen inlet.