Properties of Diamine Chain Extended Polyurethane Urea Coatings

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Abstract

An effort has been made to understand the structure property correlation with different chain extender structure. For these, different moisture cured polyurethanes were synthesized and partially chain extended with various aromatic diamines. The remaining excess isocyanates in the polyurethane matrix were reacted with atmospheric moisture. Viscoelastic properties of these cured films were determined by Dynamic Mechanical Thermal Analyzer (DMTA). The mechanical properties such as tensile strength, adhesion strength and hardness were related to chemical composition and cohesion of the hard segment. Angle resolved X-ray Photoelectron Spectroscopy (AR-XPS) was used to determine the surface properties. The combined analysis indicates the degree of phase separation is the cause for the overall macroscopic properties and is dependent on the chain extender structure.

Key-words : *Moisture cured polyurethanes, Hard segment structure, Mechanical, Adhesion and surface properties.*

1. Introduction

Moisture cured polyurethane (MCPU) is an attractive class of polymers which, through the variations of the hard and soft segments, can exhibit diverse physico-chemical properties and are widely used in the coating and adhesives industries. The attractive mechanical properties results from the microphase-separated morphology brought about by the partial mutual insolubility of different chemical sequences in the prepolymer. One microphase is the soft segment that derived from the macrodiol and imparts softness and extensibility and the other phase is the hard segment, which results from the diisocyanate/chain extender, provides cohesive strength to the polymer matrix and is relatively immiscible with the soft phase. Actually, this type of system forms tri-phase morphology, wherein the third phase arises from the interface of soft and hard segments. It is desirable to have the highest possible phase separation, but at the phase boundaries there is always a chance of partial phase mixing. The

morphology and mechanical properties of the diverse MCPUs are affected by several factors, such as polymerization conditions, nature and length of soft and hard segment, chemical constituents, molecular weight of the polymer, interfacial thickness, the amount of by-products like biuret, allophanate and the presence or absence of additional crosslinking etc.¹⁻¹⁰. The hard segment cohesion phenomenon is one of the important parameter that has to consider for developing a good protective coating and is the major concern in this investigation. The investigation of the mechanical properties of the MCPUs with respect to hard segment domain cohesion due to variation in composition would be important to tailor make the products with desirable properties. Two isocyanate-terminated polyurethane prepolymer based on PPG/TMP/TDI and PPG/TMP/IPDI was synthesized. In the second stage, the prepolymers were partially reacted with different aromatic diamines and the excess isocyanate was completely cured with atmospheric moisture. The paper correlates the structure property relationship in terms of hard segment domain cohesion.

2. Experimental

2.1 Materials

PPG-1000, TMP, IPDI (Z and E isomer in 3 : 1 ratio),

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Scheme 1. The structures of different diamines and diisocyanates used in the present study.

4-aminophenyl disulfide (DIS), 4,4'-diamino-diphenyl methane (MET) from Aldrich (USA), TDI (9 : 1 ratio of 2,4 and 2,6 isomer), 4,4'-diamino-diphenyl sulfone (SUL) from Fluka (USA), 2-Ethoxyethyl acetate and sulfur free toluene from S. D. Fine Chem. (Mumbai, India) were used. The structures of different diamines and diisocyanates used in the present study are shown in **Scheme 1**.

2.2 Preparation of NCO Terminated Prepolymers

NCO terminated oligomers were prepared from PPG in the presence of TMP and TDI/IPDI. 50 g polyether diol and 9 g TMP mixture was taken in 2-ethoxyethyl acetate and reacted at $80 \pm 2^\circ\text{C}$ with diisocyanate (NCO : OH ratio of 1.6 : 1) for six hours. Synthesized PPG/TMP/IPDI (Series 1) and PPG/TMP/TDI (Series 2) were chain extended with different aromatic diamines. The chain extension was carried out by reacting excess NCO groups (based on a NCO : OH ratio of 4 : 1) with aromatic diamines. The prepolymers were mixed with chain extenders and catalyst before casting the films. **Scheme 2** shows the synthesis, chain extension and curing of the MCPUs. Possible side product formation during synthesis as well as moisture curing is also shown.

2.3 Preparation of Free Film of Coatings

These prepolymers were coated on tin foil by using a power driven automatic applicator and were left for 3 months at 25°C and 40% relative humidity for complete cure. The cured coatings were placed in a clean mercury bath to amalgamate the tin substrate. The underside of the unsupported coating films was cleaned of mercury or amalgam adhering to it¹¹⁾. The free films with thickness 0.1–0.15 mm were used for tensile, dynamic mechanical and XPS measurements. In a similar way coatings were applied on Aluminium and MS panels and spin coated on metal discs (Al, MS and Cu). The samples were named as chain extender (as given in bracket in section 2.1) along with series number. Thus SUL-1 shows 4,4'-diamino-diphenyl sulfone chain extended polyurethane prepared from PPG/TMP/IPDI.

2.4 Test Procedures

Dynamic mechanical measurements were performed with a DMTA IV instrument (Rheometric Scientific, USA) in the tensile mode, at a frequency of 1 Hz and a heating rate of 3°C min^{-1} . The temperature range of study was from -60 to 150°C . The adhesion strength of coatings was determined by pull-off test (Microtech

Scheme 2. Synthesis, chain extension and curing of the MCPUs. Possible side product formation during synthesis as well as moisture curing is also shown.

Tensiometer, UK). The impact resistance and flexibility were assessed by falling weight (a 10.5 pound weight is allowed to fall from a height of 23 inches) and conical mandrel (Sheen Instruments, UK), respectively.

Pencil hardness was measured according to the test method of ISO 15184: 1998(E). Tensile properties were measured at room temperature using Universal Testing Machine (Shimadzu, Japan) with a crosshead

speed of 10 mm/min. Reported data are the average of five to eight measurements.

2.5 ESCA- Measurements

Electron Spectroscopy for Chemical Analysis (ESCA) is one of the most popular and useful techniques for analyzing the surface compositions of coatings. XPS probes a coating layer to a depth of about 7.5 nm. Angle resolved XPS is a technique by which a thin layer can be analyzed, with the sample tilted to change the angle of the surface with respect to the detector¹²⁾. At high takeoff angles, the detector will only collect the emitted photoelectrons and auger electrons from the shallow region near the surface. At small takeoff angles, the detector will collect electrons emitted from both the shallow region and the deeper layer. Therefore, with a change in the takeoff angle, a concentration depth profile can be obtained¹³⁾.

ESCA measurements were obtained on a KRATOS AXIS 165 X-ray Photoelectron Spectrometer instrument using monochromatic Al K_{α} radiation. Survey scan (0-1000 eV binding energy range) was used to identify the surface elemental compositions of MCPUs. High-resolution scans of the C 1s were obtained to provide chemical bonding details of carbon. The X-ray gun was operated at 15 kV voltage and 20 mA. Survey and high-resolution spectra were collected using 80 and 40 eV pass energy respectively. The pressure in the analyzer chamber was $\sim 1.33 \times 10^{-6}$ Pa. The C 1s of hydrocarbon was taken at 284.6 eV as an internal reference.

3. Results and Discussion

3.1 Dynamic Mechanical Analysis

The dynamic mechanical spectra of moisture cured polyurethane prepared from different diamine chain extenders are shown in Fig. 1(a)-(c). Fig. 1(a) shows that the polyurethane prepared from SUL chain extender of series-1 was more rigid and having more E' value at 25°C than the other two chain extended polyurethanes. Similar observation was also observed for the chain extended polyurethanes prepared from series-2 system (Fig. 1(b)). This phenomenon is due to the more polar nature of sulphone groups, which results in harder segment domain cohesion than the other diamine chain extended polyurethanes. In Fig. 1(c), the $\tan \delta$ vs. temperature plot of series-2 diamine chain extended polyurethanes are shown. Glass transition temperatures are generally defined as the temperature at which $\tan \delta$ reach the maxima. The hard segment T_g (Table 1) values were 100, 98.4 and 97.8°C for SUL-2, MET-2 and DIS-2, respectively. The presence of polar sulphone group in SUL-2 produces strong cohesive force and

results in selective hardening of hard segment, thereby reduce the segmental mobility. One more T_g that arises around 49°C, could be due to the mixed phase. From the value of $\tan \delta_{\max}$ i.e., the height of the mixed phase T_g supports the difference in phase separation of these polyurethanes. The $\tan \delta_{\max}$ values at the mixed phase/interphase of the evaluated systems were 0.09, 0.06 and 0.04 for DIS-2, MET-2 and SUL-2, respectively. Therefore, the height of the $\tan \delta_{\max}$ at the mixed phase T_g was less for SUL-2 and more for DIS-2. These observations suggest that the phase mixing is more for DIS-2, whereas phase separation is more for SUL-2. The polar nature of the sulfone group in SUL chain extended

Fig. 1(a)-(c) The representative E' and $\tan \delta$ vs. temperature curves of various diamine chain extended moisture cured polyurethane coatings.

Table 1 The coating properties of various diamine chain extended polyurethanes of series 1 and 2.

Coating	Series 1 (IPDI)			Series-2 (TDI)		
	SUL-1	MET-1	DIS-1	SUL-2	MET-2	DIS-2
$E' \times 10^{-8}$, [Pa.], 25°C	2.6	0.54	0.34	3.0	1.65	0.7
$E'' \times 10^{-7}$, [Pa.], 25°C	2.56	0.04	0.02	1.13	0.77	0.12
$E' \times 10^{-6}$, [Pa.], 80°C	3.52	3.26	3.0	27.6	19.2	17.2
$\nu_e \times 10^3$, mol/cm ³	0.4	0.37	0.34	3.14	2.18	1.95
$M_c \times 10^{-3}$, g/mol	28.04	29.75	32.77	3.5	5.05	5.64
T_g , °C	84.0	81.2	73.1	100.0	98.4	97.8
Tensile strength (Kgf/ cm ²)	290	278	263	270	238	215
% Elongation	150	136.4	128	130	110	107
Pencil Hardness	5 H	5 H	5 H	5 H	5 H	5 H
Impact Resistance	Pass	Pass	Pass	Pass	Pass	Pass
Flexibility 1/16"-Conical Mandrel	Pass	Pass	Pass	Pass	Pass	Pass
Adhesive Strength (Kg /cm ²) Mild Steel Copper Aluminum	157.9	140.3	140.3	140.3	122.8	122.8
	105.3	87.7	87.7	80.7	70.2	70.2
	70.2	52.6	52.6	59.6	45.6	45.6

polyurethane enhances the hard segment segregation phenomenon and as a result the hard segment cohesion.

3.2 Determination of Crosslink Density, ν_e and M_c

The E' values in rubbery region at $T > T_{gH}$ are taken to calculate ν_e by using equation (1) and M_c (weight of sample in grams which contains one mole of elastically effective network chain) was calculated by using equation (2)¹⁴⁻¹⁶ :

$$\nu_e = E' / 3 RT \quad \text{.....(1)}$$

$$M_c = \rho / \nu_e \quad \text{.....(2)}$$

where, R is universal Gas Constant, T is temperature ($T > T_{gH}$) and ρ is the density of coating films. Density values were determined experimentally by displacement method (found to be in the range of 1.04-1.17 g/cm³ of all the coating films). Crosslink density is an important parameter that has to consider while developing a good protective coating. In general a coating with high ν_e is brittle, while for a coating with low ν_e , the premature failure may occur due to environmental stress or fatigue that generate while servicing. Therefore the coating formulator should design a coating by considering different parameters.

From Table 1, we can say that the E' (at 25°C) of series 2 coatings were higher than series 1 coatings for the same chain extender. The ν_e values of coatings prepared from IPDI lies in between $0.4-0.34 \times (10^{-3} \text{ mol/cm}^3)$, much less than those prepared from TDI ($3.14-1.95 \times 10^{-3} \text{ mol/cm}^3$). Since in the pre-polymer-

ization step, the reaction was continued for six hours in absence of any catalyst for both the PPG/TMP/TDI and PPG/TMP/IPDI system ; therefore it is expected that TDI based MCPUs contains more urethane bonds due the high reactivity of TDI than IPDI and MCPUs prepared from IPDI contains more urea bonds. Again more polar nature of urea bond than urethane bond, possibly produce more hydrogen bonding association and enhancement in the hard segment domain cohesion should possibly leads to more E' (at 25°C) for IPDI based coatings than the TDI based MCPU coatings. But the observed reverse trend in E' (at 25°C) and crosslink density is due to the possibility of formation of side products like biuret and allophanate, which is more for TDI based system due to its more reactive nature than IPDI based MCPUs¹⁷). The side product formation may takes place during the prepolymer synthesis as well as during solid state network maturation.

3.3 Tensile Properties, Hardness, Flexibility and Impact Resistance

The degree of phase separation and the orientation of the phase-separated domains inside the polymer matrix control the mechanical and tensile properties of MCPUs. The elasticity, toughness, hardness and other physical properties of these materials are determined largely by the size, crystallinity, and interconnectivity of the hard domains i. e., hard domain cohesion as well as the nature of the domain interface and the amount of

mixing of the hard segment in the soft segment¹⁸⁻¹⁹. The tensile behavior generally depends on the size, shape, and concentration of the hard domain, intermolecular bonding within the hard domains, and the ability of the soft segments to crystallize under strain. Generally two factors can enhance the toughness and plastic character of two-phase polyurethanes i. e., the interconnectivity and crystallinity of the hard segment domains²⁰. The tensile strength, percentage elongation and modulus values are reported in Table 1. The tensile strength values of SUL-1, MET-1 and DIS-1 were 290, 278 and 263 Kg/cm² and % elongation values were 150, 136.4 and 128 respectively. This value clearly shows that the tensile strength as well as % elongation was more for SUL-1 and less for DIS-1. Similar observations were noted for series-2 system also. It is the sulphone groups that selectively increases the cohesion of the hard domains and thereby dramatically modify the tensile properties while comparing other diamine chain extended polyurethanes.

The general comparison of the effect of diisocyanate structure on tensile properties from the reported data suggests that IPDI generate more flexible films than TDI based systems. This phenomenon is due to the cycloaliphatic and aromatic structure of IPDI and TDI, respectively. The pencil hardness, flexibility and impact resistance tests are not quantitative and give qualitative indication about the hardness and toughness of the system. It was observed that hardness was in the range of 5 H. All the samples passed the flexibility and impact resistance test.

3.4 Adhesion

The adhesion of coatings to a particular type of substrate is an important property and knowledge of it helps in assessing the performance of coatings in service. Therefore it is essential to know the adhesive behavior between the substrate and the macromolecules, and according to that the coating chemist should formulate a coating that protects the substrate in a better way. There are many factors that are responsible for adhesion of the coating. It is the substrate-induced crystallization at the metal polymer interface that has taken place during the curing of the MCPU matrix on the substrate (MS, Cu and Al). Even the smoothest surface contains impurities or nano-defects like tiny cracks, hills, craters etc., which accelerate the nucleation phenomenon and crystallite growth easily takes place on the nucleated sites. It is the higher surface area of these active sites on the metal surface that accelerate surface segregation. The hard segments aggregate closer to the interface at the substrate surface and form the crystal domains and soft segments

migrate to near the air surface²¹⁻²². Therefore it is the surface segregation phenomenon that is responsible for the high adhesive strength of these materials, and it is the mobility of hard segment and its polarity that form the chelate with the metals at the surface and cohesive energy density inside the hard domain determines the adhesive strength. The adhesion strength of SUL-1 on MS, Cu and Aluminum were 157.9, 105.3 and 70.2 Kg/cm², was much higher (Table 1) than the other chain extended polyurethanes. This was due to the increased cohesive energy density and chelating effect of the polar sulphone group. The other observation from this study was the change in adhesive strength with the substrate and it was higher for MS and lower for Aluminum. This phenomenon could be attributed to the susceptibility of corrosion of the measured substrate, which is more for MS and less for Aluminum. Since the formation of iron (III) oxide takes place easily at the active sites on the metals like defects, craters, cracks, fewer crevice, hills etc. than CuO or Al₂O₃, the adhesive bonding on the MS will be much more, because the number of active sites which are responsible for enhancing the hard segment nucleation and segregation phenomenon and as a result, cohesive energy density for a particular polymeric materials is more for MS. Here corrosion enhances the number of active sites for MS. One more observation from adhesion study was that the IPDI based polyurethane showed higher adhesion than TDI based polyurethane.

3.5 ESCA-Analysis

In the survey spectra, the peaks at 535, 400, and 285 due to oxygen (1s), nitrogen (1s), and carbon (1s), respectively were observed. Tin contamination on the surface was observed due to casting film on tin foil. Fig. 2 shows high-resolution C 1s spectra of PPG/TMP/IPDI moisture cured polyurethane at takeoff angle 0 and 80 degree. High-resolution spectra of the carbon signal shows an envelope that can be curve fitted into a series of peaks corresponding to different

Fig. 2(a) and (b) High-resolution C 1s of PPG/TMP/IPDI at takeoff angle 0 and 80 degree, respectively.

functional groups. The C 1s spectra were resolved into three sub-peaks centered at 284.6 eV, 286.2 eV and 289.0 eV, representing aliphatic or cycloaliphatic carbon atoms bound to hydrogen or carbon atom ($\underline{\text{C}}\text{-C}$ and $\underline{\text{C}}\text{-H}$), etheral carbon ($\underline{\text{C}}\text{-O}$), and carbonyl carbon ($\underline{\text{C}}\text{=O}$), respectively. While curve fitting, we have considered $\underline{\text{C}}\text{-O}$ and $\underline{\text{C}}\text{-N}$ are having similar chemical shift with respect to $\underline{\text{C}}\text{-C}$ peak.

The $\underline{\text{C}}\text{-O}$ peak arises from the PPG soft segments, and higher intensity of this peak with increasing takeoff angle suggests that, etheral carbons preferentially reside towards the surface. The decrease in peak intensity of $\underline{\text{C}}\text{=O}$ peak with increasing takeoff angle suggests that urethane and urea groups segregate toward the bulk of the polymer^{23–25}. The high resolution O 1s XPS spectra (Fig. not shown) are consistent overall with the C 1s profiles, and are comprised mainly of $\underline{\text{C}}\text{-O}$ (531.5–532.5 eV) and in $\underline{\text{C}}\text{=O}$ moieties (532–534 eV). These experimental investigations confirmed the segregation behavior of hard segments towards the bulk and away from the surface^{26–28}. Similar observation was made for the other chain extended MCPUs.

4. Conclusions

In this paper, two series of NCO terminated polyurethane prepolymers were prepared and chain extended with various diamine chain extenders, and the structure to hard segment domain cohesion and degree of phase separation was compared for the completely cured coatings. The dynamic mechanical properties showed that polyurethane containing sulphone groups in the hard segment was more phase separated and showed good tensile and mechanical properties. It was observed that IPDI based polyurethane gives more adhesion on metals than TDI based MCPUs, whereas TDI based coatings generate more hardness and having more crosslink density than IPDI based MCPUs. The surface segregation phenomenon was observed from ESCA analysis. From a practical point of view, this result opens new possibilities for the paint formulator to improve the performance and the durability.

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ジアミン鎖伸長ポリウレタン尿素樹脂塗膜の特性

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要 旨

本研究では、異なる鎖伸長剤構造とその構造特性との関係を理解することを目的とした。この目的のため、異なる湿気硬化形ポリウレタンが合成され種々の芳香族ジアミンにより部分的に鎖伸長が行われた。ポリウレタンマトリックス中の過剰未反応イソシアネートは大気中の水と反応した。これらの硬化塗膜の動的粘弾性を DMTA により測定した。引張強度、接着強度、硬度などの機械的性質はその化学組成と剛直セグメントに依存した。角度可変型 X 線光電子分光分析により塗膜表面の性状をしらべた。これらの結果から、相分離の程度は塗膜全体の巨視的性状を決定し、また鎖伸長剤構造に依存することが示唆された。