



Phase morphology and surface properties of moisture cured polyurethane-urea (MCPU) coatings: Effect of catalysts

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ABSTRACT

Effect of catalysts on curing behaviour, phase morphology and surface properties of a moisture cured polyurethane-urea (MCPU) coating has been studied. The prepolymer, prepared by capping hydroxy terminated polybutadiene (HTPB) with isophorone diisocyanate (IPDI), was cured with moisture using different urethane catalysts at 30 °C and relative humidity of 60%. Fourier transform infrared spectroscopy (FTIR) was used to monitor the curing process. Gel fraction studies through solubility method, show catalyst induced shortening of induction period for gelation and increase in gel fraction. Effect of catalysts on phase morphology of the MCPU was evaluated by X-ray diffraction, small angle X-ray scattering (SAXS) and differential scanning calorimetry (DSC). The results show that the heat of fusion and interdomain distance of hard segments are influenced by the choice of catalysts. The effect on surface properties was evaluated by FTIR-ATR and contact angle goniometry. The type of H-bonding interaction was identified by deconvolution of the FTIR spectra. The results show that the surface polar group concentrations increase with increasing efficiency of the catalysts. Consequently there is a clear observation of catalyst induced surface energy changes of the MCPU.

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1. Introduction

Moisture cured polyurethane-ureas contain NCO-terminated polyurethane prepolymer [1], which on curing in the presence of atmospheric moisture produce highly crosslinked networks. MCPUs are widely used in the high performance coating applications as well as reactive hot melt adhesive industries. The advantages of one component polyurethane-urea systems have been summarized by Gardner [2]. First of all they can be manufactured as one package system and their application is easier. Secondly since the reactant is water, the formulations have less VOC than two component systems. In comparison to two component polyurethanes, the MCPUs have good adhesion, abrasion resistance, thermal stability, hardness, chemical and solvent resistance [3]. Further these materials adhere well to visibly damp surfaces as they penetrate into pores and tight crevices, where moisture is present. In order to obtain adequate modulus and strength development, the cure of NCO-terminated polyurethane prepolymer with moisture requires a careful control of processing conditions. The parameters affecting the cure process are relative humidity, isocyanate content in the prepolymer and catalyst type [4,5].

Phase morphology of segmented polyurethanes has been studied extensively by researchers [6–10]. The factors which influence

phase separation include segmental polarity difference [11], segmental length [12], crystallizability of either segment [13], intra- and intersegment interactions such as hydrogen bonding [13,14], overall composition and molecular weight [11]. Extensive phase mixing of soft and hard segments of PTMG/IPDI based MCPUs and their effect on surface properties are reported [15]. In comparison to segmented polyurethanes, the phase morphology studies on MCPUs have been relatively scanty.

The behaviour of the MCPUs at the surface and interfaces has a significant effect on various properties and plays a vital role in coating applications. The surface composition of multicomponent MCPUs during cure progress has been studied in detail by many researchers [16–18]. XPS studies have shown the enrichment in soft segments on the air-side surface of polyurethanes [19–21].

In the present study, hydroxy terminated polybutadiene capped with isophorone diisocyanate has been used as the prepolymer for MCPU formation. Effect of catalysts on curing, thermal properties, phase morphology and surface properties of MCPU have been studied.

2. Experimental

2.1. Materials

Isophorone diisocyanate (IPDI) from E-Merck was used as received. Hydroxy terminated polybutadiene (HTPB) (functionality 2.4, OH value 50) was purchased from ORION Chem Ltd., India.

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Dibutyltin dilaurate (DBTDL) was purchased from Fluka and used as received. Ferric chloride and triethyl amine (TEA) were purchased from S.D. Fine Chemicals, India. Triethyl amine was vacuum distilled before use.

2.1.1. Synthesis of prepolymer

The prepolymer from IPDI and HTPB was synthesized at 60 °C in a three-necked R.B. flask equipped with a mechanical stirrer. The molar ratio of NCO to OH groups was 2:1. The reaction was carried without use of any catalysts under a dry nitrogen blanket until the desired isocyanate content is obtained. Isocyanate content in the prepolymer was determined by titration with diethyl amine [22]. The NCO value was 3.48% compared to the theoretical value of 3.64%.

2.2. Preparation of films

The prepolymer was mixed with different catalysts (0.05 wt%) and the films were cast on a Teflon mould. The films were cured with moisture at 30 °C and 60% RH. The progress of curing was monitored by monitoring the decay of the isocyanate band by FTIR spectra. The time for complete cure for various catalysts were found to be 1120 h (unanalysed), 1080 h (FeCl₃), 930 h (TEA) and 820 h (DBTDL).

2.3. Characterization techniques

2.3.1. FTIR analysis

FTIR spectra of the samples were recorded using a PerkinElmer 1650 FTIR spectrophotometer with a resolution of 4 cm⁻¹ and 32 scans. Crosslinking for the one component system was followed by monitoring the disappearance of isocyanate band. In the FTIR analysis, integrated intensities of the absorbance bands were corrected for sample thickness differences using the CH₂ stretching band near 2980 cm⁻¹ as normalising factor.

For calculating the degree of curing it is assumed that there are no side reactions [11]. From the isocyanate conversion the degree of curing was calculated as follows

$$\text{Isocyanate conversion } (p) = 1 - \frac{A_t - A_\infty}{A_0 - A_\infty}$$

Where A_0 is the normalised area of absorption at the initial time, A_t is the normalised area of absorption at a certain time during the cure process, and A_∞ is the final normalised area of absorption at infinite time. For a completely cured system A_∞ will be zero, because no NCO functionality will be available for IR absorption in such a case.

2.3.2. Determination of sol and gel fraction

The sol and gel fraction of the MCPUs with progress of cure was evaluated by Soxhlet extracting the MCPUs with toluene. The sol fraction was determined using the following equation

$$\text{Sol fraction } (\%) = \left(\frac{W - W_1}{W_1} \right) \times 100$$

where W is the initial weight and W_1 is the weight of the sample after extraction

$$\text{Gel fraction } (\%) = 100 - \text{sol fraction } (\%)$$

2.3.3. TGA

The thermal stability of the polymer film with progress of cure was studied in Nitrogen environment using TA instruments Hi Res 2950 Thermogravimetric Analyser. The measurements were carried out from 30 to 800 °C at a heating rate of 10 °C/min.

2.3.4. Wide-angle X-ray diffraction

The crystallinity of the MCPUs was evaluated by using Cu K α ray of wavelength 1.54 Å between 10 and 30° at 0.2°/10 s in a Philips X-ray diffractometer.

2.3.5. SAXS

Small angle X-ray scattering, SAXS (Ariton Paar, Austria) experiments was performed on moisture cured polymer films using an X-ray source having wavelength 1.54 Å. The samples were scanned for 15 min at 25 °C. The scattering patterns were recorded using the collimation technique. The scattering patterns were integrated to generate an $I(q)$ versus q curve, where $I(q)$ is the intensity of the scattered X-rays and q is the scattering vector.

2.3.6. DSC

Calorimetric measurements of the completely cured MCPUs were carried out using TA instruments DSC Q-100, from -80 °C to 120 °C at a heating rate of 5 °C/min under nitrogen atmosphere. The instrument was calibrated with Indium standards before measurements.

2.3.7. FTIR-ATR

Attenuated total reflectance (ATR) analysis was carried out in a Thermocom Nicolet 5700 spectrometer with a horizontal flat plate ATR accessory. The ATR crystal was diamond with an end-face angle of 45°. The substrate-facing side of the polymer film was placed against the crystal and clamped into position. Each sample was scanned 100 times at a resolution of 4 cm⁻¹ and the scans were signal averaged. In ATR the depth of penetration for a non-absorbing medium, defined as the distance required for the electric field amplitude to fall to e⁻¹ of its value at the surface, has been given by Harrick [23].

$$d_p = \frac{\lambda}{2\pi n_1 (\sin \theta - (n_1/n_2)^2)^{0.5}}$$

Where n_1 is the refractive index of the sample and n_2 is the refractive index of the ATR element. Micebella and Harrick [24] has shown that sampling depth for polymeric materials is about three times d_p .

2.4. Surface energy analysis through goniometry

The surface free energies of polymer samples were determined by contact angle goniometer using a Kruss G10 goniometry interfaced to image capture software. The surface energy system measures and averages contact angles of various liquids and calculates the surface energy. Advancing (θ_A) contact angles were measured for droplets (2–10 μ L) of double distilled water and diiodomethane using the movable protractor scale of the goniometer. The spatial size probed (in the plane of the surface) was 1–2 mm in diameter. The images of three droplet liquids of each test liquid are taken by a CCD camera and the contact angles were determined using automated image analysis.

3. Results and discussion

3.1. Cure behaviour of MCPUs

Hydroxy terminated polybutadiene with a functionality of 2.4 has been used for prepolymer synthesis. Hence during the cure process a three dimensional network is formed without the aid of an external crosslinker. The evidence of a crosslinked network is apparent from the evaluation of the gel fraction by extraction of the MCPUs with toluene. Fig. 1 shows the effect of catalysts on cure time dependant gel fractions of the MCPU. From the results it is seen

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