



Trends in
**Applied Sciences
Research**

ISSN 1819-3579



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Automotive Clear Coat Polyurethane (Desmodur Z4470+Different Desmophen) with Respect to Some Physical and Self-healing Properties

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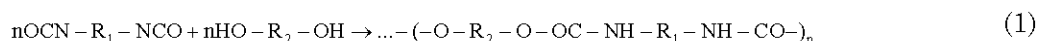
ABSTRACT

Desmodur Z4470 having isocyanate group was used to find optimum formulation of Polyurethane (PU) having self-healing property, with different desmophens as polyalcohol: desmophen 670 BA, desmophen 1800 and desmophen A 665 both in the present and absent of ethylene glycol as the chain extender agent. The obtained results showed that a hard polymer coating is obtained using desmophen A665 polyalcohol in the absence of any chain extender, however a corrosion resistant and transparent coating is obtained using desmophen 1800 and a ratio of NCO/OH = 2 for prepolymer formation stage and NCO/OH = 0.85 in polymerization stage by adding proper amount of ethylene glycol. This obtained PU shows the best self-healing properties.

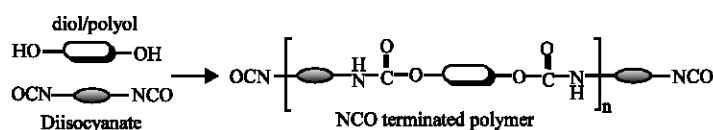
Key words: Polyurethane, self-healing, desmophen, chain extender, pre-polymer

INTRODUCTION

Polyurethane are manufactured by polyaddition process where a di-or poly-isocyanate and two or multi-functional polyols having a hydroxyl group at the end side of the molecule are the main elements of PU structure:



Using a multistage manufacturing process in PU production, where the reaction ingredients are added and mixed in different stage, different structures of produced polymeric chains were obtained (Azizi *et al.*, 2011). In most cases, a prepolymer is synthesized and the additional amount of one main reactant (polyol or polyisocyanate) is reacted at later stages (Piotr, 2007). For example using excess amount of isocyanate (B) in reaction with stoichiometric polyol (A) will produce a prepolymer having NCO group at the tail as shown at scheme 1:

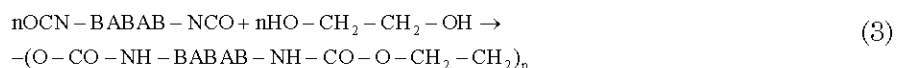


Scheme 1: PU prepolymer preparation

Such groups are linked to each other at the later stage by chain extenders producing urethane groups. On adding a polyol to a polyisocyanates, the mole fraction of reactants will determine the size of formed polymer molecule:



The synthesized urethane-isocyanate pre-polymer either in BAB or BABAB form, will reacted with low molecular weight diols such as ethylene glycol to produce larger macromolecules having greater molecular weights:



Self-healing property of PU: PU elastomers recover their original shape due to the action of cross chemical and/or physical links, i.e., the reaction of isocyanate and chain extender produce rigid sections in the molecular structure, such section which have isocyanate functional groups at their ends, are linked to the polyols which form soft section by chemical reactions. As a result, a block copolymer is formed. After forming hard section, their molecular interactions occur by hydrogen bonding. Due to this interaction, the hard sections are positioned beside each other and a secondary structure of both soft and hard sections is formed. The formation of hard and soft phases depends on incompatibility of both hard and soft parts, as well as that of hydrogen bonding between hard parts. The symmetry of isocyanate molecule helps to have a compact structure on positioning the hard block besides each other. In this way, the formed PU is composed of hard sections which are floated in a soft phase. The molecular motion in PU elastomer also depends on the phase separation of hard and soft sections. Kang and Stoffer (2000) and Chu *et al.* (1992) have studied the effect of thermodynamic properties on PU formation. PU obtained from aliphatic diisocyanates has shown less separation in comparison to that of aromatic diisocyanates and they represent no evidence of kinetic parameters. The effect of kinetic parameters on PU production were studied by Trevino *et al.* (2008) and Liaw (1997). The microphase separation on polyether PU production occurs by stronger interactions between ester and urethane group (Liaw, 1997). More separation was observed for PUs with low molecular weights. The phase separation in PU elastomer increases by cross linking (Desai *et al.*, 2000; Eceiza *et al.*, 2008).

Automotive coating by PUs: PU coatings are shiny, clear and strong against abrasion and corrosion and are widely used in overcoating of automobiles. It has high mechanical strength at ambient temperatures and shows elastic properties at higher temperatures and self-healing characteristics (Sonntag, 2009).

In two component PU coatings, so called 2K-PUR, the applied components have a lower viscosity in comparison to that of other PU's and hence they need less amount of solvent used for coating formation and more environmental friendly character. The overcoat determines the final strength of the coating against scratch where this layer has a thickness of 40 microns, only. This protecting can be taking place at the temperatures between +70 to -30°C using UV radiation as well as high humidity.

EXPERIMENTAL

Material and instrument: Commercial grade polyols are obtained from Bayer Company (Germany) under different types of desmophen trade mark, including desmophen 670 BA, 1800 and A665 BA, respectively. Desmophen 670 BA is the 80% solution of polyester polyalcohol in buthyl acetate, while desmophen 1800 is a polyester polyalcohol without any solvent with average viscosity of $21,500 \pm 2,500$ mPa.s and desmophen A 665BA is polyacrylate polymer with hydroxylic group prepared as the 70% solution in butylacetate solvent. Commercial grade polyisocyanate was obtained from Bayer company (Germany) under the trade mark of desmodur N 3800 which is hexamethylene diisocyanate trimmer (an aliphatic polyisocyanate). Analytical grade ethylene glycol (99.9% pure) was obtained from Merk (Germany) and used as the chain extender agent to improve elastomer property of PU. Ethyl methyl ketone (99% pure) and benzene chloride (99.5% pure), were obtained from Merk (Germany) and Fluka (Swiss), respectively and used as solvents.

PU is synthesized in a 500 mL Pyrex balloon having three inlet equipped to a thermometer and blanketed by nitrogen and water bath was used to maintain reaction mixture at 80°C . A magnetic mixer and electrical heater were used for mixing and heating the reaction mixture. IFS-88 model FTIR (Brooker Co., Germany) used to determine the end point of polymerization reaction using CaF_2 liquid cell and CCl_4 solvent.

Determination of polymerization reaction time: To determine the time for complete polymerization reaction of PU formation, desmophen (having OH group function), desmodur (having NCO group function) and ethylene glycol were reacted at $r = \text{NCO}/\text{OH} = 0.85$ and FTIR spectrums for different time intervals were obtained and NCO absorbance values are obtained at $2265/\text{cm}$ wave length. After 5 h, NCO absorbance decreases as a significant of trace amount of remaining NCO functional group in the solution phase. Complete conversion of NCO groups takes more time. To ensure the complete reaction of NCO groups all samples were left in reaction condition for 7 h for PU formation.

Quality assessment of the polymer coating: The pendulum hardness rocker counter (Persoz 240, Italy) was used to measure the hardness of polymer coating. It is equipped to a 500 g pendulum and the ball of radius of 8 mm with a quadratic frame and vibration angle of 12 degrees. Micro-TRI-gloss (200IR, Iran) equipment with a radiation angle of 20 degrees was used to shiny measurement.

Measurement of self-healing capacity: The self healing test was designed and applied in the present study based on measuring the preservation of the brightness of the surface after scratching. The more brightness preserved after scratching means the more having the self healing capability of the coating. Taking into account the average value of the coating brightness (light transparency) before and after scratching, the Self Healing Index (SHI%) is defined as:

$$\text{SHI}\% = \frac{\text{Average value of the coating brightness (light transparency) after scratching}}{\text{Average value of the coating brightness (light transparency) before scratching}}$$

The index varies between 0 to 100%. The higher value of the index means the more the selfhealing character of the coating.

RESULTS AND DISCUSSION

Desmodur Z4470 was selected as the isocyanate agent in all the studied cases and different polyols including desmophen 1800, 670 BA and A665 were added to desmodur Z4470, respectively. The obtained PU coatings were applied to the standard plates and tested under the same conditions for polymer formation, i.e., for all polymers ethylmethyl ketone was used as the solvent and the polymerization reaction time was 7 h at 80°C where NCO/OH was adjust at 0.85 which is the common value used in different coating technologies (Jacobs and Yu, 1993).

At the beginning of the polymerization reaction the ratio is different but by adding ethylene glycol as the alcoholic agent (C.E.) the NCO/OH value is adjusted at 0.85. Three different experiments were carried out for each set of selected desmodur and desmophen pairs: (i) the proper masses of the two components were selected to adjust the stoichiometric ratio without adding any chain extender (C.E.) agent, (ii) desmodur/desmophen ratio was selected as 2 to form a pre-polymer after 2 h and followed by adding the chain extender agent to adjust NCO/OH at 0.85 and (iii) desmodur/desmophen ratio was selected as 3 and the chain extender was added according to (ii).

Hardness test: The results of this test are shown in Fig. 1.

The hardness of the resulted polymers is increased as the applied polyol changed from desmophen 1800 to 670BA and A665. Also the hardness is increased when no chain extender is used and the NCO/OH ratio was adjusted to 0.85. In addition, on preparing the pre polymer, the more the ratio of desmodur/desmophen the more the hardness of the formed polymer is resulted.

The more ratio of NCO/OH before pre polymer formation means the more ethylene glycol should be used to adjust the ratio at 0.85. In other words there are more dialcohol groups in the polymer structure than polyalcohol groups. The polyalcohols are responsible to form the soft sections of the final polymer and by increasing the size of the polyalchol, the resulting polymer become softer. In contrast the more the amount of ethylene glycol used will yield hard and tough polyurethane and hence the poor self-healing characteristics of resulted polyurethane. The minimum level of approved hardness is 180 s based on Iranian standard protocols for automotive coating. These results is on adapted by some similar works about PU (Simon *et al.*, 2006; Togay *et al.*, 2009).

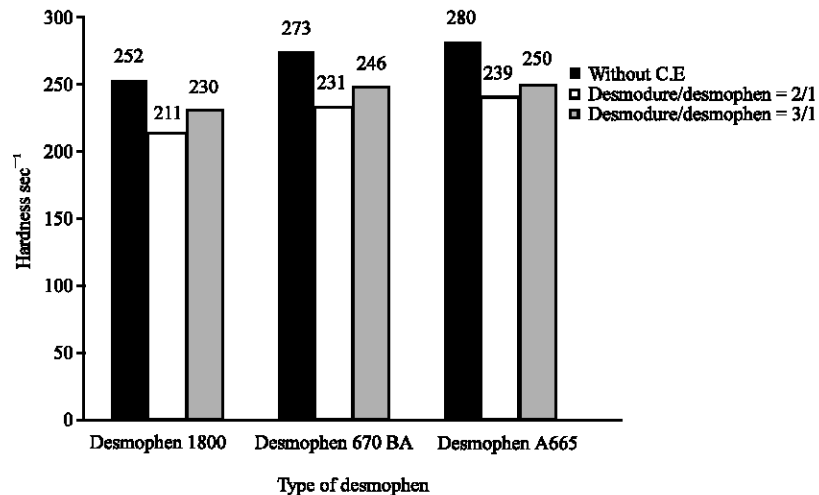


Fig. 1: The hardness of different polymers obtained by reacting desmodur Z4470 and different polyols

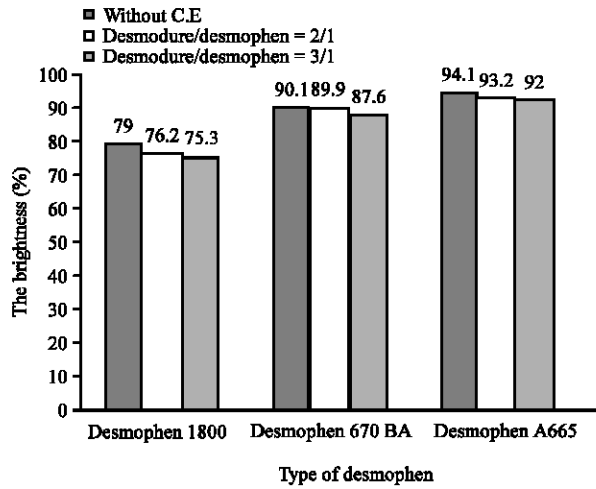


Fig. 2: The brightness test results for the coatings obtained using desmodur Z4470 as an isocyanate agent and different polyols

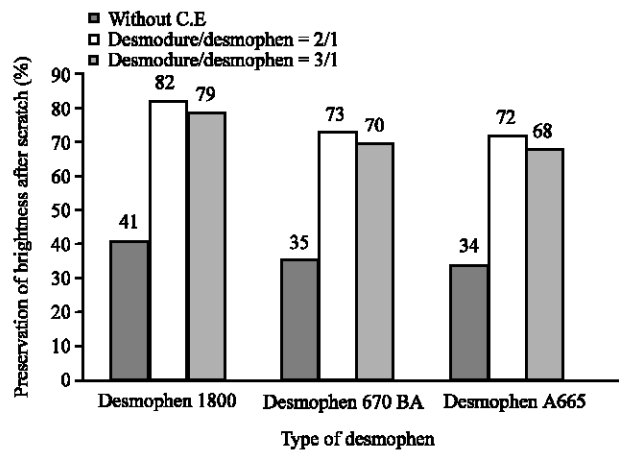


Fig. 3: The results of the test for preservation of brightness after scratching for different coatings prepared using desmodur Z4470 as the isocyanate agent and different polyols

The brightness test: Figure 2 shows the brightness test results for different coatings. The brightness of the coating is increasing in the absence of the chain extender agent. The standard brightness value is 80% based on Iranian standard protocols for automotive coatings. The results show that desmophen 665 A which is an acrylic based polyol will yield the maximum brightness in the coating when reacted with desmodur Z4470 at NCO/OH = 0.85 in the absence of any chain extender agent.

The test of the preservation of brightness after scratching (self-healing test): Piin *et al.* (2005) studied on scratch resistance assessments of polymeric coatings. They showed the relation of monomer formulation and the scratch resistance of PU. In contrast of their tests, at present work we proposed a test method which used as a measure of self-healing property in coatings. As it is shown in Fig. 3, those coatings prepared using desmophen 1800, shows the maximum preservation of brightness and self-healing property. The maximum is obtained when desmodur/desmophen ratio is adjusted to 2 and increasing the ratio will decrease the self-healing property. The minimum

Self-healing property was observed in the absence of chain extender agent, which is due to the blocky structure of polyurethane polymer. The optimum result were obtained using desmophen 1800 and NCO/OH = 2.

CONCLUSIONS

Polyurethanes are widely used in automotive coating industries since they show high mechanical strength at normal temperature and more elastic properties at higher temperatures. They have enough resistance against abrasive agents and show self-healing properties. In the present study an optimum polyurethane formulation is obtained using desmodur Z4470 as the isocyanate agent and different polyols including desmophen 1800, 670BA and A665. The hardness of the resulted polymer is increased as the polyol changed from desmophen 1800 to 670BA and A665. The application of ethylene glycol as the chain extender agent will increase the hardness of the resulted polyurethane and hence lower the self-healing characteristic of the polymer. Also in the absence of the chain extender agent, the brightness of the polymer is increased and the maximum brightness and self-healing is obtained using desmophen 1800. When the ratio of desmodur/desmophen is adjusted to 2, the maximum self-healing is observed and increasing the ratio will decrease the self-healing character of the obtained polymer. The minimum self-healing was observed when no chain extender agent was applied.

ACKNOWLEDGMENT

The author is grateful Islamic Azad University, Qaemshahr Branch for its financial support.

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