



## Effect of NCO/OH Ratio on the Physico-Mechanical Properties of Polyurethane-Polyurea Hybrid Spray Coatings



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### Abstract

Polyurethane- polyurea hybrid spray coating was prepared by two steps polymerization. In the first step, polyurethane prepolymers (PUs) were prepared by polyaddition reaction based on 4,4'-methylene dipheyl dissocyanate (4,4' MDI), poly(oxytetramethylene) glycol (PTMG), polyoxypropylene glycol (PPG), and triol (trade name FA-703) with different NCO/OH molar ratios. IR spectroscopy and acid-base titration were used to check the NCO content of the prepolymers. In the second step, polyurethane-polyurea hybrid resin was prepared by mixing the polyurethane prepolymer (PU) with polyoxypropylenediamine (POPA) at constant molar ratio (1: 1). The effect of NCO/OH ratios on physico-mechanical properties of the polyurethane-polyurea hybrid coating films was studied including viscosity, tensile strength, elongation at break, tear strength, contact angle and adhesion. The results obtained showed that tensile strength, contact angle and hardness increased, while viscosity, elongation, adhesion and tear strength decreased with increasing NCO/OH molar ratio.

**Keywords:** Polyurea, Polyurethane, Hybrid coatings, NCO/OH ratio, Mechanical properties;

### Introduction

Polyurethane-polyurea hybrid technology represents a major type of resins in development of the coating for different substrates including metal, concrete, wood and asphalt [1, 2]. This technology is based on preparation of polyurea based on the reaction of polyurethane prepolymer with a resin blend [3-7]. The resin blend mad up of amine terminated polymer resin or an amine chain extender. Polyurethane prepolymer with an isocyanate terminated consists of reaction between an excess of isocyanates and polyols to yield [6-9]. Isocyanate can be aromatic or aliphatic. Polyurethane-polyurea hybrid resins are 100% solids, and compliant with the strictest VOC regulations [6-8]. A key advantage of polyurea hybrid coating is that the amine/isocyanate reaction. It is fast curing even at low temperature and moisture resistance [9]. Furthermore, hybrid has excellent chemical resistance, high mechanical properties and durability. In addition, it makes coating for the widest range of applications including anticorrosion, tank linings, roof coatings and

roof coating. The performance of polyurethane-urea hybrid coatings depends on the type of diisocyanate, the degree of branching of polyols/amine and isocyanates as well as NCO/OH ratio [10, 11]. Mara et al. [12] showed that the coating with the highest NCO/OH ratio in polyurethane-urea hybrid presented high performance properties and corrosion properties. Negim et al. [13] studied the effect of polyol on physico-mechanical properties of polyurethane-urea hybrid films. It was observed that on increasing the soft segments in the prepolymer, physico-mechanical properties of polyurethane-urea hybrid films improve significantly and become flexible with high adhesion. A great variety of polyurethane-urea hybrid coating properties including flexible, hard, brittle and semiflexible films can be obtained by controlling the NCO/OH ratio [14]. This paper describes the

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preparation of polyurethane-urea hybrid coating based on prepolymer polyurethane (PU) and resin blend polyoxypropylenediamine (POPA). PU was also prepared by polyaddition of polyol and isocyanate with different NCO/OH ratios. The influence of NCO/OH ratios on the physical and mechanical properties of polyurethane-urea hybrid films was studied.

## Experimental

### Materials

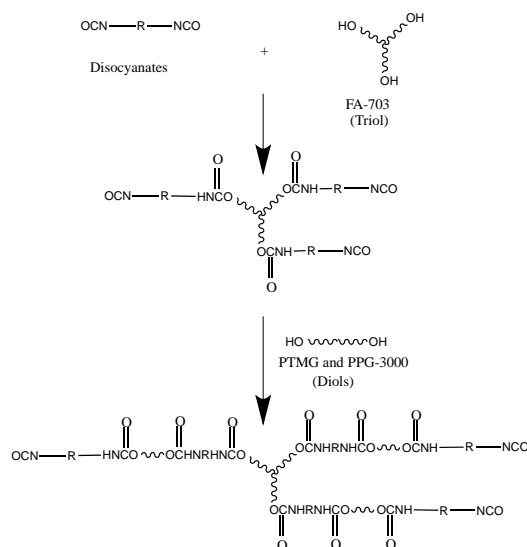
4,4'-methylene diphenyl diisocyanate (4,4'-MDI, NCO content 33.8%;  $M_w = 250.25$  g/mole) (Sigma Aldrich), polyoxypropylenediamine (POPA,  $M_w = 2000$  g/mole) (Jeffamine Chemicals) curing agent (Aldrich), polypropylene glycol diol (PPG,  $M_w = 3000$  g/mole, OH number = 37.5 mg/g) (Aldrich), poly(oxytetramethylene) glycol (PTMG,  $M_w = 2000$ , OH number = 55 mg/g, Korea PTG, Korea), triol trade name (FA-703,  $M_w = 3200$ , OH number = 33 mg/g, Korea polyols, Korea) were used as received.

### Preparation polyurethane prepolymers (PU)

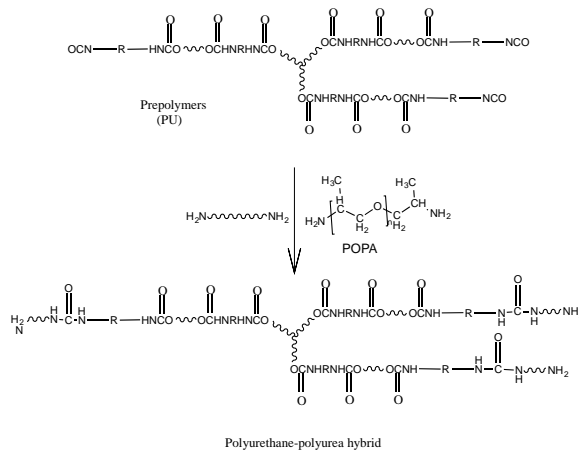
The polyurethane prepolymers were prepared as previously described in the literature [15-17]. Polymerization was performed in a 500 mL round-bottom, four-necked separable flask with a mechanical stirrer, thermometer, and condenser with drying tube. Reaction was carried out in inert  $N_2$  atmosphere at constant temperature oil bath. MDI and FA-703 were charged into the reactor and the mixture was heated at 100 °C for 1 h. After that, PTMG and PPG-300 were added to the mixture and the reaction proceeded at the same temperature until the theoretical NCO value was reached (15.5 %), as determined by di-n-butylamine titration method according to ASTM D 2572 [19-20]. The reaction scheme for the polyurethane prepolymer preparation is shown in Scheme 1. Samples were prepared at different NCO/OH ratios as shown in Table I.

### Preparation of polyurethane-polyurea hybrid films

The polyurethane-polyurea films were prepared by mixing the polyurethane prepolymers with POPA at constant volume ratio 1: 1 and applied by spraying method with high pressure (150-180 bar) spray machine into sheets. The gelation time for resins was five seconds and the films were cured after 15 seconds. Different samples were synthesized to study the effect of NCO/OH ratios of the prepolymer on physical and mechanical properties of the polyurethane-polyurea hybrid films. The structure of the polyurethane-polyurea hybrid films is shown in Scheme 2.



**Scheme 1:** Synthesis of polyurethane prepolymer (PU).



**Scheme 2.** The structure of polyurethane-polyurea hybrid films.

### Measurements

FTIR spectra were recorded on a Bruker Tensor 37 FTIR spectrometer. The viscosity ( $\eta$ ) of the polyurethane-polyurea hybrid resins (liquids) were measured using a Brookfield viscometer (Model LVTDV-II) at a shear rate of  $100\text{ S}^{-1}$  at 25 °C. The contact angle formed between the water drops and the surface of the cured coating films was measured using contact angle measuring system (CAHN DCA-322 analyzer) operated at 25 °C with water drop, and a velocity of 100  $\mu\text{m/s}$ . The drop of water was

**Table 1: Feed compositions of polyurethane prepolymer synthesized at different NCO/OH ratios.**

Samples No.	1		2		3	
	Wt (g)	Wt (%)	Wt (g)	Wt (%)	Wt (g)	Wt (%)
PP-3000	99.59	37.82	86.18	37.34	94.31	47.20
FA-703	81.71	31.02	91.92	39.83	59.70	29.80
PTMG	42.13	15.99	12.76	5.52	6.50	3.25
MDI	39.94	15.17	39.94	17.40	39.49	19.75
Total	263.37	100	230.8	100	200	100
Mole of OH (g/mole)	0.0798		0.06384		0.0532	
Mole of NCO (g/mole)	0.1596		0.1596		0.1596	
NCO/OH ratio	2.0		2.5		3.0	

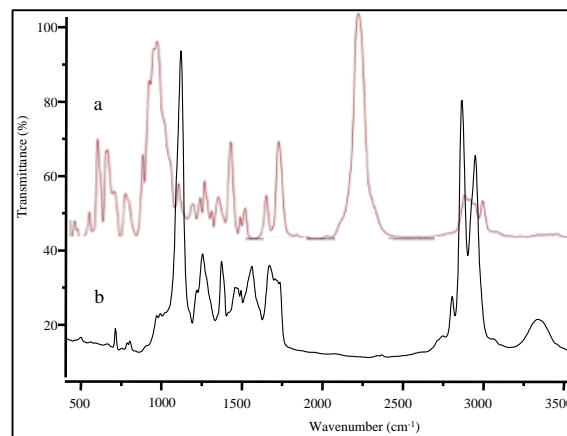
mounted on the surface to be tested using a micro-syringe, and the contact angle was measured from the view of water drops as observed on monitor. Results are the mean value of three measurements on different parts of the cured coating film. The tensile properties of the cast films were measured by using MTS 10/M tensile testing machine (1-kN load cell) at a crosshead speed of 50 mm/min. The average of at least four measurements was taken. Shore A hardness was measured using an indentation hardness tester according to ASTM D2240-75 [21]. A universal testing machine (DCS-500, Shimadzu Crop, Kyoto, Japan) at a crosshead speed of 0.5 mm/min. was used to conduct the bond strength test. The bond strength was calculated by dividing the force at which bond failure occurred by the bonding area.

## Results and discussion

### FTIR analysis

IR spectrum of 4,4'-methylene diphenyl diisocyanate (MDI) is presented in Figure 1a. The characteristic absorption peak of the isocyanate groups (NCO) (stretching vibration) appeared at  $2260\text{ cm}^{-1}$ . The peaks ranging from  $1500\text{ cm}^{-1}$  to  $1700\text{ cm}^{-1}$  are related to the double bond of the benzene ring. Figure 1b showed a new broad peak ranging from  $3250\text{ cm}^{-1}$  to  $3450\text{ cm}^{-1}$  which is attributed to the N-H stretching vibrations of polyurethane-urea hybrid. The aliphatic C-H stretching vibration peak appeared in the range from  $2750\text{ cm}^{-1}$  to  $3000\text{ cm}^{-1}$ . The characteristic peak at  $1750\text{ cm}^{-1}$  is related to the urethane carbonyl group. In addition, C-O-C stretching absorption band corresponding to the ether oxygen of the soft segment was observed at  $1000\text{--}1150\text{ cm}^{-1}$ . From Figure 1b, it can be seen that the disappearance of the NCO at  $2265\text{ cm}^{-1}$  can be attributed to the consumption of NCO in

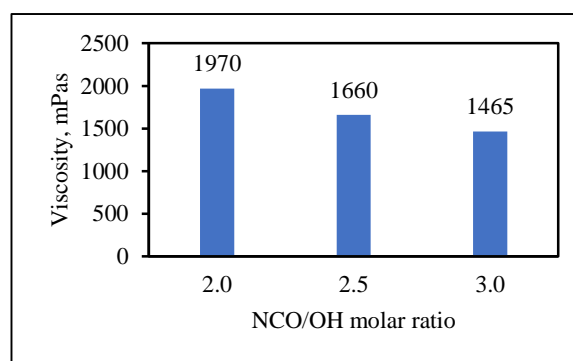
the reaction with POPA forming the polyurethane-polyurea hybrid (Scheme 2)



**Figure 1:** FTIR spectra of (a) 4,4'-methylene diphenyl diisocyanate and (b) polyurethane-polyurea hybrid resin.

### Viscosity measurements

Viscosity is a critical factor that directly affects the coating process in various methods including final thickness and flow of coating on the surface. Figure 2 shows increasing viscosity of the polyurethane-polyurea hybrid resins with decreasing NCO/OH ratio. This can be attributed to increase in the free volume within the prepolymer molecule which furthermore increases the segment and mobility of the polymer [22].

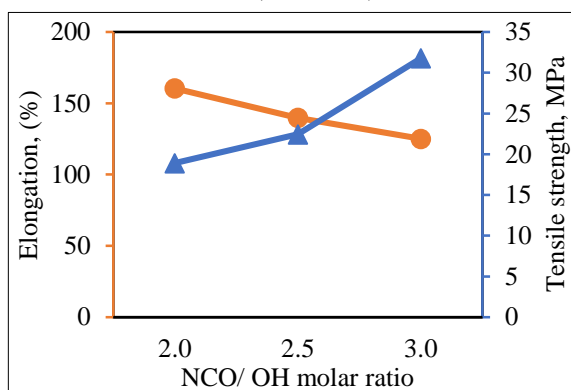


**Figure 2:** Effect of NCO/OH molar ratio on the viscosity of polyurethane-polyurea hybrid resin.

### Mechanical properties

The effect of NCO/OH ratio on tensile strength and elongation at break of polyurethane-polyurea hybrid cured resin films is given in Figure 3. It is evident that, the elongation at break decreased, while tensile strength increased with increasing NCO/OH ratio. The sample with (NCO/OH = 2) possessed low tensile

strength (18.9 MPa) and high elongation at break (160.5%), while the sample with (NCO/OH = 3) displayed high tensile strength (31.78 MPa) with low elongation at break (125.1 %). The increase in tensile strength is attributed to increasing the hard segments (NCO) in polyurethane-polyurea hybrid resin which increased with increasing NCO/OH ratio [22, 23]. On the other hand, the increase in elongation at break is due to the soft segments (polyol) in polyurethane-polyurea hybrid which increase with decreasing NCO/OH ratio. The high tensile strength of the films confirmed that polyurethane-polyurea hybrid films were well cross linked (Scheme 2)

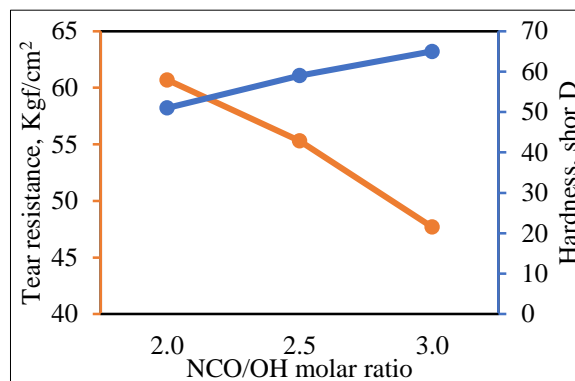


**Figure 3:** Effect of NCO/OH molar ratio on the mechanical properties of polyurethane-polyurea hybrid cured resin film.

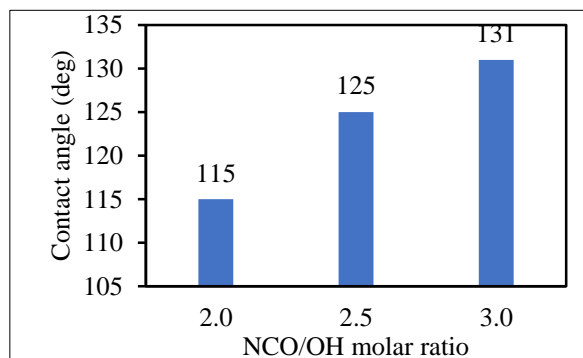
The results of hardness and tear resistance of polyurethane-polyurea hybrid films are presented in Figure 4. The hardness of hybrid films increased, while tear resistance decreased with increase NCO/OH ratios. The increase in hardness is mainly due to increase in crosslink content in the main chain of polyurethane-polyurea hybrid with increasing NCO/OH molar ratio [22]. The results also detect that tear resistance is directly related to NCO/OH molar ratio, where tear resistance decreases with increasing NCO/OH ratio. Wettability (surface polarity) of the polyurethane-polyurea hybrid films were characterized by contact angle measurement as shown in Figure 5. It is clear that the contact angle of the cured resin films increased up to 131° as NCO/OH increase, demonstrating its high hydrophobic character due to high crosslinking density of the cured resin films. It is known that the hydrophobic surface gives a high contact angle, while hydrophilic surface gives a low contact angle [23 - 30].

From Figure 6, it is clear that the adhesion strength of the cured resin films increased with decreasing NCO/OH molar ratio of the polyurethane prepolymer (PU). Polyurethane-polyurea hybrid film with the lowest NCO/OH ratio (2.0) showed the

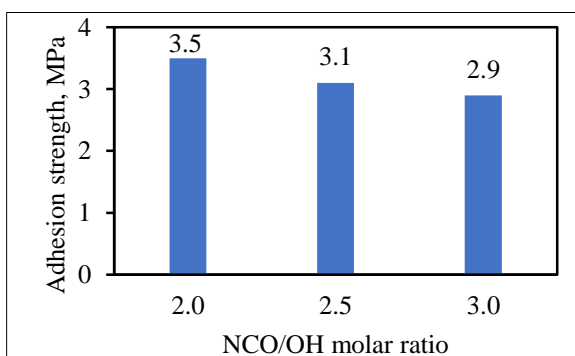
highest adhesion strength (3.5 MPa) to the metallic substrate. This can be attributed to the soft segments in the polyurethane prepolymer which improved adhesion of the polyurethane-polyurea hybrid film and exhibited good compatibility with the metallic substrate. These results are in agreements with contact angle measurements.



**Figure 4:** Effect of NCO/OH molar ratio on the mechanical properties of polyurethane-polyurea hybrid cured resin film.



**Figure 5:** Effect of NCO/OH molar ratio on contact angle of polyurethane-polyurea hybrid cured resin films.



**Figure 6:** Effect of NCO/OH molar ratio on the adhesion strength of polyurethane-polyurea cured resin films on metallic substrate.

## Conclusions

Polyurethane-polyurea hybrid resins based on the reaction of polyurethane prepolymers (with different NCO/ OH molar ratios) with POPA at volume ratio 1: 1 was prepared. The polyurethane (PU) prepolymers were prepared by poly addition reaction of MDI as isocyanate (NCO) monomer with different polyols including FA-303 (triol), and PTMG and PPG-3000 (diols). The effect of NCO/OH molar ratios on the physico-mechanical properties of polyurethane-polyurea hybrid films was studied. The results showed that viscosity, elongation at break, tear resistance, and adhesion increased by decreasing NCO/OH molar ratio from 3 to 2, while tensile strength, hardness and contact angle increased with increasing NCO/OH molar ratios from 2 to 3. The increase in tensile strength, hardness and contact angle is interpreted in terms of increasing hard segments (NCO) while increase in viscosity, elongation at break, tear resistance, and adhesion with decreasing NCO is due to increasing the soft segments (polyol) in the prepared resin. However, polyurethane-polyurea hybrid resin with low reactivity results in higher flexibility with excellent adhesion to metal substrate.

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## References

1. Yeh F., Hsiao BS., Sauer BB., Michel, S. and Siesler, H. W. In-situ studies of structure development during deformation of a segmented poly(urethane-urea) elastomer, *Macromolecules* **36**, 1940-1954 (2003).
2. Qiao J., Amirkhizi AV., Schaaf K., Nemat-Nasser S. and Wu, G. Dynamic mechanical and ultrasonic properties of polyurea, *Mech Mater*, **43**,10, 589-607 (2011).
3. Zur A. Polyurea - The new generation of lining and coating, *Adv. Mater. Res.* **95**, 85-86 (2010).
4. Toutanji HA., Choi H., Wong D., Gilbert J.A., Alldredge DJ. Applying a polyurea coating to high-performance organic cementitious materials, *Construction and Building Materials* **38**, 1170-1179 (2013).
5. Lu PF., Zhang YF., Jia C., Li YF., Mao ZQ. Use of polyurea from urea for coating of urea granules, *Springer Plus* **5**, 457, 1-6 (2016).
6. Negim ES., Mahyuddin R., Bahruddin S., Bekbayeva, L., Muhammad IS. Preparation and characterization of water dispersion polyurethane, *J. World Applied Sciences* **12**, 8, 1145- 1150 (2011).
7. Pathak JA., Twigg JN., Nugent KE., Ho DL., Lin, EK., Mott PH. Structure evolution in a polyurea segmented block copolymer because of mechanical deformation, *Macromolecules* **41**, 7543-7548 (2008).
8. Hapburn C. Polyurethane Elastomers, 2<sup>nd</sup> Ed.; Elsevier: Oxford, (1991).
9. Zhao J., Knauss WG., Ravichandran G. Applicability of the time and temperature superposition principle in modeling dynamic response of a polyurea, *Mech Time-Depend Mater* **11**, 289-308 (2007).
10. Kausar A., Zulfiqar S., Sarwar MI. High performance segmented polyurethanes derived from a new aromatic diisocyanate and polyol, *Polym. Degrad. Stab.* **98**, 368-376 (2013).
11. Mishra AK., Narayan R., Raju KVS.N., Aminabhavi TM. *Prog. Org. Coat.*, **74**, 134-141 (2012).
12. Mara CLO., Renato AA., Isolda C. Effect of the NCO/OH molar ratio on the physical aging and on the electrochemical behavior of polyurethane-urea hybride coatings, *Int. J. Electrochem. Sci.* **8**, 4679-4689 (2013).
13. Negim ES., Bekbayeva L., Mun GA., Abilov ZA., Saleh MI. Effects of NCO/OH ratios on physico-mechanical properties of polyurethane dispersion, *World Applied Science Journal* **14**,13, 402-407 (2011).
14. Primeaux DJ. Spray Polyurea-Versatile High Performance Elastomer for the Polyurethane Industry, Polyurethane '89, The SPI 32<sup>nd</sup> Annual Technical/Marketing Conference, Francisco, California, p.126-130 (1989).
15. Negim ES., Khatib JM., Faizova E., Shilibekov S., Mussylmanbek S. The Effect of Diamine Extender on the Properties of Polyurethane Dispersions, *Middle-East Journal of Scientific Research* **16**, 7, 890-895 (2013).
16. Patrycja K., Tamara CC., Arantxa E., Janusz D. Synthesis and characterization of polyurethane elastomers with semi-products obtained from polyurethane recycling, *European Polymer Journal* **85**, 26-37 (2016).
17. Zhang H., Chen Y., Zhang Y., Sun X., Ye H., Li W. Synthesis and Characterization of Polyurethane Elastomers, *Journal of Elastomers & Plastics* **40**, 2, 161-177 (2008).
18. Szycher M. Szycher's Handbook of Polyurethanes, 1.1-9. CRC Press, Boca Raton (1999)
19. Oertel G. Polyurethane Handbook, Carl Hanser, Munich, 31, (1985).

20. ASTM D 2572. Standard method of test for isocyanate group in urethane materials or prepolymer (1979).
21. ASTM D2240-75. Standard test methods for hardness (2006).
22. Runumi G., Alam MS., Rakesh KK. Effect of increasing NCO/OH molar ratio on the physico-mechanical and thermal properties of isocyanate terminated, *International Journal of Basic and Applied Science* **3**, 2, 118-123 (2014).
23. Negim ES., Ketegenov T., Irmukhametova GS., Sultanbekova IN., Tastambekova TN., Mun GA. The effect of TDI, PTMG and DMPA on the physico-mechanical properties of polyurethane dispersion containing aromatic isocyanate, *International Journal of Biology and Chemistry* **9**, 1, 68-72 (2016).
24. Jin H., Lina Z. Effect of NCO/OH molar ratio on structure and properties of graft-interpenetrating polymer networks from polyurethane and nitrolignin, *Polymer* **43**, 2287-2294 (2002).
25. Soma AE, Rabab SY., Anhar AA. Processing of polyurethane nanocomposite reinforced with nanosized zinc oxide: effect on mechanical and acoustic properties, *Egypt. J. Chem.* **62**, 2, 333-341 (2019).
26. Negim SM., Bahrudin S., Mahyuddin R., Idiris MS. Effect of TDI and FA- 703 on physico-mechanical properties of polyurethane dispersion, *J. Applied Polymer Science* **121**, 8-13 (2011).
27. Garbassi F., Mora M., Occhiello E. Polymer Surfaces, From Physics to Technology, John Wiley & Sons, Chichester (1998).
28. Zawadzki SF., Akcelrud L. HTPB-based polyurethanes: a correlation study between morphology and mechanical behavior, *Polymer International* **42**, 422- 428 (1997).
29. Negim ES., Bekbayeva, L., Omurbekova, K., Mohamad, NMI. Effect of polyol on physico-mechanical properties of polyurea film, *AIP Conference Proceedings* **2124**, 1, 020051-6 (2019).
30. Bashandy MS., Abd El-Fattah M., Abd El-Wahab H., El-Eisawy RA., Abd El-Hai F., Mohamed S. Synthesis and characterization of thiazole derivatives and evaluating their performance as additives in polyurethane coating, *Egypt. J. Chem.* **59**, 1, 115-129 (2016).