

Preparation of novel UV-curable methacrylated urethane resins from a modified epoxy resin and isocyanatoethylmethacrylate (IEM)

Tülay Yılmaz İnan^{1,2}, Ekrem Ekinci¹, Abdülkadir Kuyulu^{1,3}, Attila Güngör^{1,4} (✉)

¹ Marmara Research Center, Material and Chemical Technologies Research Institute, P.O. Box 21, 41470, Gebze-Kocaeli, Turkey

² Department of Chemical Engineering, Istanbul Technical University, Maslak-İstanbul, Turkey

³ Department of Chemical Engineering, Yıldız Technical University, 34210, Esenler-İstanbul, Turkey

⁴ Faculty of Art&Sci., Department of Chemistry, Marmara University, Göztepe-İstanbul, Turkey

Received: 26 June 2001/Revised version: 5 April 2001/Accepted: 5 April 2001

Summary

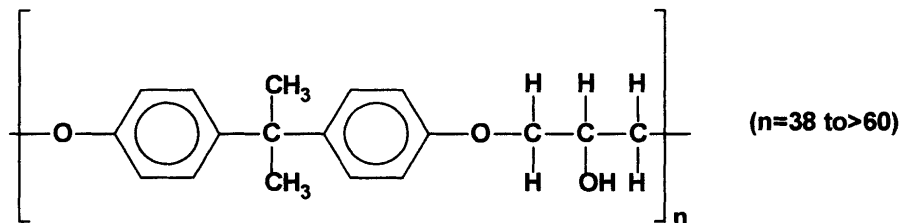
New UV curable methacrylated urethanes (PAPHEN-XIEM) were synthesized by substituting X percent (e.g., 10, 20, 30 %) of the total OH content of the PAPHEN-301 (Scheme 1) with isocyanatoethyl methacrylate (IEM). These resins were used alone (neat resin formulation) or as a mixture of 5, 10 and 13 % (w/w) respectively with methacrylated urethane prepolymer (PTHFUMA) in UV systems. For neat resin formulations, tensile strength and modulus values were observed to be inversely proportional with the modification degree of PAPHEN-301 as opposed to what is normally expected. This may be explained as a result of screening effect of increasing unsaturation. The water absorption capacities for neat resins and PTHFUMA-included formulations were decreased as the modification degree increased due to the replacement of hydrophilic OH groups of PAPHEN-301 by the hydrophobic methacrylate groups. TGA thermograms of neat resin formulation show that, initial weight loss temperatures are lower; possibly owing to the higher methacrylate content in the formulations.

Introduction

Radiation curable coating applications have been increasing due to the advantages such as lower energy consumption, less environmental pollution and very rapid curing (1-3). In general, UV curable coating formulations are consisted of primarily three major components; namely, a reactive oligomer, end-capped with a functional group such as acrylic or methacrylic, a mono or polyfunctional reactive diluents, and a photoinitiator. Nonreactive additives such as pigments, adhesion promoters, surface active agents, may be used in formulations depending on the specific application. However, reactive oligomers, which govern the mechanical properties of the UV-cured films, are the major ingredients in these formulations (1-7).

In this study, we used N-vinyl-2-pyrrolidone (NVP) as the reactive diluent (NVP) due to its powerful solvating effect, diethylene glycol dimethacrylate (DEGDA) as crosslinking agent and isobutyl benzoin ether (IBuBE) and dibutyltin dilaurate (DBTDL) as photoinitiator and catalyst, respectively.

PAPHEN-301 (Scheme 1) is a tough, ductile epoxy based thermoplastic resin with good cohesive strength and good impact resistance. Its ether linkage and pendant hydroxyl groups promote wetting and bonding to polar substrates and fillers. It is compatible with many polymers and is an efficient flexibilizer for cross-linked formulations. It improves the performance of metal primers and coatings for metal, wood, and flexible substrates. It imparts outstanding properties in magnetic tape, adhesive, molding and extrusion applications (8).



Scheme 1: PAPHEN-301

In order to transfer the above-mentioned properties to the UV-curable formulations, PAPHEN-301 was modified with isocyanatoethyl methacrylate (IEM). The amount of IEM used to modify PAPHEN-301 was varied to consume 10,20, 30 % (w/w) of the total hydroxyl groups of PAPHEN-301. The respective modified resins thus obtained were coded as PAPHEN-10IEM, PAPHEN-20IEM, PAPHEN-30IEM (PAPHEN-XIEM) (Scheme 2) and used as oligomers in the formulations. These oligomers were used either alone (neat resins) or in a mixture with the methacrylated urethane prepolymer (PTHFUMA). PTHFUMA was synthesized from IEM and polytetrahydrofurandiol (PTHF) via one step reaction (Scheme 3). The effect of urethane content on mechanical, thermal and physical properties were investigated for the two systems.

Experimental

Materials

Isocyanatoethyl methacrylate (IEM, Dow Chemical Co.) was used without further purification. Purity was determined to be 90.8 % analytically (9). Polytetrahydrofuranediol (PTHF, BASF Inc.) was vacuum dried before use. Its hydroxyl number was determined to be 104 mg KOH/g (10). *N*-vinyl-2-pyrrolidone (NVP, GAF Corp.) was dried over 4A° molecular sieve before use. Diethylene glycol dimethacrylate (DEGDA, Alcolac Int. Inc.), PAPHEN-301 (Phenoxy Associates) having a hydroxyl equivalent weight of 499 were used as received. Isobutyl benzoin ether (IBuBE, Stauffer Chemicals) and dibutyltin dilaurate (DBTDL, Merck) were used without further purification.

Characterization Methods

¹H NMR spectra data were taken in DMSO-d₆ using a Bruker AC 200 spectrometer operating at 200.132 MHz. employing TMS as internal standard. FTIR spectra of the KBr discs or films of the samples were taken using a Nicolet-510P FTIR spectrometer.

Gel content of the UV-cured films were determined by extraction using acetone-toluene mixture (1/1, v/v) in a Soxhlet apparatus for 12 hours. The insoluble gel fraction was vacuum-dried at 60 °C for 24 hours and was weighed to calculate the gel content by difference. In all formulations, gel contents were found to be greater than 95 %.

Stress-strain measurements were performed on UV-cured free films using an Instron tensile testing machine according to ASTM D 882-91 (11). All stress-strain measurements were carried out uniaxially at ambient conditions.

Test samples were initially conditioned at 50 °C before immersing them in deionized water at 25 ± 0.5 °C for 24 h. The water absorption capacities of the samples were calculated from the weight differences between the dry films and those soaked in deionized water (12).

Thermal characterization of UV-cured polymeric films with PTHFUMA and without PTHFUMA was carried out using a DuPont 990 modular thermal analyzer system.

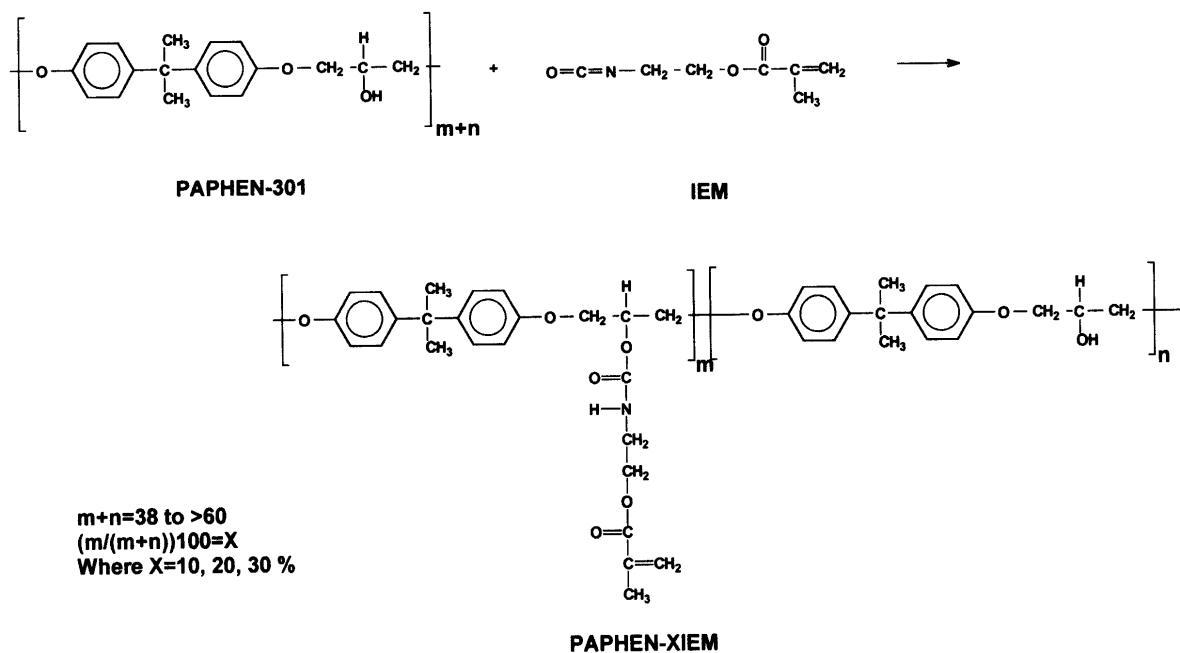
Thermogravimetric analyses (TGA) were performed using a DuPont 951 thermogravimetric analyzer with a heating rate of 10 °C/min in air.

Preparation of PAPHEN-XIEM prepolymers (X=10, 20 and 30 % IEM)

PAPHEN-301 (40.00 g) was charged into a flame-dried three-necked 250 ml round-bottom flask, equipped with a nitrogen inlet and a dropping funnel, and it was dissolved in 57.14 ml NVP (40 % w/w). DBTDL (0.08 % by weight) was added into the reaction flask as catalyst. Then, IEM (1.367 g, 0.008 mol, equivalent to 10 % of the total hydroxyl content of PAPHEN-301) was added dropwise to the well-stirred reaction mixture over a period of 1 h. The reaction was kept at 15-20 °C for 8 h. At the end of the reaction, the disappearance of the -NCO peak at 2275 cm⁻¹ and the OH peaks at 3500 cm⁻¹ confirmed that the reaction was completed. Furthermore, NH peaks at 3400 cm⁻¹ appeared.

The preparation of IEM modified PAPHEN-301 urethane methacrylate (PAPHEN-XIEM) is shown in Scheme 2. Resin thus obtained was precipitated in methanol and vacuum-dried in an oven at 30 °C, and characterized by FTIR and ¹H NMR techniques.

FTIR (KBr): 2275 (-N=C=O), 3350 (-NH, stretching), 1730 (C=O, amid I, stretching) 1520 (-CNH) ¹H NMR (DMSO-d₆): δ=1.6 (s, 3H, CH₃) 4.0 (m, 4H, OCH₂-CH₂-N), 5.2 (s, 1H, NH), 5.36 (m, 2H, CH₂)

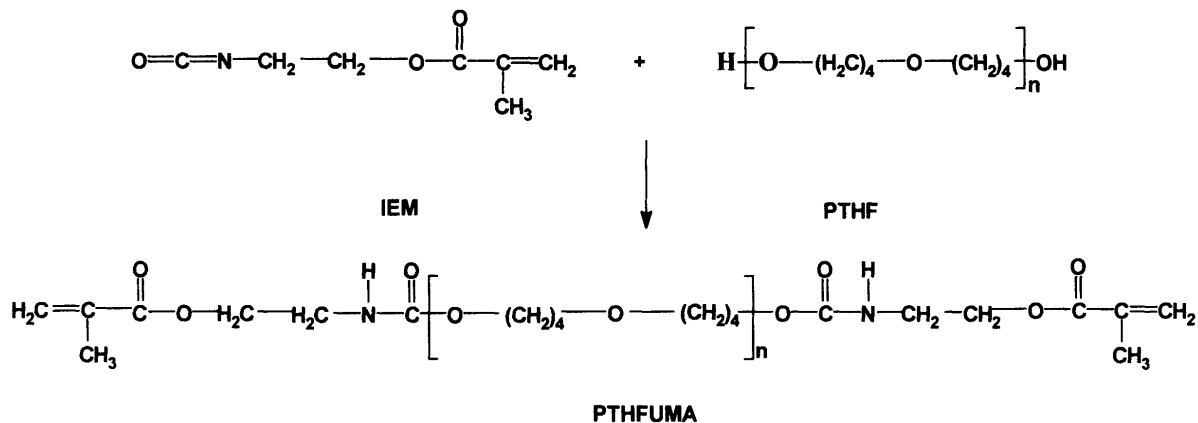


Scheme 2: Preparation of PAPHEN-XIEM prepolymer

PAPHEN-20IEM and PAPHEN-30IEM were also prepared according to this procedure using 2.734g, 0.016 mol and 4.102 g, 0.024 mole of IEM, respectively.

Preparation of PTHFUMA prepolymer

PTHFUMA prepolymer was prepared from IEM and PTHF as described previously (7) as shown below (Scheme 3).



Scheme 3: Preparation of PTHFUMA prepolymer

Polymeric Film Preparation

The UV-curable methacrylated urethane formulations were prepared by mixing PTHFUMA and PAPHEN-XIEM (PAPHEN-10IEM, PAPHEN-20IEM and PAPHEN-30IEM) with NVP and IBuBE homogeneously. The amount of PAPHEN-XIEM in the formulation was varied from 5 to 10 and to 13-wt. %. IBuBE concentration was kept constant as 2-wt. % in all formulations. Air bubbles formed during mixing were removed under moderately reduced pressure at room temperature. Approximately 200 μ thick polymeric films were obtained by pouring the viscous liquid resins onto a Teflon[®]-coated mold. In order to decrease the viscosity and obtain better flow, the mold was kept at 35 °C. Moreover, to prevent oxygen inhibition, resin in the mold was covered with a 25 μ thick transparent Teflon film. Before irradiation, a quartz plate was placed over the Teflon[®] film to obtain a smooth surface with desired thickness. Finally, the formulation on the mold was irradiated for 210 s, under high pressure UV lamp (OSRAM-300W), placed 15 cm above the film. The exposure time of 210 s, necessary for the disappearance of unsaturation of methacrylates, was pre-determined from a test experiment. For quantification, 763 cm^{-1} band, which was raised by aromatic rings within IBuBE, was used as an internal standard against the 810 cm^{-1} band of unsaturation of methacrylate.

Results and Discussion

New UV-curable methacrylated urethane resins were synthesized from the epoxy based commercial resin PAPHEN-301 and IEM (isocyanatoethyl methacrylate) which was used to consume 10, 20 and 30 % of the total hydroxyl groups of PAPHEN-301. UV-curable methacrylated urethane resin formulations were prepared by varying the amount of PAPHEN-XIEMs resins while keeping the other components (NVP, IBuBE, and DEGDA) constant. In both Tables, the numbers in front of the designation codes represent the wt % of each component in the final formulation.

As seen from Table 1, an increase in the (PAPHEN-XIEM) (Scheme 2.) content caused an increase both in tensile strength and elongation values of UV-cured polymeric films (1,2,3-5,6,7-9,10,11), except film 7. Maximum stress, stress-strain slope and maximum strain values found to be increasing with the ratio of modified PAPHEN-XIEM and PTHFUMA. As seen from the bold lines in Table 1 (4, 8, 12), tensile strength and modulus (slope) values decrease whereas maximum strain (elongation) increases with the increasing IEM content of the neat resins. This could be attributed to increasing unsaturated acrylic functionality that was resulted from replacement of -OH by IEM; the higher amount of -OH replaced by IEM, the higher

unsaturation. This higher than normal unsaturation at and/or close to the surface of the film leads to fast curing that eventually prevents light from penetrating into deeper areas, which may be termed as screening effect, resulting in decreased mobility of growing chains and insufficient crosslink density. Therefore, these abnormal elongation and tensile strength values shown in Table.1 can be eminently explained by presence of insufficient crosslink density of the produced films.

Table 1. Mechanical and water absorption values for PAPHEN-XIEM included films

NO	COMPOSITION	Tensile Strength (MPa)	Elongation (%)	Modulus (N/mm)	Water abs. (%)
	PAPHEN-301	-	-	-	0.22
0	68PTHFUMA/20NVP	3.04	19	18.73	8.8
1	63PTHFUMA/5PAPHEN-10IEM/20NVP	6.67	42	3.13	9.0
2	58PTHFUMA/10PAPHEN-10IEM/20NVP	7.76	44	3.32	8.9
3	55PTHFUMA/13PAPHEN-10IEM/20NVP	8.05	46	3.99	9.1
4	0PTHFUMA/35PAPHEN-10IEM/53NVP	13.55	36	66.07	33.7
5	63PTHFUMA/5PAPHEN-20IEM/20NVP	6.05	34	2.72	8.3
6	58PTHFUMA/10PAPHEN-20IEM/20NVP	7.39	39	2.82	8.1
7	55PTHFUMA/13PAPHEN-20IEM/20NVP	7.22	39	3.38	7.4
8	0PTHFUMA/35PAPHEN-20IEM/53NVP	9.14	59	24.33	20.6
9	63PTHFUMA/5PAPHEN-30IEM/20NVP	8.33	43	2.22	8.6
10	58PTHFUMA/10PAPHEN-30IEM/20NVP	8.43	44	3.59	8.0
11	55PTHFUMA/13PAPHEN-30IEM/20NVP	8.72	45	5.34	7.6
12	0PTHFUMA/35PAPHEN-30IEM/53NVP	7.49	69	20.99	19.5

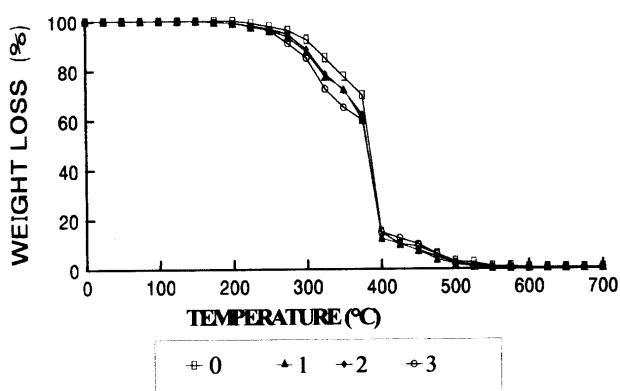
* All formulations contain 10 % DEGDA and 2 % IBuBE

For PTHFUMA included formulations, tensile strength and elongation values first decrease as the IEM modification increases from 10 % to 20% than increase as the modification degree increases from 20 % to 30 % (1,5,9-2,6,10-3,7,11). Similar behavior was also observed previously (13). For samples 1,2,3 - 5,6,7- 9,10,11, as modified PAPHEN-XIEM content increased both tensile strength and elongation values showed an increasing trend except for sample 7. Additionally, as seen from Table 2., tensile strength, elongation and modulus values of 20 % IEM modified formulations (5,6,7) are slightly lower than 10 and 30 % modified counterparts (1,2,3 and 9,10,11). Cooper et al (14) and Oraby and Walsh (15) noted that when urethane content was kept constant and soft segment molecular weight increased, Young modulus, and tensile strength decreased in acrylated urethane oligomers. On

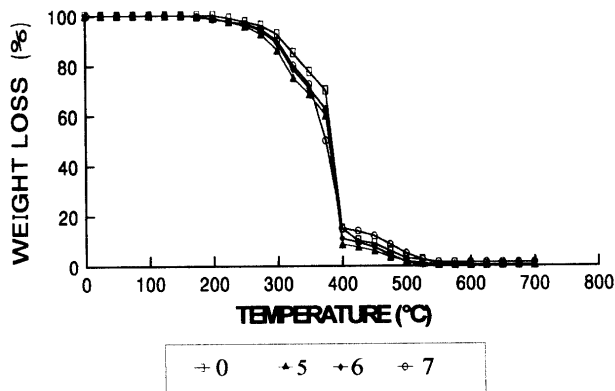
the other hand, Dai et al. (16), and Yu et al. (17), showed that when the hard segment content of the polyurethane acrylate samples increased, tensile strength also increased.

As far as water absorption characteristics of these films are concerned, it is clear from the Table.1 that water absorption values decrease drastically as the degree of IEM modification increases (4,8,12) for neat resin formulations. This could be due to the replacement of hydrophilic OH groups of PAPHEN-301 by the hydrophobic methacrylate groups (IEM). However, when these modified PAPHEN resins are used in the formulations with PTHFUMA (1,2,3-5,6,7-9,10,11) water absorption affect is not as strong as neat resin formulations (4, 8, 12) because of the small amounts (% 5, %10, % 13) of modified resins in the formulations. As shown from Table 1, water absorption value of original PAPHEN-301 is 0.22 %. However, when this resin is used as a non-reactive resin (making 5-20 % of the formulation) in the formulation, water absorption values are observed to increase up to 18.8 %. This increase in the water absorption of the formulation is probably due to OH groups and O linkages in the structure of PAPHEN-301 leading to strong H-bonding and resultant high water absorption of the formulation.

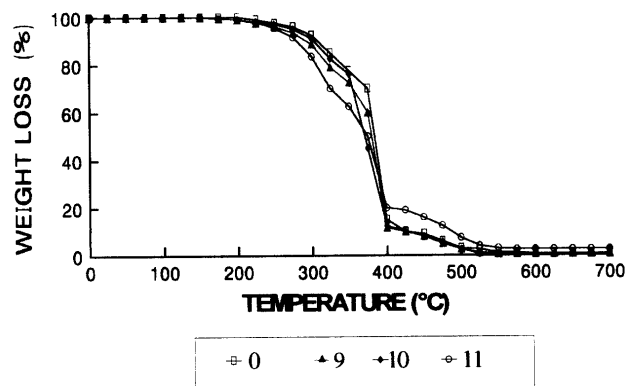
TGA thermograms showed no significant differences at the initial weight loss temperatures for any resin combinations (Figure 1, A, B, C). On the other hand, due to the low decomposition temperature of polymethacrylates, approximately around 160 °C, higher methacrylates containing neat resins have greater initial weight loss values (Fig 1-D). All the films showed approximately 5 % weight loss at around 200 °C and decomposed rapidly at around 300 °C (Figure 1, A, B, C, D).



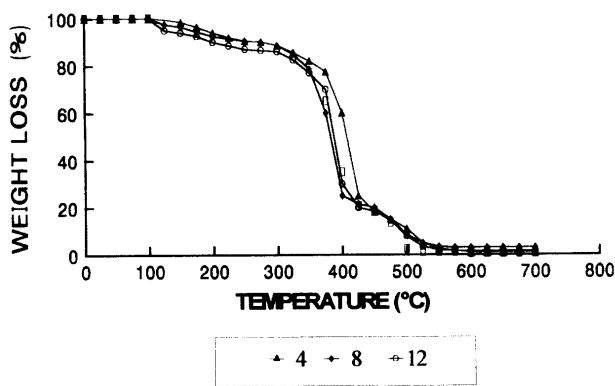
(A)



(B)



(C)



(D)

As seen from Table 2, although it is difficult to suggest a strong relation between the modification degree of IEM and T_m values, it is observed that increasing the IEM modification degree caused a decrease in PAPHEN-301's T_m values. However, while PTHFUMA-free formulations having only T_m , others have T_g as well. This could be explained by phase separation in the network.

Table 2. Glass Transition Temperatures for PAPHEN-XIEM included films

COMPOSITION	DSC (°C)					
	PAPHEN-10IEM		PAPHEN-20IEM		PAPHEN-30IEM	
	(T_g)	(T_m)	(T_g)	(T_m)	(T_g)	(T_m)
63PTHFUMA/5PAPHEN-XIEM//20NVP	-8	48	-4	42	-3	42
58PTHFUMA/10PAPHEN-XIEM//20NVP	-5	45	-8	46	-6	46
55PTHFUMA/13PAPHEN-XIEM//20NVP	-4	45	-4	43	-1	40
0PTHFUMA/35PAPHEN-XIEM/53NVP	-	43	-	38	-	40
PTHFUMA (T_g)	-11					
PAPHEN (T_m)	56					

* All formulations contain 10 % DEGDA and 2 % IBuBE

Acknowledgement

The authors kindly acknowledge Phenoxo Associates (Rock Hill, SC), BASF, GAF Corp. (U.S.A), and Gibaka Trading & Industrial Corp. (Zoetermeer, Holland) for their kind support of chemicals used in this work.

1. Photopolymerisation and Photoimaging Science and Technology, Edited by Norman S. Allen, Elsevier Applied Sci., (1989).
2. Anne M. Grosset, Wei-Fang A.Su, Ind.Eng.Chem.Prod.Res. Dev., 24, 113-120, (1985).
3. Sami A. Shama, Anthony J. Tortorello, J. Appl. Polymer Science, 43,699-707, (1991).
4. Wen-Yen Chiang and Shao-Ching Chan, J. Appl. Polym. Sci., 41, 2971-2985, (1990).
5. Giuseppe Li Bassi, Journal of Radn. Curing, 18-31, (1987).
6. E. Yıldız, H. Güçlü, A. Kuyulu, H. Yıldırım, A. Güngör, Angew. Makromol. Chem., 236:169-176, (1996).
7. T. Yılmaz, Ö. Özarslan, E. Yıldız, A. Kuyulu, E. Ekinci, A. Güngör, J. of Appl. Polym.,Sci. 69:1837-1845 (1998).
8. PAPHEN Phenoxo Resins Catalog, 1995.
9. ASTM D 2572, (1993). Test Method for Isocyanate Groups in Urethane Materials or Prepolymers, Vol. 6.03.
10. ASTM D 4274-83, (1993). Standard test Methods for Testing polyurethane Raw Materials: Determination of Hydroxyl Numbers of Polyols, Vol. 8.02,
11. ASTM D 882-91,(1993). The Method for Tensile Properties of Thin Plastic Sheeting, Vol.8.01.
12. ASTM D 570, (1993). Standard Test Method for Water Absorbtion of Plastics, Vol. 6.03.
13. Güngör, A., PhD. Thesis, "The Preparation, The Characterization and Various Applications of UV-Cured Polymeric Films", (1987), Istanbul Technical University.
14. Lin, S. B., Tsay, S.Y., Spechard, T. A., Hwang, K.K.S., Jezerc, J.J., Cooper, S. L., Properties of UV-Cured Polyurethane Acrylates: Effect of Polyol Type and Molecular Weight, Chem. Eng. Commun., 30, 251-273 (1984).

15. Oraby, W., Walsh, W. K., Elastomeric Electron Beam-Cured Coatings: Structure-Property Relationship, I. Oligomer Structure, *J. of Appl. Polym. Sci.* **23**, 3227-3242 (1979).
16. Dai, J., Gao, X., Jiang, G., Studies of structure and Properties of Photocrosslinked Polyurethane Acrylates, *Macromol. Chem.*, **192**, 177-184 (1991).
17. Yu, X., Grady, B. P., Reiner, R. S., Cooper, S. L., Mechanical and Thermal Properties of UV-curable polyurethane and Polyurea Acrylates, *J. of Appl. Polym. Sci.*, **49**, 1943-1955 (1993).