

# Effect of catalyst type on film forming properties of moisture curing polyurethane prepolymer

<sup>1</sup>Altan A, <sup>2</sup>Esen HE, <sup>1</sup>Arca M and <sup>3</sup>Arca E

<sup>1</sup>Caran Kimya San. ve Tic. Ltd. Şti., Izmir, Turkey

<sup>2</sup>Vocational High School, BiruniUniversity, Istanbul, Turkey

<sup>3</sup>Faculty of Engineering Marmara University, Istanbul, Turkey

Corresponding author: aysun.altan@gmail.com

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## ABSTRACT

**Aim:** This study was aimed to investigate effect of catalyst type on curing behavior, morphology, mechanical and surface properties of a moisture curing polyurethane (MCPU) prepolymer.

**Method and Materials:** The prepolymer was prepared by the reaction of polypropylene glycol and methylene diphenyl diisocyanate (MDI). It was cured using 2-Dimorpholinodiethylether (DMDEE) and Dibutyltindilaurate (DBTL) at 25°C, and relative humidity of 45%. Fourier transform infrared spectroscopy (FTIR) was used to monitor the curing rate. Morphology of the MCPU was evaluated by tapping mode Atomic Force Microscopy (AFM). The results showed that the orientation of hard segments within the matrix of soft segments was influenced by the choice of curing catalyst.

**Results:** The effect of the catalyst on surface properties was analyzed by contact angle measurements and surface free energy (SFE) calculations. Elongation, tensile strength and elastic modulus measurements were performed in order to analyze the mechanical properties.

**Conclusion:** It was concluded that surface free energy and mechanical properties of MCPU differentiate depending on the type of curing catalyst.

**Keywords:** Catalyst effect, curing rate, mechanical properties, morphology, surface free energy, polyurethanes.

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## Introduction

Polyurethanes are segmented copolymers. Urethane bonds are formed by the reaction of isocyanates and polyols. Urethane blocks are called hard segments of the polyurethane chains and they are higher in polarity. Soft segments of the polyurethanes with lower polarity are formed by the polyol components (Szycher, 2013). It is possible to create polyurethane materials in enormous variety by changing the properties of hard and soft segments (Zhu et al., 2017, Nakamae et al., 1996, Ni et al., 2002, Miller et al., 1985, Sun et al., 2018, Gogoi et al., 2014 and Janik and Vancso, 2005). Isocyanates and NCO terminated polyurethane prepolymers can be cured by the reaction with active hydrogen containing materials including water. By taking the advantage of isocyanate-water reaction many moisture curing polyurethane (MCPU) systems are designed.

Isocyanates and NCO terminated polyurethane prepolymers can be cured by the reaction with active hydrogen containing materials including water. By taking the advantage of isocyanate-water reaction many moisture curing polyurethane (MCPU) systems are designed. MCPU is one of the significant type of polyurethanes for coatings industry due to their good adhesion, abrasion resistance, thermal stability, hardness, chemical and solvent resistance. All these properties are related to the morphology of the polyurethanes that is affected by structure, length, polarity of hard and soft segments. Distribution of hard and soft segments during curing process (Fig 1) has a crucial impact on morphology and thus performance parameters of polyurethane coatings (Szycher, 2013, Prisacariu et al., 2011, Jiang et al., 2018 and Rath et al., 2008). Formation of three dimensional polyurethane matrix and the interaction between the soft and hard segments change with curing in time (Zhu et al., 2017 and Lepene et al., 2002).

Curing time of MCPU can be altered by using catalysts. It is has been known that amine and

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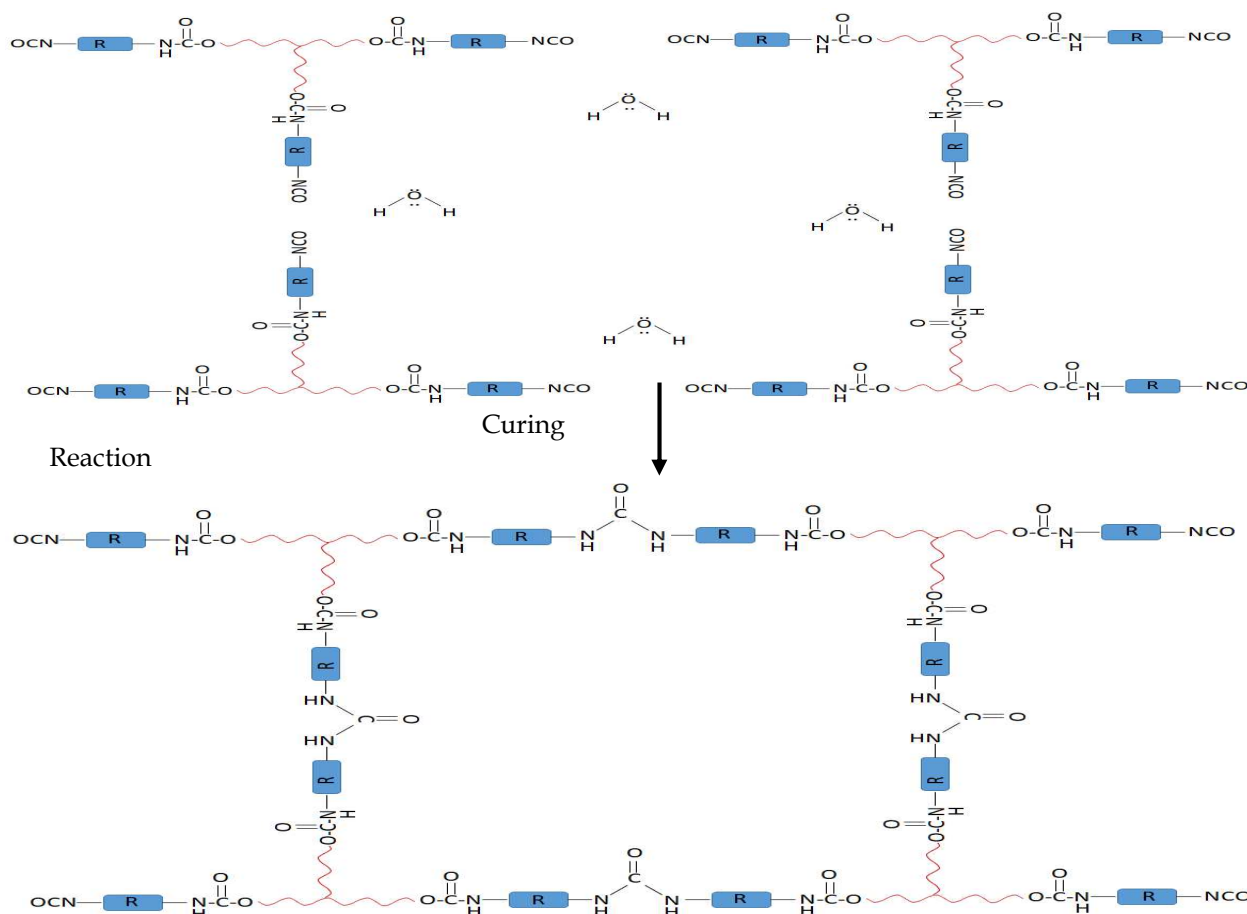


Fig 1. Moisture curing reaction of NCO-terminated polyurethane prepolymer

metal catalysts used to catalyze the reactions between isocyanates and active hydrogen compounds. There are many tertiary amine and tin catalysts available for carrying out the synthesis and crosslinking of MCPU (Szycher, 2013, Ning et al., 1997, Arnould et al., 2020, Gogoi et al., 2012 and Mukherjea and Saha, 1980).

The effect of metallic and organic catalysts on the cross linking rate and mechanical properties of polyurethane prepolymers was reported that the type of catalyst has an impact on chemical and physical network structure of MDI based moisture curing polyurethanes which are extended with inorganic fillers (Arnould et al., 2020).

It was investigated the impact of catalysts on curing behavior, phase morphology and surface properties of a moisture curing polyurethane prepolymer which is the reaction product of isophorone diisocyanate (IPDI) and hydroxyl terminated polybutadiene (HTPB). They suggested that the interdomain distance of hard segments are influenced by the choice of catalysts

and the polar group concentrations on the surface increase with increasing efficiency of catalysts (Prisacariu et al., 2011). The 2-Dimorpholinodiethyl ether (DMDEE; Fig. 2a) and Dibutyltin dilaurate (DBTL; Fig. 2b) were used to accelerate the curing rate of a polyurethane prepolymer, made up of methylene diphenyl diisocyanate and polypropylene glycol. The effect of the type and the amount of catalyst on the curing time of the prepolymer, mechanical and surface properties of the cured polyurethane films were studied.

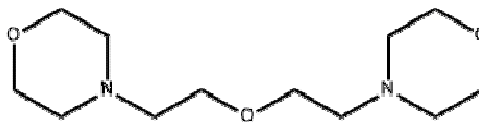


Fig. 2a. DMDEE

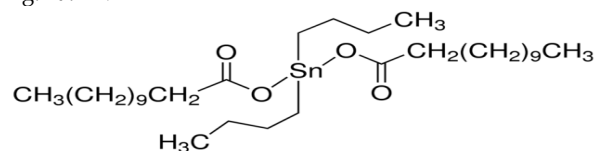


Fig 2b. DBTL

## Materials and Methods

The isocyanate was the mixture of 4,4'-methylene diphenyl diisocyanate and 2,4'-methylene diphenyl diisocyanate and purchased from Wanhua Chemical Group Co, Ltd. Two types of polypropylene glycols (MW: 2000 g, f: 2 and MW: 450 g, f: 3) were supplied from Shell Chemicals. The catalysts DBTL and DMDEE were purchased from Borchers and Huntsman Performance Products respectively. Materials were used without any further purification.

### Synthesis and Curing of Prepolymer

The prepolymer was synthesized under nitrogen blanket, at 60 °C, in 2L glass reactor with mechanical stirrer, temperature probe and nitrogen inlets. The molar ratio of NCO to OH groups was 1, 9: 1. The final NCO content of the prepolymer was determined as 3,52 % by the back titration of dibutylamine with normalized HCl solution. The titration method was applied in accordance with ISO 14896. Prepared prepolymer was cured with 0, 15 % DMDEE (Sample A) and % 0, 15 DBTL (Sample B) separately. Their curing rate was monitored with FTIR measurements.

### FTIR Analysis

FTIR analyses were carried out with Alpha II Platinum FT-IR Spectrometer with Platinum Diamond ATR (Bruker) in the optical range of 4000  $\text{cm}^{-1}$  - 400  $\text{cm}^{-1}$ , by averaging 12 scans.

### AFM Measurement

AFM measurements were performed in the tapping mode with Flex Axiom AFM from Nanosurf AG, Switzerland. Samples were scanned in the area of 50 X 50  $\mu\text{m}$  and the phase images were recorded in 2D and 3D.

### Surface Free Energy (SFE) Measurement

Static contact angle measurements of water, glycerol and liquid paraffin were performed by using a computer controlled homemade experimental setup which is equipped with a video camera. The measured contact angles and the surface tensions of the given liquids were used for the calculation of SFE of the cured prepolymers. SFE calculations were conducted with Matlab.

## Results and Discussion

The effect of catalysts on the curing rate of prepolymers was investigated with FTIR spectroscopy. The decreasing rate of the NCO concentration in the sample is an indication of the curing rate of the prepolymers. In order to analyze the change in the NCO amount in time, the area of

the FTIR absorption band which is attributed to NCO (Fig. 3) was integrated between 2220 and 2320  $\text{cm}^{-1}$  and interpreted in terms of percentage by using Equation 1.

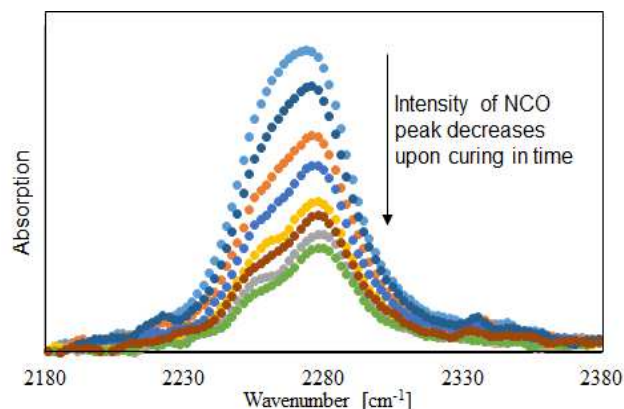


Fig 3. Changes in the FTIR absorption peak of NCO group during curing reaction

$$\text{Area (\%)} = [\text{Area}(t_0)/\text{Area}(t_n)] \times 100$$
 Equation 1  
where Area ( $t_0$ ) is the area of the FTIR absorption band of NCO at the initial time, and Area ( $t_n$ ) is the area of the same band at a certain time.

The change in the area of the absorption band of NCO group in 120 minutes for both systems was represented (Fig. 4). The decay profiles displayed that the concentration of NCO decreased linearly in Sample A while it was decreasing polynomially in Sample B in the same period of time. The equations and  $R^2$  values obtained from regression of these profiles were given (Table 1). From the slope of the decay graphs, it was observed that decreasing rate of NCO concentration in Sample B was higher compared to Sample A which means that film formation and viscosity gaining of Sample B was faster than Sample A.

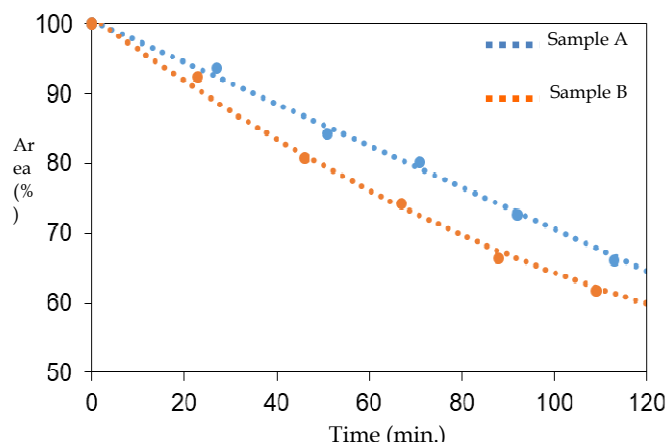


Fig 4. Change in the area of the absorption band of NCO group

Table 1. Regression equations and R<sup>2</sup> values for the decrease of the area of NCO peak

Sample	Catalyst	Regression Equation	R <sup>2</sup>
A	DMDEE	$y = -0.2984x + 100.48$	0.996
B	DBTL	$y = 0.0012x^2 - 0.4882x + 101.08$	0.995

The viscosity change rate affects the alignment of the hard segments within the systems. If the viscosity of the system builds up rapidly, mobility of the hard segments is hindered. The hard segments which cannot find enough time to diffuse away from the bulk are dispersed among the soft segments.

The differences in the distribution of the hard segments sample films were monitored with AFM imaging. In the AFM images, hard segments appeared as lighter areas and the rest represents the continuous matrix of soft segments (Pergal et al., 2013 and Chattopadhyay and Raju, 2007). The analysis of AFM images demonstrated that the hard segments of Sample A were aligned at specific areas. On the other hand, the hard segments in Sample B were dispersed more evenly within the soft segments. The difference in the phase morphology of Sample A and Sample B were relevant to their viscosity building up rate.

The mechanical and surface properties which were observed (Table 2 and Table 3) in accordance with the phase morphology of the samples monitored with the AFM images.

It was known that the mechanical properties of the polyurethanes were primarily dependent on the hard segment content (Szycher, 2013 and Chattopadhyay and Raju, 2007). Although Sample A and Sample B having the same composition except the type of catalyst, they indicated different mechanical properties (Table 2). The distinction between the mechanical properties of Sample A and B was associated with the degree of ordering of hard segments during the curing reaction. It

was proved with the AFM images, the hard segments of Sample B indicated higher segment mixing which makes it more resistant to mechanical stress resulting in higher elastic modulus and lower elongation values. Higher degree of ordering of hard segment in Sample A causes higher elongation and lower elastic modulus values.

Table 2. Mechanical properties of Sample A and Sample B

Sample	Tensile Strength at break [N mm <sup>-2</sup> ]	Elastic Modulus [MPa]	Elongation at break [%]
A	6	4.2	1042
B	6.1	6.5	785

Table 3. Surface free energy estimations of the polyurethane films (Sample A and B)

Sample	Surface Free Energy [mJ m <sup>-2</sup> ]			
	Fowkes	Owrk	Wu	Neumann
A	45.1	45.0	46.2	49.7
B	31.0	30.2	33.1	44.3

Since the surface free energy of the materials cannot be measured directly, models that based on the contact angle measurements have been proposed. In our study, glycerol, water and liquid paraffin were used for contact angle measurements. Fowkes, Wu, Owrk and Neumann models were employed for the surface free energy estimations.

It was noticeable that surface free energy of Sample A was higher than Sample B regardless of the calculation method. The surface energy measurement results were consistent with the analysis of AFM images. The polar hard segments of Sample A were available at the air interface of the film surface as detected on the AFM images that results in higher surface free energy. Surface free energy of Sample B was lower since the hard segments were dispersed in the matrix of soft segments away from the air interface.

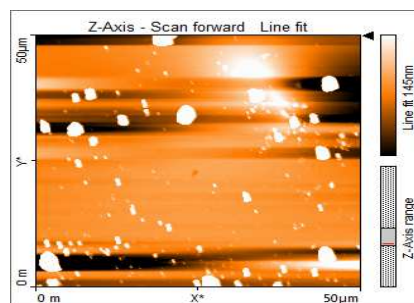
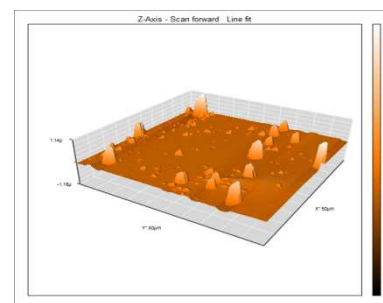
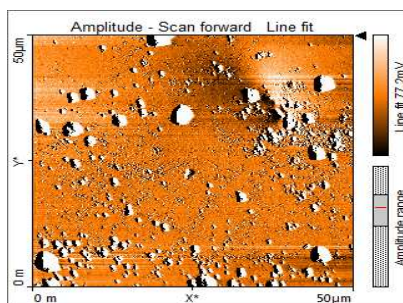


Fig 5a. AFM images of Sample A





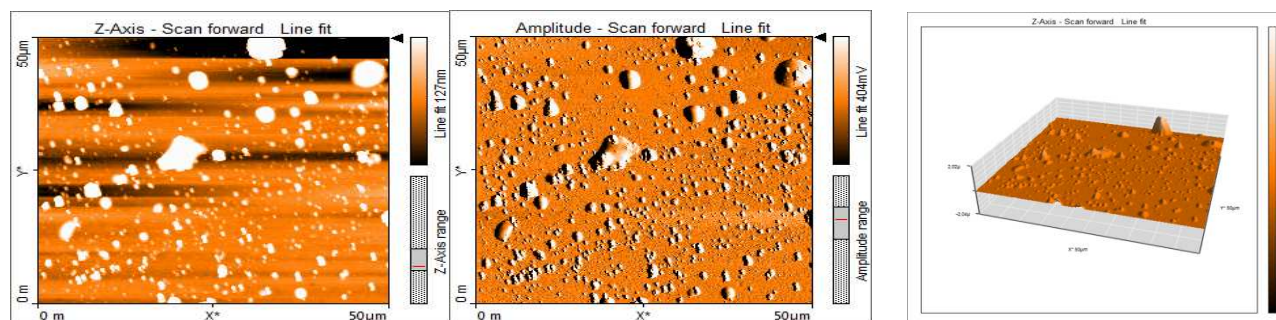


Fig 5b. AFM images of Sample B

## Conclusion

It was concluded that one of the most important factors affect the curing rate and the extent of cross linking of MCPUs is the type of catalyst. The choice of catalyst thoroughly has a crucial impact on the mechanical, morphological and surface properties of MCPU. While designing a MCPU system, it is a prerequisite to take into account the type of the curing catalyst in order customize the properties of the material.

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