

Synthesis, Characterization and Performance Evaluation of

Dual-Cure UV-Curable OH-Terminated Polyurethane Acrylate Systems

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Introduction and Aim

Today, the demand for both fast production and long-term durability in industrial coatings, medical devices, and functional surfaces increases the need for advanced curing technologies. UV-curable systems offer rapid processing and environmental advantages due to their solvent-free nature, but they may lack chemical and mechanical resistance. As an innovative and sustainable approach, UV-curing is widely adopted in modern industries; however, its limitations have led to growing interest in dual-curing systems. These systems combine fast UV-initiated photopolymerization with a secondary chemical curing step, enabling high-performance films. The results demonstrated that the polyol type significantly influences the UV curing behavior and final film properties.

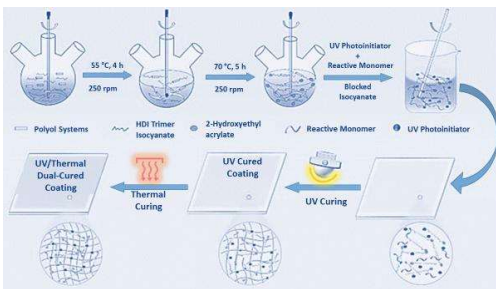


Fig. 1: UV/Thermal Dual-Cure System

Objective

In this study, PUA systems prepared with polyether, polyester, and bio-based polyol contents were subjected to secondary curing using thermally activated blocked isocyanates, taking advantage of the remaining –OH groups after initial UV curing. The final film properties were systematically compared.

The prepolymer backbone was constructed using an HDI trimer as the isocyanate source and end-functionalized with 2-hydroxyethyl acrylate (2-HEA) to introduce UV-reactive acrylate groups. To evaluate the influence of polyol structure on curing behavior and performance, three different polyols—castor oil-based for higher crosslinking density, polyether triol for flexibility, and polyester diol for mechanical strength—were used [1-3]. This approach enabled a comprehensive evaluation of how backbone composition and formulation design affect photoreactivity and the efficiency of subsequent thermal crosslinking via blocked isocyanates.

Results

UV curing efficiency was evaluated by monitoring the conversion of C=C bonds via FTIR. Yellowing resistance was assessed using a standardized aging chamber at 0.7 W/m² UV intensity and 40° C for 24 hours. Mechanical performance was tested via Shore hardness measurements and cross-cut adhesion tests. Optical and physical properties such as gloss, transparency, and flexibility of the cured films were also evaluated. All comparative results are presented in tables and images below.

Table 2: Efficiency values of PUA Prepolymers with monomer addition

Product	Viscosity Value	Pass	Efficiency (Height)	Efficiency (Area)
Polyether System	338 mPa·sec	7 (70 sec)	% -54	% 21
Polyester System	335 mPa·sec	6 (60 sec)	% 2300	% 33
Bio-based System	344 mPa·sec	5 (50 sec)	% 175	% 44

Table 3: Efficiency values of PUA Prepolymers at their respective viscosity

Product	Viscosity Value	Pass	Efficiency (Height)	Efficiency (Area)
Polyether System	6402,6 mPa·sec	6 (60 sec)	% -	% 34
Polyester System	14030 mPa·sec	7 (70 sec)	% -	% 26
Bio-based System	11127 mPa·sec	8 (80 sec)	% 88	% 50

Table 4: Yellowing test results of PUA Prepolymers with monomer additions

Product	Delta b Value	Delta E Value
Polyether System	3,77	3,75
Polyester System	5,54	5,70
Bio-based System	2,55	3,48

Table 5: Yellowing test results of PUA Prepolymers at their respective viscosity

Product	Delta b Value	Delta E Value
Polyether System	4,21	4,29
Polyester System	4,25	4,32
Bio-based System	3,41	3,48

Table 6: Shore Hardness Test results of Dual-Cure PUA systems

Product	Shore Hardness Value
Polyether System	98 HA
Polyester System	95,5 HA
Bio-based System	93 HA

Table 7: Curing speeds of Dual-Cure PUA systems

Product	Curing Speed
Polyether System	5 sec
Polyester System	10 sec
Bio-based System	15 sec



Fig. 5: Cross-Cut Test of Dual-Cure PUA systems



Fig. 6: Appearance of Dual-Cure PUA systems after curing

Materials and Method

Three different PUA prepolymers were synthesized separately using HDI trimer and one of three polyols: polyether triol, polyester diol, or castor oil-based bio-polyol. Based on NCO/OH ratios, acrylate functionality was adjusted to 3 using 2-hydroxyethyl acrylate. Reactions were carried out in a heated, stirred setup. First, HDI trimer and 2-HEA were reacted, monitored by FTIR [4]. Then, the respective polyol was added and the reaction continued until –NCO groups were fully consumed (~2270 cm⁻¹). Final products were clear, viscous, colorless liquids; FTIR spectra and viscosities were recorded.

Table 1: Viscosity Values of PUA Prepolymers

Product	Viscosity Value
Polyether System	6402,6 mPa·sec
Polyester System	14030 mPa·sec
Bio-based System	11127 mPa·sec

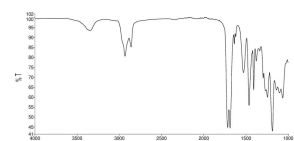


Fig. 2: FTIR spectra of Polyether System PUA Prepolymer

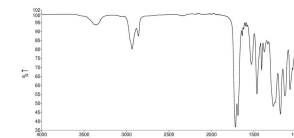


Fig. 3: FTIR spectra of Polyester System PUA Prepolymer

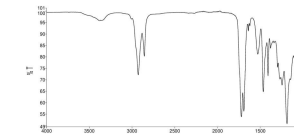


Fig. 4: FTIR spectra of Bio-based System PUA Prepolymer

Notable differences in polymerization, yellowing resistance, and mechanical properties emphasized the role of polyol selection in dual-curable PUA systems.

Resources

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- [4] Yun Hu, Qianqian Shang, Caiying Bo et al., ACS Omega, 2019, 4 (7), 12505-12511.