

EFFECTS OF NCO/OH RATIO ON THE PROPERTIES OF RADIATION CURABLE WATERBORNE POLYURETHANE ACRYLATE

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ABSTRACT

A series of radiation-curable waterborne polyurethane dispersion was synthesized with two different NCO/OH ratios of 1.5 and 2.0. The polyurethane prepolymer was synthesized by reacting polypropylene glycol (MW=2000) with isophorone diisocyanate to produce -NCO end-capped polyurethane prepolymer. The prepolymer chain was then terminated with hydroxyethyl acrylate and dispersed with deionized water to produce waterborne polyurethane acrylate (WPUA) dispersion. The WPUA dispersions were mixed with two types of photoinitiators, Irgacure 500 and Darocur 1173, and cured under a medium pressure mercury ultraviolet lamp with a wavelength of 365 nm to produce PUA films. The effects of NCO/OH ratios and different types of photoinitiators on the properties of WPUA dispersion and PUA film were studied. Both dispersions with NCO/OH ratios of 1.5 and 2.0 exhibited similar properties, with a pH value of approximately 7 and good dispersion stability. The zeta potential was measured at -60.9 for the NCO/OH ratio of 1.5 and -48.78 for the NCO/OH ratio of 2.0. The viscosity of the dispersions increased as the NCO/OH ratio increased. Regarding the curing speed of the WPUA dispersions, it was observed that Irgacure 500 performed better than Darocur 1173 for low film thicknesses of 50 μm at 5 passes. However, as the thickness of the PUA film increased to 100 μm , the curing speed became similar for all dispersions, requiring 9 passes, irrespective of the NCO/OH ratio or type of photoinitiator. The hardness of the PUA films was evaluated using a pendulum hardness test. It was found that the type of photoinitiator did not have an impact on the film hardness. However, the NCO/OH ratio influenced the hardness, with higher ratios resulting in increased hardness. These findings contribute to the understanding of the properties and performance of radiation curable waterborne polyurethane dispersions and provide valuable insights for their potential applications.

Keywords: *Radiation curable, Prepolymer, Dispersion, Polyurethane Acrylate*

INTRODUCTION

Waterborne polyurethane has attracted a lot of interest lately and is widely used as coatings because of its nontoxic and environmentally friendly appeal. Coatings are essential in many different industries because they provide protection and aesthetic improvement to a variety of substrates. Conventional polyurethane (PU) coatings frequently use organic solvents to improve their ability to adhere to various surfaces. These solvents, however, usually contain hazardous air pollutants and volatile organic compounds (VOC) that are dangerous towards the environment and health (Jiménez-López, A. M., 2022). In addition, most organic solvents are toxic and carcinogenic in nature. In response to the increased emphasis on environmental awareness, many countries have started to issue various regulations and laws related to the production of coatings. Due to this, waterborne coatings

have gained rapid development in coatings, adhesives, and textile industry (Honarkar H., 2018; Zhou X., 2015; Santamaria-Echart, 2021; Kang, S.Y., 2018). Because of their low toxicity, decreased emissions of hazardous compounds, and enhanced eco-friendliness, waterborne PUs represent a promising alternative. However, a major drawback of water-based PUs is that they take longer to cure at room temperature than solvent-based PUs.

To address this challenge, radiation curing technology offers a viable solution. By incorporating radiation curable property into the formulation of water-based coatings, instant drying can be achieved, providing both environmental and energy-friendly benefits. Radiation curing offers a rapid and efficient curing process that minimizes the need for extended drying times, allowing for enhanced productivity and reduced energy consumption (Zareanshahraki, F., 2020). Waterborne PU coatings derived from radiation induced polymerization are becoming progressively more attractive due to increasing environmental demands and owing to their good physicochemical, rheological and optical properties (Agnol, L. D., 2021).

Although radiation curable waterborne PUs have drawn more interest, there is not much work on the factors that influence the properties of radiation curable waterborne PU. Waterborne polyurethane acrylate dispersion (WPUA) was synthesized from the flexible polyol as the soft segment while diisocyanates and hydroxyl acrylate act as the hard segment. Apart from adjusting the NCO/OH ratio, the performance of PUA can be altered by changing the structure of polyol, diisocyanates and hydroxyl acrylate used in the formulation [8], the performance of PUA can be tailored to meet specific requirements. This paper aims to investigate the effects of isocyanate to hydroxyl (NCO/OH) ratios of WPUA dispersion and PUA films. Furthermore, this paper also evaluates the effects of different types of photoinitiators on the properties of polyurethane acrylate (PUA) films.

METHODOLOGY

Materials

Polypropylene glycol (PPG; MW = 2000), dimethylol propionic acid (DMPA), N-methyl-2-pyrrolidone (NMP), hydroxyethyl acrylate (HEA) and deionized water were procured from Acros Organics (Belgium). Tin-II-2-ethylhexanoate and isophorone diisocyanate (IPDI; 98%) were procured from Sigma Aldrich (Germany). Triethylamine (TEA), hydrochloric acid, di-n-butylamine, toluene and bromophenol blue indicator were procured from Fisher Scientific (USA). Isopropyl alcohol was procured from System (Malaysia). Irgacure 500 and Darocur 1173 were procured from Ciba Specialty Chemicals (Switzerland).

Synthesis of Waterborne Polyurethane Acrylate

The molar ratio between the isocyanate (NCO) group from IPDI and the hydroxyl (OH) groups from PPG polyol and DMPA was calculated to reach the NCO: OH molar ratio of 1.5 and 2.0. Initially, to produce polyurethane acrylate (PUA) prepolymer, PPG and DMPA were added and allowed to mix with NMP as co-solvent in a 3-neck flask equipped with a heating mantle, overhead mechanical stirrer, and thermometer as in Figure 1. The reaction temperature was maintained constant under 80°C and stirrer continuously until all the chemicals were homogenous. Then, IPDI was added drop wise using a dropping funnel for 30 minutes followed by addition of catalyst. The reaction is monitored hourly with titration (ASTM D2572) until NCO content reaches theoretical value. Next, HEA was dropped gradually and allowed to react at 60°C until all remaining NCO had been fully consumed. The carboxylic acid group of the DMPA was then neutralized with TEA for 30 minutes. Finally, the

PUA prepolymer was then dispersed in deionized water. The dispersion was prepared at 40% solid content, the volume of deionized water was calculated and added into the reactor flask over the course of 30 minutes with vigorous stirring.

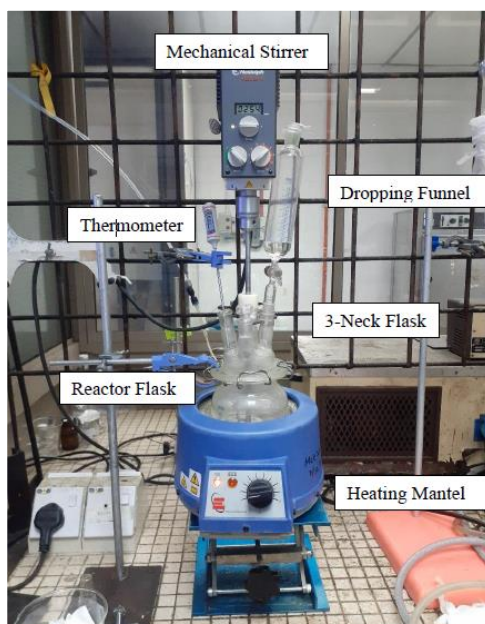


Figure 1: WPUA synthesis setup

Characterisation of WPUA Dispersion

i. Viscosity

The viscosity of both WPUAs were measured with rotational viscometer (DV2T Touch Screen, AMETEK Brookfield, USA) at ambient temperature, for 60 seconds at different speed of 1, 10 and 50 rpm with a Spindle-51.

ii. pH

The pH was measured using pH meter (PB-10, Sartorius, German) by dipping the probe into the sample at room temperature. After each usage, the probe was rinsed with distilled water to clean the probe.

iii. Isocyanate Standard Test Method (ASTM D2572)

Along the synthesis step, the amount of NCO content remaining in the mixture was monitored with dibutylamine back titration method (ASTM D2572) (Figure 2) to calculate the amounts of HEA needed to end-cap the remaining NCO group. The standard test method for calculating the content of NCO groups in urethane prepolymers was done by reacting the remaining NCO in the prepolymer with excess dibutylamine in toluene.

The NCO content was calculated as below:

$$NCO \text{ content } (\%) = \frac{[(B - V) \times N \times 0.0420]}{W} \times 100 \quad \text{Eq...}(1)$$

Where:

- B = Volume of titration of blank, mL
- V = Volume of titration with sample, mL
- N = Normality of HCl
- 0.0420 = milliequivalent weight of NCO group
- W = Weight of sample, g

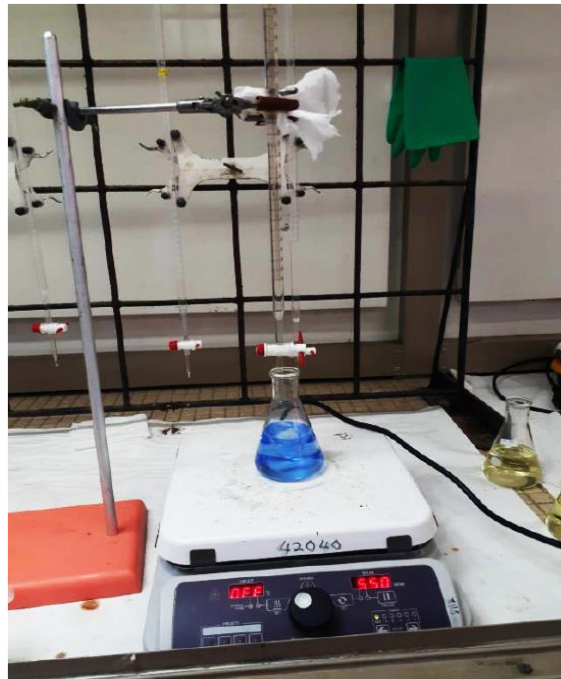


Figure 2: ASTM D2572 titration set up

iv. Zeta Potential

The WPUA 1.5 and WPUA 2.0 dispersion was diluted with deionized water to a solid content of 1 wt%. Then, a single drop of the mixture was further diluted with distilled water in the equipment's sample cell–electrode assembly and measured by zeta potential analyser (ZetaPlus, Brookhaven, USA).

v. Solid Content

The solid content of WPUAs were calculated by weighing 1.0 g of the sample in a weighing boat and dried in the oven at 80°C until the dried film reaches a constant weight. The weight difference of before and after were recorded, and the solid content were calculated with the formula:

$$\text{Solid content } (\%) = \frac{W_f}{W_i} \times 100 \quad \text{Eq...}(2)$$

where:

- W_f = Net weight of dry sample
- W_i = Net weight of original sample

Preparation of PUA Film

The samples of both WPUA 1.5 and WPUA 2.0 were placed inside a vacuum oven to release air that was trapped in the dispersion during synthesis. The two samples of WPUA were added with different photoinitiators; Darocur 1173 and Irgacure 500 and were let sit for 24 hours at room temperature. The prepared coatings were then applied to a glass substrate using a 4-sided bar coater with a thickness of 50 and 100 μm wet films. The wet films were then cured using a UV-IST, UV-curing machine equipped with a medium-pressure mercury lamp at 365 nm to induce free radical polymerization with a conveyor speed of 10 m/min. The film was checked with a thumbprint test until the film has fully cured.

Characterisation of PUA Film

i. Gel Content

The gel content was measured through Soxhlet extraction method following the works of Wang *et al.* (2021). The cured PUA films were sliced into small pieces and weighed about 0.1 g, after which the sample was immersed in acetone for 17 h before being dried for 24 hours at 60°C until it reached a constant weight. The gel content was calculated with the formula:

$$\text{Gel content}(\%) = \frac{W_f}{W_i} \times 100 \quad \text{Eq...}(3)$$

where:

W_f = Weight of gel fraction*

W_i = Weight of original sample

*Gel fraction refers to the weight of the cross-linked portion of the polymer that remains after the solvent extraction and drying process.

ii. Pendulum Hardness

The PUA films hardness with different PI and different thickness were measured through the deflection angles of pendulum oscillation on the film samples, using a Pendulum Hardness Tester, TQC Sheen, SP0500, Netherlands, using a König pendulum, in accordance with ASTM D4366.

RESULT AND DISCUSSION

In this study, WPUA prepolymers were synthesised by reacting polyols and diisocyanate followed by termination with an acrylate. This process provides an unsaturated carbon double bond (C=C) site from acrylate functionality. The WPUA prepolymer was then dispersed in deionized water to form WPUA dispersion.

Properties of WPUA Dispersion

i. Viscosity

The waterborne PUA dispersion was commonly used as adhesives and coatings. One of the most crucial factors influencing the workability as well as the rate of photopolymerization and properties of the cured film is the viscosity of the dispersion (Xu, J., 2013). The viscosity of WPUA dispersion

needed to be controlled to prevent sagging and difficulty to apply due to very high viscosity (Asif, A., 2004). The produced WPUA 1.5 and WPUA 2.0 are in the range of acceptable viscosity as compared to conventional WPUA coatings as shown in Table 1.

The viscosity values of both WPUA 1.5 and WPUA 2.0 dispersions shows that the NCO:OH ratio did not greatly affect the viscosity. The viscosity of the emulsion can be adjusted by controlling the volume of water added during the dispersion step.

Table 1: Comparison between in-house WPUA and commercial products

Company	Product	Solid content (%)	Viscosity (mPa·s)	pH
Nuklear Malaysia	WPUA 1.5	39	28.16	7.27
Nuklear Malaysia	WPUA 2.0	40	29.44	7.41
Allnex	UCECOAT® 7230	40.5 to 43.5	< 200	6.0 to 8.0
BASF	Joncryl® HYB 6340	40	50	7.6
UBE Corp.	UVPUD-7009E	30	20	8.0
UBE Corp.	UVPUD-7009E-C2	30	15	7.0
Covestro	Bayhydrol® UV 2282	38 to 40	< 800	7.8 ± 0.8

ii. pH

According to Szycher (1999), the viscosity of the dispersion increases with increasing pH, but decreasing pH makes the dispersion unstable by causing the solids to settle. The pH of WPUA 1.5 and WPUA 2.0 are in the range of conventional coating, with 7.27 and 7.41 respectively, as shown in Table 1. The low acidity values of the resins are the result of a neutralization reaction that took place when the carboxylic acid groups were neutralized by the addition of TEA during synthesis.

iii. Stability of WPUA

Zeta potential is an important indicator for assessing the stability of the WPUAs dispersions as it is a determining factor in particle dispersions for electrostatic interactions. The zeta potential values obtained for WPUA 1.5 and WPUA 2.0 were found to be -60.90 mV and -48.78 mV respectively, which indicates both dispersions are stable. These values indicate that both dispersions exhibit stable behaviour. The negative zeta potential values observed for both WPUA formulations suggest the presence of repulsive forces among the particles, which effectively prevents aggregation and ensures dispersion stability. These results demonstrate how well the WPUA formulations produce stable dispersions, which is essential for their use in a variety of industries like coatings and adhesives.

iv. Solid Content

The solid content of the WPUAs were both within the expected range of 40% as displayed in Table 1. According to Nanda et al. (2005), the WPUA solid content can only be dispersed in water when the water content is equal to or greater than the solid content. Thus, the solid content range was set to about 40% as to avoid having a solid-like structure in the WPUA dispersion.

Properties of PUA Film

The (C=C) site from acrylate functionality was utilized for free radical polymerization when the dispersion is exposed under electron beam or ultraviolet radiation to form PUA film. The physicochemical properties of PUA films with different photoinitiators was investigated.

i. Curing Rate

The amount of time needed to fully cure a sample is important especially for industrial use application. Low number of passes required to cure a sample imply higher curing and polymerization rate occurred to crosslink the PUA. The number of passes for both WPUAs with different PIs at different thickness are presented in Table 2. The performance difference between both PIs were significant at low thickness 50 μm , where PUA 2.0 film with Irgacure 500 shows higher curing rate. However, at a higher thickness of 100 μm , the curing performance for both NCO:OH ratios and PI types were almost the same. The reactivity of both PIs depends on the UV energy needed to initiate free radical polymerization, in which Irgacure 500 appeared to require less energy as compared to Darocur 1173. It was observed that the water particles slow down the curing process, thus more cycle is needed to cure the WPUA dispersion. In future study, the PUA films needed to be flashed off with a convection oven before curing to release water particles from the dispersion particularly at higher film thickness.

Table 2: Curing and mechanical properties of WPUA 1.5 and WPUA 2.0 with varying photoinitiators and film thicknesses

Sample	WPUA 1.5				WPUA 2.0			
	Irgacure 500		Darocur 1173		Irgacure 500		Darocur 1173	
Film thickness (μm)	50	100	50	100	50	100	50	100
Curing (Number of passes)	6	9	9	9	6	10	8	9
Gel content (%)	62	62	66	66	64	64	72	72
Film hardness (Oscillation)	28	18	29	18	46	26	44	23

ii. Crosslinking Density

The gel content test was used to measure the percent of crosslinking produced in the coating after curing. The observed gel content for the WPUAs at different PI is shown in Table 2. The gel content of WPUA 2.0 is higher than WPUA 1.5, which indicates the increase in NCO: OH ratio can improve the crosslink extent of the resin.

iii. Pendulum Hardness

The film hardness can be understood as the material's resistance to localized plastic deformation. Table 2 and Figure 3 shows the data on the pendulum hardness of WPUA 1.5 and WPUA 2.0 with film thickness of 50 and 100 μm as a function of photoinitiators Irgacure 500 and Darocur 1173. The data shows the pendulum hardness decreases with increasing thickness of coating. The pendulum hardness test is based on the idea that the harder the surface of the coating, the longer the pendulum will oscillate (Ma, X., 2013). In this study, WPUA 2.0 showed better hardness than WPUA 1.5. This occurrence can be linked with the high gel content and crosslinking density of WPUA 2.0 especially with Irgacure 500 that will induce high hardness (Hwang, H. D., 2011). There is no apparent

difference in the WPUAs trends between both PI as in Table 2, indicating the PUA film hardness is not affected by the types of PI.

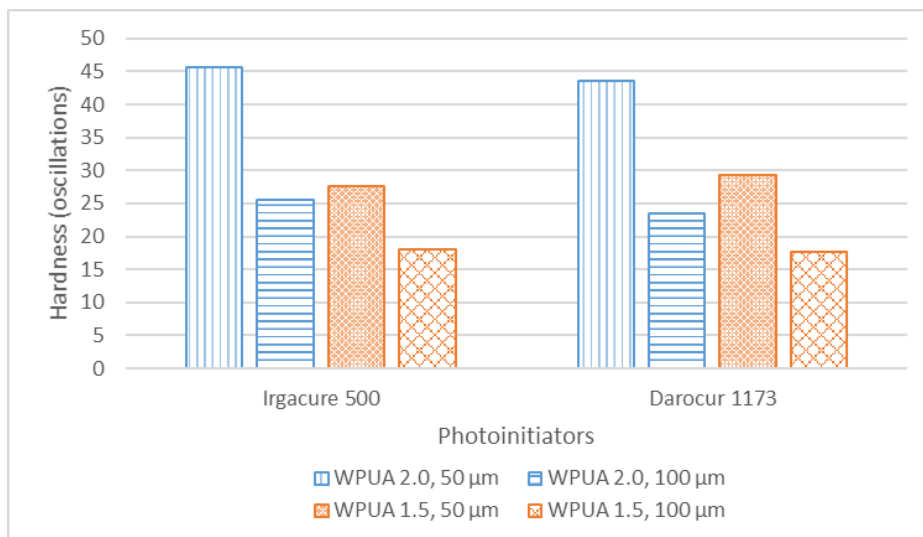


Figure 3: Film hardness of WPUA 1.5 and WPUA 2.0 with varying photoinitiators

CONCLUSION

In conclusion, the experimental results highlight several features relating to the characteristics and effectiveness of the WPUA dispersions and PUA films examined in this work. According to the zeta potential measurements, both the WPUA 1.5 and WPUA 2.0 dispersions exhibit stable behaviour, which is essential for their practical application. The WPUAs' viscosity is within the permissible range of conventional PU coating which ensures adequate workability and promotes photopolymerization during curing. Furthermore, the WPUAs' solid content is within the necessary range of 40%, allowing for good dispersion in water without producing a solid-like structure. The pH values for both WPUA dispersions are within the conventional coating range, indicating the effectiveness of the neutralization reaction carried out during synthesis. The polymerization process was discovered to be influenced by the film thickness and photoinitiator selection with regards to the cure rate. In the future, especially when working with thicker films, pre-flashing the PUA films might be needed to liberate water particles from the dispersion prior to radiation curing. Based on the hardness test, it is revealed that the type of photoinitiators does not affect PUA film hardness. However, the hardness improved with increasing NCO:OH ratio. Overall, this work offers an insight towards prospective application of WPUAs as greener coatings alternatives. Future work is suggested to compare the feasibility of natural-based polyol such as palm oil in synthesizing WPUA.

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