

Synthesis and characterization of waterborne polyurethane acrylate copolymers

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Abstract—Polyurethane acrylate copolymers were synthesized by emulsion polymerization process. To reduce the environmental hazards, organic solvents were replaced by eco-friendly aqueous system. Concentration of polyurethane and acrylate monomer was varied to investigate the effect of chemical composition on performance properties of copolymers. FTIR spectroscopy was used as a key tool to record the chemical synthesis route. The synthesized copolymer emulsions were characterized by evaluating their particle size, viscosity, dry weight content, chemical and water resistance. Thermal decomposition was studied by thermogravimetric analysis. Scanning electron microscope was used to visualize the morphological structure of copolymers. The experimental results indicate better polyurethane acrylate compatibility till the ratio of 30/70. However, these copolymers exhibited synergistic effects between the two polymers and revealed a remarkable improvement in numerous coating properties.

Key words: Polyurethane, Acrylate, Emulsion Polymerization, Copolymers, Eco-friendly, Coating

INTRODUCTION

Waterborne polyurethanes (PU) coatings are introduced as environment-friendly materials with a variety of potential applications. These are non-toxic and non-flammable materials with respect to environmental issues [1]. Based on water, they are volatile organic compounds (VOC) free or of low VOC emission. These water-based PU materials have been extensively applied in adhesives, coatings, surface finishing, paper and textile industries [2,3]. Waterborne PU technology is now growing at a prompt rate and is going to be a very common practice in the industry [4]. However, PU coatings are in general more expensive, and in some applications there are cost limitations. To take benefit of PU film-forming properties, a combination with a low cost material is now a common routine in the coating market leading to new different products. One of the most popular second components is the acrylic moiety. Acrylic polymers are known to have superior water resistance, wearing resistance, adjustable mechanical properties and low cost, though they have low solvent and abrasion resistances. Combination of polyurethane with acrylics is expected to be valuable to increase the performance of the resulting materials [5]. Acrylic polymer emulsions have been extensively used in the leather industry as coatings and also as paper and textile finishes [5]. Polyurethane acrylates are comb-like materials which can potentially merge the high abrasion resistance, toughness, tear strength, chemical and solvent resistance, and good low temperature properties of polyurethanes with the good optical properties, water resistance, wearing resistance and weather ability of the acrylates. A wide variety of properties can be engineered in polyurethane copolymer by rearranging acrylic structural units, for example, anticorrosive protective films and finish materials

for leather industry, bending matter for magnetic media, mounts for printing ink, coating for optical and carbon fibers, gas and liquid separating membranes, materials for medical usages, and as adhesives etc. [6] During the last decade the incorporation of acrylic component into PU chains has been widely studied by numerous researchers [3,7-17]. Different researchers account excellent statements about the characteristics of polyurethane acrylates. There are some research groups dealing with combinations of polyurethane with acrylic dispersions, which incorporate polyurethane as a co-binder of acrylic emulsions, dispersants [13], physical mixtures and composites [14]. Physical blends of the two different polymeric systems are an accepted approach to combine the favorable attributes of each of polymer. However, in many cases these blends present the expected characteristics and compromise the superior performance properties because of the incompatibility of the two systems in which the different polymers are present as separate particles. A more elegant way to obtain this balance is to synthesize the urethane acrylate copolymer [11]. In these systems, both components are present in a single polymer molecule [15]. According to the research writings, a chemical coupling between the urethane and the acrylic components has been established, and these systems are known as polyurethane-acrylates or acrylic-polyurethane hybrids [16,17]. Unsaturated polyurethane resins are reacted with acrylic monomers in the presence of water as a solvent in a special copolymerization process to produce solvent free polyurethane acrylates. Keeping in view all of these incentives, this study was intended in which different polyurethanes were copolymerized with acrylates. Polyurethane acrylate copolymers were synthesized with varying compositions by three-step synthesis process with water as solvent. To establish the chemistry and to evaluate the efficacy range, copolymers were subjected to special tests and characterized by different sophisticated techniques, e.g., FTIR, DSC, and TGA. This research study was a part of a project in which different series of polyurethane acrylate copolymers with

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a variety of monomers were synthesized in aqueous medium. Hence the concern of environmental pollution by volatile organic compounds was reduced. There are many efforts in the world of polymer chemistry to resolve the issue of volatile organic compounds. Moreover, the performance of these copolymers in textiles was investigated and good quality results have been discussed elsewhere [18, 19]. These successful applied consequences have made this project a valuable effort in the field of polymer engineering.

EXPERIMENTAL

1. Chemicals and Reagents

Polycaprolactone polyol, CAPA2100, (molecular weight 1000) was purchased from Perstorp UK limited, 4,4'-diisocyanato dicyclohexylmethane (H₁₂MDI, 90% mixture of isomers), polyvinylalcohol (PVA, 87-89% hydrolyzed with molecular weight 13000-23000) were purchased from Sigma-Aldrich Chemical Co, USA. Toluene diisocyanate (TDI) from Bayer Material Science, 2-Hydroxyethyl methacrylate (HEMA, 95%, 130.15) and Butyl acrylate (BA, 99%, 128.17) were received from Fluka Chemika. Ammonium persulphate (APS), sodium thiosulphate (Na₂S₂O₃·5H₂O) and sodium salt of alkyl aryl polyglycol ether sulphate from local market. Deionized water was used for the whole process. Basic formulations to prepare PUA copolymers are given in Table 1 and 2, respectively.

2. Synthesis of Polyurethane Acrylate (PUA) Copolymers

Polyurethane acrylate copolymers were synthesized by subsequent three-step synthesis processes. The PU prepolymers were synthesized according to a recommended procedure [20]. First, stoichiometric amounts of CAPA (2 moles) and isocyanate (H₁₂MDI) (3 moles) were charged into a 500 mL four-necked round bottom glass reactor equipped with a mechanical stirrer, a thermometer, a reflux condenser, heating oil bath and a nitrogen gas inlet system. The temperature of the oil bath was increased up to 60 °C. This mixture of polyol and isocyanate was stirred continuously under the blanket of nitrogen gas and temperature was increased steadily from 80-90 °C. It took approx. 2.0 h to obtain NCO terminated polyurethane

(PU) prepolymer (Fig. 1). After that, temperature of the reaction vessel was decreased to 60 °C and (2 moles) 2-hydroxyethyl methacrylate (2-HEMA) was introduced into the reaction mixture. It took approx. 1.0 h to form a thick, viscous and transparent resin material in the reaction flask [21], which indicates the formation of vinyl terminated PU resin. The Fourier transform infrared (FTIR) spectroscopy was used at every step to monitor the synthesis process (Fig. 2).

3. Copolymerization of PU Resin with Butyl Acrylate (BA)

Copolymerization of PU resin with butyl acrylate (BA) was carried out through emulsion polymerization process, polyvinyl alcohol (PVA) and alkyl aryl polyglycol ether sodium sulphate were used as emulsifier while ammonium persulphate (APS) with sodium thiosulphate (Na₂S₂O₃) as initiator. Deionized water was used during all the steps of copolymer synthesis. Water solutions of PVA 3% (w/v) and emulsifier 12% (v/v) were prepared separately, and were introduced slowly to the reaction flask with 0.2% (w/v) initiator solution. The reaction was completed in approx. 3.5 h with continuous stirring at 55 °C. 20% of the emulsion was of BA and vinyl terminated PU prepolymer, ratio of both monomers were assorted progressively. White milky emulsions were obtained at the end of process which was saved for succeeding characterization purposes. A schematic illustration of the chemical route for synthesis of PU acrylate copolymer is given in Fig. 1.

4. Characterization of Copolymers

The copolymers were characterized by different techniques. For chemical characterization, FTIR spectra were collected at every stage of the synthesis process by Bruker Equinox 55 (Germany) instrument; scanning region was from 4,000 cm⁻¹ to 500 cm⁻¹. Samples were analyzed by applying on KBr or NaCl discs.

Particle size is an important parameter for deciding the end use of copolymer emulsions in industry. Particle size and polydispersity index (PDI) were measured using SEMATEch Laboratory, SEM 633 light scattering apparatus (France).

Viscosity of PUA emulsion was measured with the help of Brookfield DV-II+Pro viscometer using UL adapter spindle. Dry weight content of PUA emulsions was determined by placing a weighed amount of emulsions in aluminum cups at 50 °C in oven for 24 h. After that, these samples were again weighed and dry weight content was calculated according to the following formula:

$$\% \text{ dry weight} = W_b/W_a * 100$$

where W_a is weight of sample before drying and W_b is weight after drying.

Chemical resistance was evaluated according to ASTM D 1647-89. The PUA emulsions were flowed onto the glass panels. The coated panels were allowed to dry for three consecutive days (72 h) at room temperature. The periphery of panels was covered with wax in order to restrain the migration of chemical solutions under the films from open ends. 3% (w/w) solutions of H₂SO₄ and NaOH were used for this purpose and changes in appearance of films were monitored after three days with naked eye.

Water resistance was evaluated according to ASTM D 1647-89. Aluminium panels were coated with PUA emulsions. Emulsions were flowed and allowed to drain onto the panels in a nearly vertical position. These coated panels were dried for 48 h. Dried coated panels were placed in a beaker containing deionized water at room tem-

Table 1. Basic ingredients for PUA copolymer emulsions

Ingredients	Amount in %
Deionized H ₂ O	66-75
APS	0.02
Na ₂ S ₂ O ₃ ·5H ₂ O	Few crystals
Emulsifier	12
PVA	3
BA	18-10
PU resins	10-50 of BA

Table 2. Formulation of PUA copolymer emulsions

Emulsion no.	PU resin composition	PU/BA (%)
AL1.1	H ₁₂ MDI/CAPA/HEMA	10/90
AL1.2	H ₁₂ MDI/CAPA/HEMA	20/80
AL1.3	H ₁₂ MDI/CAPA/HEMA	30/70
AL1.4	H ₁₂ MDI/CAPA/HEMA	40/60
AL1.5	H ₁₂ MDI/CAPA/HEMA	50/50

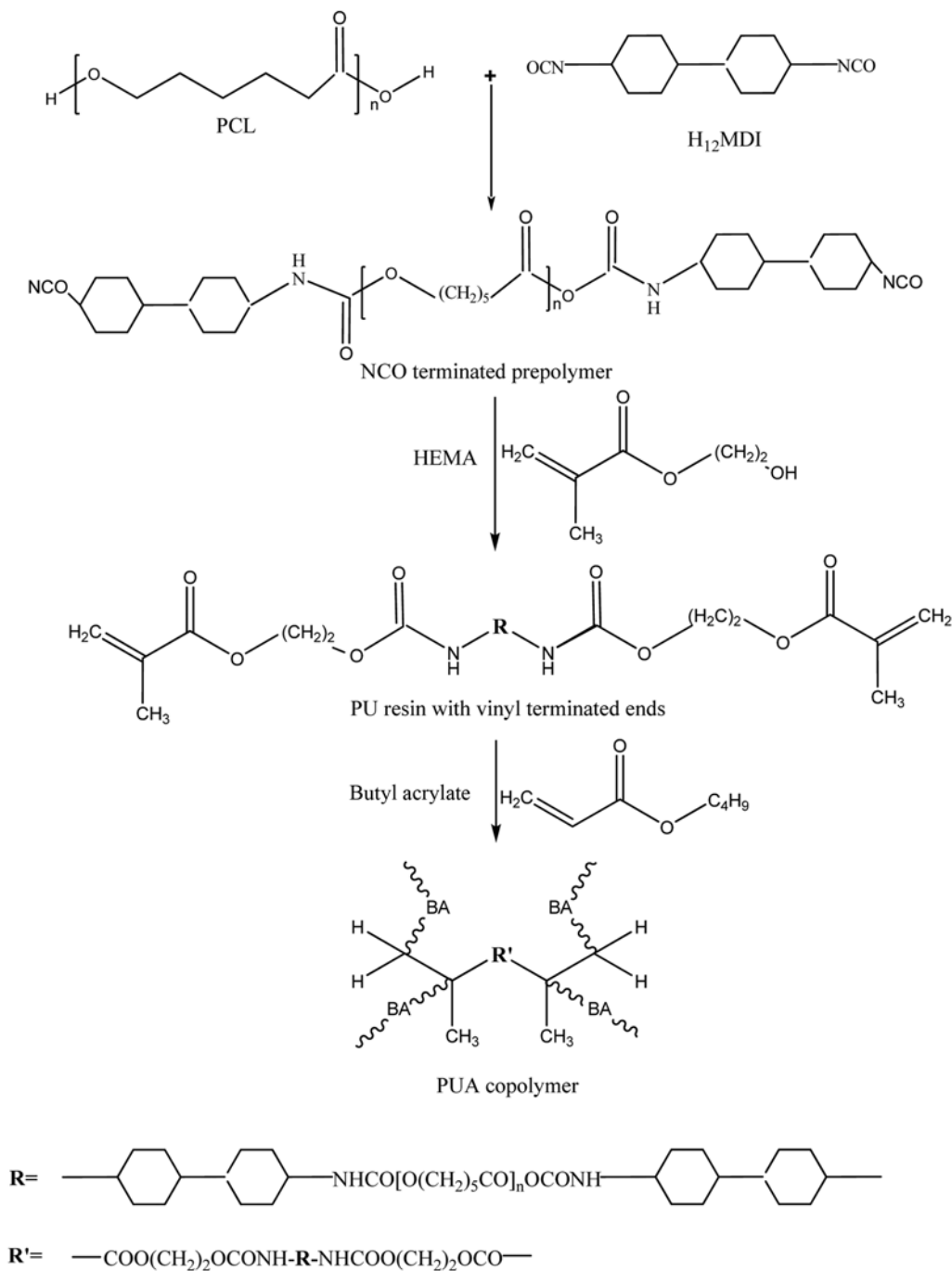


Fig. 1. Reaction scheme to prepare PUA copolymer.

perature, immersing the ends that were uppermost during drying. After 18 h panels were removed from water, wiped carefully and dried at room temperature to monitor any change.

Thermal decomposition (thermogravimetric analysis) study was carried out by TGA-PL England in platinum pan under the flow rate of 50 mL/min of nitrogen gas. Temperature scan was carried out from ambient temperature (25 °C) to 600 °C with the ramp of 10 °C. Weight loss of sample in percent (%) was recorded versus change in temperature (°C).

Morphological properties of dried samples of PUA emulsions were studied by scanning electron microscope (SEM), VEGA 3

SBH\ TESCAN, Brno, Czech. In the SEM samples were imaged at 20 kV accelerating voltage. The samples without any dilution were coated with a thin layer of gold to reduce any charge build-up on the fracture surface.

RESULTS AND DISCUSSION

Fig. 2 demonstrates stepwise IR spectra of all of the monomers and product species during the course of PUA copolymer preparation. The IR spectral analysis is mainly used to evaluate and confirm the completion of PUA copolymerization reaction in terms of

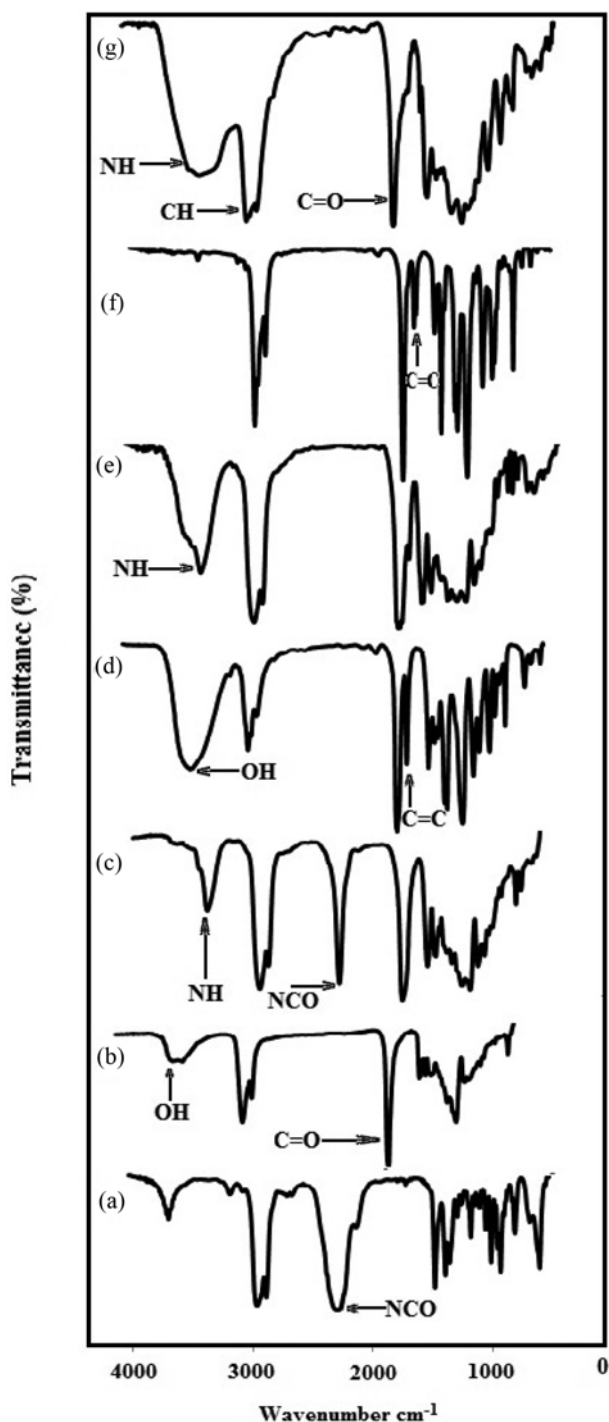


Fig. 2. FTIR spectra for synthesis of PUA copolymers, (a) H_{12} MDI, (b) PCL, (c) PU prepolymer with free NCO groups, (d) 2-HEMA, (e) vinyl terminated PU prepolymer, (f) BA, (g) PUA copolymer.

disappearance of the NCO band of isocyanate near $2,260\text{ cm}^{-1}$ and the appearance of N-H band at $3,000\text{--}3,400\text{ cm}^{-1}$ [15]. In this figure spectrum of H_{12} MDI and polyol Capa shows characteristic stretching vibration bands of NCO at $2,259\text{ cm}^{-1}$ and OH at $3,439\text{ cm}^{-1}$, respectively. In PU prepolymer spectrum OH broad band of polyol is replaced by comparatively narrow band of N-H at $3,373\text{ cm}^{-1}$. However NCO band is still visible with relatively less intensity at

$2,263\text{ cm}^{-1}$. Next spectrum of 2-HEMA shows typical broad band of OH at $3,438\text{ cm}^{-1}$ and a stretching vibration peak of C=C at $1,635\text{ cm}^{-1}$ with strong carbonyl peak at $1,714\text{ cm}^{-1}$. In spectrum of vinyl terminated PUA resin, the broad band of OH is replaced by relatively narrow band of N-H at $3,374\text{ cm}^{-1}$, and NCO band of PU prepolymer completely vanishes, which confirms the completion of reaction between OH groups of 2-HEMA and NCO groups of PU prepolymer. The spectrum of BA shows characteristic peaks of C=O and C=C at $1,726\text{ cm}^{-1}$ and $1,636\text{ cm}^{-1}$, respectively, with a strong peak of C-O at $1,191\text{ cm}^{-1}$. In the copolymerization step BA reacts with PU resin and produces PUA copolymer, which was analyzed by IR after drying in oven at $50\text{ }^{\circ}\text{C}$ for 24 h. The spectrum of PUA copolymer does not contain any peak for C=C, IR region from $1,500\text{--}1,700\text{ cm}^{-1}$ is completely clear with a bending vibration peak of C-H at 841 cm^{-1} , which is a strong evidence of complete copolymerization of PU with acrylate. But stretching band of N-H at $3,349\text{ cm}^{-1}$ is wide, which may be because of some remaining amount of moisture in the film.

PU molecular chains with vinyl terminals undergo vinyl addition with unsaturated sites of BA. Resulting copolymer is a cross-linked polymer with particle sizes in the range of nm scale. A glance of Table 3 and Fig. 3 reveals that particle size increases as PU/BA ratio increases from 10/90 to 30/70 from 47.1 nm to 198.4 nm , but after this it decreases till 50/50 to 40.2 nm again. These particle sizes are analogous to the sizes reported by Chai et al. [5], even better other than the size of emulsion AL1.3. It is possible that when PU concentration was increased from 10-30% of BA, the fusion of particles resulted in large particles along with the tendency of acrylates to swell. But after that, the concentration of BA was low regarding

Table 3. Particle size, viscosity and dry weight content of PUA copolymers

Emulsion no.	PU/BA (%)	Particle size (nm)	PDI ^a	Viscosity (cp)	Dry weight (%)
AL1.1	10/90	47.1	0.148	50.6	38.15
AL1.2	20/80	53.3	0.046	29.2	37.40
AL1.3	30/70	198.4	0.717	17.0	30.00
AL1.4	40/60	84.6	0.328	15.3	29.00
AL1.5	50/50	40.2	0.216	17.4	28.60

^aPolydispersity index

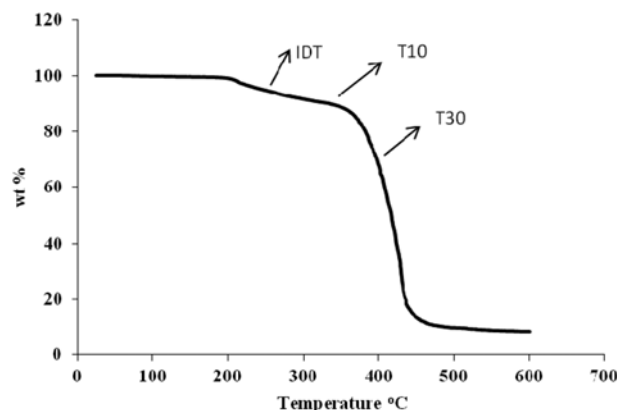


Fig. 3. Thermogravimetric analysis of PUA copolymer.

swelling of monomer-swollen particles, even the concentration of PU was increased further. Also, stability of emulsions was observed to decrease for last two concentrations as compared to first three ones.

Viscosity of PUA copolymer emulsions is presented in Table 3. In this copolymerization process, acrylate monomer-swollen micelles, stabilized by emulsifier, were first formed, and then inside these micelles further process of copolymerization was continued. It is obvious from the data that viscosity of emulsions decreases with the decrease of acrylate concentration. It might be because of decrease in the count of monomer-swollen micelles, which leads to a decrease in cross linked polymer chains.

Dry weight content of PUA copolymers decreases gradually from higher PU/AC ratio to lower one. Highest dry weight content is 38.15% and lowest is 28.6%. However, it is not very low dry weight; usually emulsion products with 30–40% dry weight content are appreciated in industrial applications. By the addition of BA at the initial stage of emulsion polymerization, monomer-swollen particles were generated. When vinyl terminated PU resin was introduced, copolymerization was carried out inside these monomer-swollen particles. It is probable that at higher concentrations of BA monomer-swollen particles were richer in concentration of monomer with greater ability of acrylate to swell and copolymerize with vinyl terminals of PU prepolymer, as compared to the situation when concentration was lower. So, the dry weight content of final PUA copolymers was decreased gradually. Also, remaining unreacted monomers might be vaporized during drying of PUA copolymer emulsions. This inclination has already been proved by variation in viscosity and stability of copolymer emulsions.

To evaluate the overall performance of the PUA copolymers, the coated films were subjected to action of acid and alkali according to standard methods. From the data presented in Table 4, it can be revealed that all the copolymer emulsion coatings had excellent resistance to acids and also valuable very good to good resistance to alkalis or bases. These better results of chemical resistance of PUA copolymers could be due to exceptional performance of acrylates [15].

Water resistance of PUA copolymer coatings is very important regarding their end applications in industry. Since one of the key drawbacks compared with the solvent-based products, the water resistance of water-based PUA copolymers has attracted broad attention [22]. Several factors influence the water resistance of PUA copolymers. Here, this property was evaluated according to standard

Table 4. Chemical and water resistance of PUA copolymers

Emulsion no.	PU : BA (%)	Acid resistance	Alkali resistance	Water resistance
AL1.1	10/90	E ^a	VG ^b	E
AL1.2	20/80	E	G ^c	VG ^d
AL1.3	30/70	E	G	VG
AL1.4	40/60	E	G	VG
AL1.5	50/50	E	G	VG

^aExcellent resistance with no visible effect

^bVery good resistance with slight haziness

^cGood resistance with haziness

^dVery good resistance, blooming disappear in 2 h

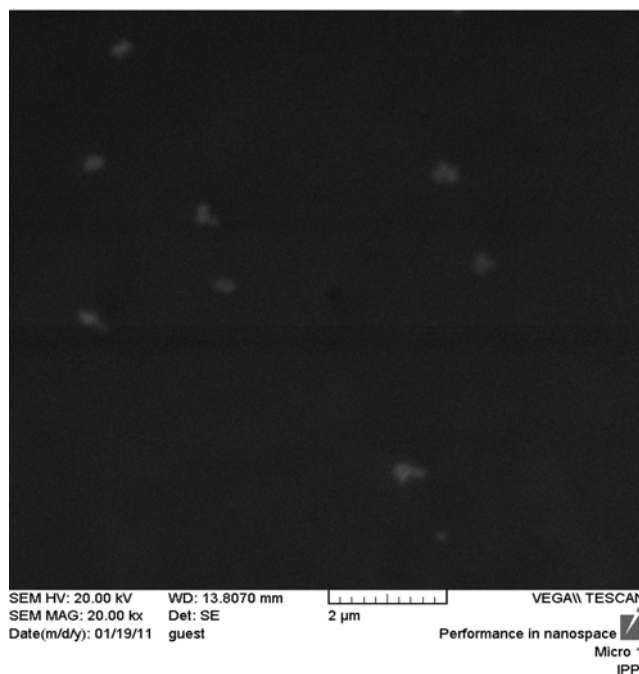


Fig. 4. Scanning electron microscope micrograph of PUA copolymer.

method, and results displayed in Table 4 depict the excellent to very good water resistance of PUA copolymer coatings. It can be because of incorporation of acrylates to PU chains in a cross linked manner [15].

The decomposition of PUA copolymer was investigated by thermogravimetric analysis of its film. Generally, polyurethane exhibits a relatively poor thermal stability, owing to dissociation of the urethane bond occurring around 200 °C [23,24]. However, by the chemical incorporation of acrylate in polyurethane, enhanced thermal stability was observed (Fig. 3). The thermal stability was evaluated by using initial decomposition temperature (IDT, 5% degradation) and the thermal indexes T_{10} and T_{30} (10% and 30% weight loss). There was no great loss before 245 °C (IDT) and T_{10} and T_{30} were 333.64 °C and 397.18 °C respectively. These results present quite stable thermal behavior of PUA copolymer as compared to reported in literature [15].

Morphological properties of dried samples of PUA emulsions were studied by SEM. Fig. 4 SEM micrograph of dried PUA copolymer displays structural morphology of particles. The spherical rounded PUA micelles are visible in this image; however, coagulation of particles is also detectable, which may happen during drying of solvent from emulsion sample.

CONCLUSIONS

To reduce environmental hazard and to obtain cost/performance properties, aqueous polyurethane acrylate emulsions were successfully prepared with different concentration ratios by using emulsion polymerization process. The chemical route of synthesis was traced by FTIR spectral analysis. Experimental results indicate an increase in particle size till 30/70 ratio (PU/BA) with relatively more stable emulsions. Dry weight content and viscosity of emulsion de-

crease with the decrease in acrylate content. Synergism of polyurethane and acrylate resulted in good to excellent chemical and water resistance. Thermal decomposition analysis shows the quite stable behavior of copolymers till 245 °C. The spherical rounded microphase structure of copolymers was further confirmed by SEM. Thus by careful selection of monomers and weight ratio of PU and acrylates, tailor-made cross linked copolymers can be developed to fulfil the industrial demand of high performance to low cost products that can comply with increasingly stringent regulations of volatile organic compounds.

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