Click Cross-Linking-Improved Waterborne Polymers for Environment-Friendly Coatings and Adhesives

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S *Supporting Information*

ABSTRACT: Waterborne polymers, including waterborne polyurethanes (WPU), polyester dispersions (PED), and polyacrylate emulsions (PAE), are employed as environmentally friendly water-based coatings and adhesives. An efficient, fast, stable, and safe cross-linking strategy is always desirable to impart waterborne polymers with improved mechanical properties and water/solvent/thermal and abrasion resistance. For the first time, click chemistry was introduced into waterborne polymer systems as a cross-linking strategy. Click cross-linking rendered waterborne polymer films with significantly improved tensile strength, hardness, adhesion strength, and water/solvent resistance compared to traditional waterborne polymer films. For example, click cross-linked WPU (WPU-click) has dramatically improved the mechanical strength (tensile strength increased from 0.43 to 6.47 MPa, and Young's modulus increased from 3 to 40 MPa), hardness (increased from 59 to 73.1 MPa), and water resistance (water absorption percentage dropped from 200% to less than 20%); click cross-linked PED (PED-click) film also possessed more than 3 times higher tensile strength (∼28 MPa) than that of normal PED (∼8 MPa). The adhesion strength of click cross-linked PAE (PAE-click) to polypropylene (PP) was also improved (from 3 to 5.5 MPa). In addition, extra click groups can be preserved after click cross-linking for further functionalization of the waterborne polymeric coatings/adhesives. In this work, we have demonstrated that click modification could serve as a convenient and powerful approach to significantly improve the performance of a variety of traditional coatings and adhesives.

KEYWORDS: *waterborne polymers, click chemistry, polyurethanes, coating, polyacrylate emulsions*
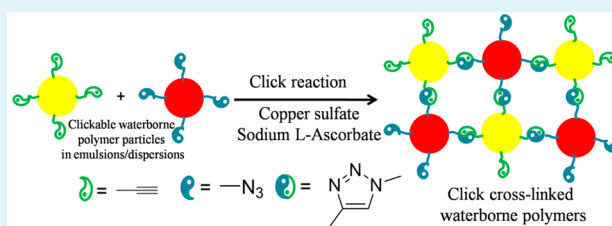
1. INTRODUCTION

Waterborne polymers, including waterborne polyurethanes (WPU), polyester dispersions (PED), and polyacrylate emulsions (PAE), have been extensively used in the coatings industry, such as wood coating, metal coating, printing inks, architectural coatings, and plastic coatings, among others mainly due to their environmental friendliness, low cost, and longer pot life and storage time compared to solvent-based polymers.[1−5] However, waterborne polymers possess some inherent drawbacks such as poor mechanical strength, low hardness, water sensitivity, and heat-softening. Significant efforts have been undertaken to improve the film properties of waterborne polymers, among which cross-linking modification is one of the most attractive methods. Cross-linking of waterborne polymers can enhance mechanical strength, adhesion strength, water resistance, and durability of the formed films.

Among currently available cross-linking strategies used for preparing waterborne polymers, self-cross-linking systems based upon *N*-methylolacrylamide (NMA)[6,7] have been widely used in vinyl-based polymers. However, these polymers tend to release formaldehyde, thus posing significant risks to human health. Although using *N*-ethylolacrylamide instead of NMA can completely eliminate the formation of formaldehyde,[8,9] it releases acetaldehyde that could result in the formation of low molecular weight polymers which fail to achieve desired mechanical strength. Cross-linking systems based on pendent acetoacetate groups, such as acetoacetoxyethyl methacrylate (AAEM),[10,11] normally have a very short shelf life and require the addition of a blocking agent, which tends to severely retard curing. Self-cross-linking systems based on reversible keto-hydrazide reactions[12] have a relatively slow reaction rate and yield minimally improved mechanical properties, and moreover toxic hydrazine can also cause health hazards. None of the above cross-linking strategies can be broadly applied in all the three kinds of waterborne polymer systems, WPU, PED, and PAE. Thus, there is an urgent need to develop an efficient, fast,
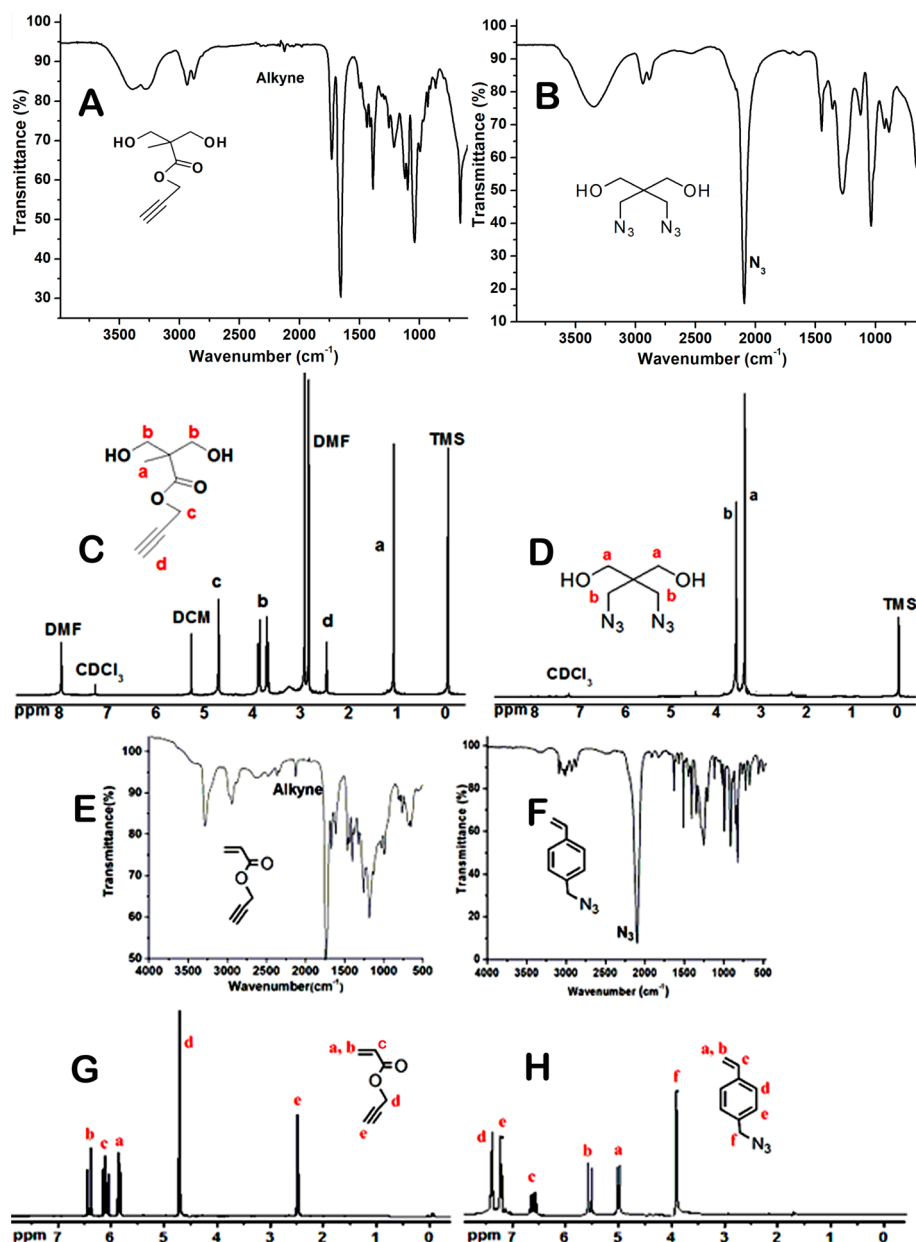
Figure 1. FTIR spectra of click-suitable monomers, (A) M1, (B) M2, (E) M3, and (F) M4; ^{1}H NMR spectra of click-suitable monomers: (C) M1, (D) M2, (G) M3, and (H) M4.

stable, safe, and broadly applicable cross-linking strategy for such waterborne polymers.

Click chemistry, especially copper-catalyzed 1,3-dipolar azide−alkyne cycloaddition (CuAAC), is insensitive to oxygen, water, solvents, and a wide range of functionalities and can be site-specifically performed at room temperature[13,14] with high reaction rates and quantitative yields.[15] As one of the most effective chemical reactions, click chemistry has been widely used in the synthesis, modification, and engineering of polymers, to obtain linear or branched polymers,[16,17] to conjugate or link small molecules or macromolecules,[18−21] and to cross-link click-suitable polymers.[22−26] The highly stable aromatic structure of triazole has the advantages of being tolerable to acidic, basic, and oxidative mediums,[27] mimicking amide groups, and acting as hydrogen bond acceptors to improve mechanical strength.[28,29] Although some research toward improving mechanical properties[30,31] using click

chemistry has been reported, application of CuAAC in the cross-linking of waterborne polymers has not been reported to date.

In this work, click chemistry was introduced into waterborne polymer systems as a cross-linking strategy for the first time. First, click-suitable alkyne- or azide-containing monomers were introduced into waterborne polyurethanes (WPU), polyester dispersions (PED), and polyacrylate emulsions (PAE) to create novel types of waterborne polymers with side alkyne or azide groups. Waterborne polymers with side alkyne groups could undergo click reaction with waterborne polymers with side azide groups in the presence of copper catalysts. The click reaction simultaneously improved the overall film properties of the waterborne polymers suitable for coatings and adhesives.

Table 1. Reagent Amounts Employed for the Preparation of Waterborne Polyurethanes (WPU), WPU-Al, and WPU-N$_3$

	WPU		WPU-Al		WPU-N$_3$	
	amount (g)	weight (%)	amount (g)	weight (%)	amount (g)	weight (%)
IPDI	40.00	50.60	40.00	47.70	40.00	47.14
PEG (1 kDa)	25.00	31.63	25.00	29.82	25.00	29.46
DMPA	3.50	4.43	3.50	4.17	3.50	4.12
1,6-hexanediol	7.20	9.11	0.00	0.00	0.00	0.00
M1	0.00	0.00	12.00	14.31	0.00	0.00
M2	0.00	0.00	0.00	0.00	13.00	15.32
triethylamine	2.55	3.23	2.55	3.04	2.55	3.01
ethylenediamine	0.80	1.01	0.80	0.95	0.80	0.94
total polymer	79.05	100	83.85	100.00	84.85	100.00
water	184.80	–	195.60	–	198.00	–
solid content, wt %	29.96	30.01	30.00			
M_n (10^4 g/mol)	2.11		2.19		2.01	
M_w (10^4 g/mol)	5.81		5.50		5.29	
PDI	2.76		2.51		2.63	
average particle size (nm)	106.3		100.2		99.6	
particle size distribution (PDI)	0.173		0.181		0.194	

2. EXPERIMENTAL SECTION

2.1. Materials. All chemicals were purchased from Sigma-Aldrich and used without further purification unless otherwise mentioned.

2.2. Characterization. The FTIR spectra analysis was carried out with a Nicolet 6700 FTIR spectrometer (Nicolet Instrument Co., Madison, WI). ^{1}H NMR spectra of polymers were recorded with a JNM ECS 300 spectrometer (JEOL, Tokyo, Japan) using tetramethylsilane as an internal standard and CDCl$_3$ as a solvent. The thermal properties of cross-linked polymers were characterized by differential scanning calorimetry (DSC, −50 °C to 50 °C, or −100 °C to 100 °C for WPU series) at a heating rate of 10 °C/min under nitrogen atmosphere. The glass transition temperature (T_g) was determined at the first heating run to avoid the effect of further thermal click cross-linking in the measurement process.

2.3. Synthesis. *2.3.1. Synthesis of Propargyl 2,2-Bis-(hydroxylmethyl)propionate (M1).* Propargyl 2,2-bis-(hydroxylmethyl)propionate (M1) was prepared according to a previous procedure.[32] Briefly, 26.8 g of 2,2-bis(hydroxymethyl)-propionic acid (0.2 mol) and 12.8 g KOH (more than 0.2 mol) were added to 150 mL of dried *N,N*-dimethylformamide (DMF). The mixture was stirred at 100 °C for 2 h until a transparent solution was formed. The reaction temperature was then reduced to 45 °C, followed by the addition of 24.7 mL of propargyl bromide (0.217 mol, 80 wt % solution in toluene). The mixture was then reacted at 45 °C for another 72 h. After removing DMF and excess propargyl bromide under vacuum at 80−120 °C, the crude product was dissolved in 30 mL of DI water and extracted with dichloromethane (DCM) or chloroform (100 mL × 4). The combined organic phase was dried by anhydrous MgSO$_4$ or Na$_2$SO$_4$ and filtered. The solvent was removed by rotary evaporation, and the final product (yellowish liquid, yield: 79%) was then placed under vacuum for at least 3 days before use. The ^{1}H NMR and FTIR results are shown in Figure 1.

2.3.2. Synthesis of 2,2-Bis(azidomethyl)propane-1,3-diol (M2). 2,2-Bis(azidomethyl)propane-1,3-diol (M2) was synthesized as described by Xu et al.[33] Briefly, 40 g of 2,2-bis(bromomethyl)-propane-1,3-diol (150 mmol) and 40 g of sodium azide (NaN$_3$, 620 mmol) were mixed in 150 mL of DMF. The mixture was stirred at 120 °C overnight. After removal of DMF under vacuum at 80−120 °C, the crude product was then dissolved in acetone, the solid byproduct NaBr salt and excess NaN$_3$ were filtered, and the solvent was removed by rotary evaporation. The crude product was then dissolved in diethyl ether or dichloromethane (DCM) (200 mL) and extracted by saturated NaCl solution (50 mL × 3). The organic phase was separated and dried by anhydrous MgSO$_4$ or Na$_2$SO$_4$ and filtered. The solvent was removed by rotary evaporation, and the final product (brown liquid, yield: 87%) was then placed under vacuum for at least 3

days before use. The structure of the obtained monomer was determined by ^{1}H NMR and FTIR.

2.3.3. Synthesis of Propargyl Acrylate (M3). Propargyl acrylate (M3) was synthesized according to Malkoch et al.[34] Briefly, 14.43 mL of propargyl alcohol (0.25 mol) and 34.85 mL of triethylamine (TEA, 0.25 mol) were added into 300 mL of dichloromethane (DCM), and the solution was cooled to 0 °C. Acryloyl chloride (18.102 g, 0.2 mol) was then added slowly over a 30 min period, and the reaction was continued for an additional 16 h at room temperature. The reaction mixture was washed with brine and water, dried over magnesium sulfate, and concentrated under reduced pressure to give a pale yellow liquid (yield: 85%). The structure of the copolymer was determined from ^{1}H NMR and FTIR.

2.3.4. Synthesis of 4-Azidomethylstyrene (M4). 4-Azidomethyl-styrene (M4) was synthesized according to Guo et al.[35] Briefly, 15 mL of distilled 4-chloromethylstyrene (CMS, 106.4 mmol) was dropped into a solution of NaN$_3$ (13.8 g, 212.9 mmol) and tetrabutylammo-nium bromide (TBAB, 0.75 g) in 30 mL of distilled water at room temperature. The reaction mixture was stirred at 50 °C under nitrogen atmosphere for 5 h. Then the mixture was poured into 20 mL of ice−water and extracted with DCM three times (100 mL × 3). The combined organic phase was then dried over anhydrous MgSO$_4$, and DCM was removed using a rotary evaporator. The product was obtained as a brown yellow liquid (yield: 83%). The structure of the copolymer was determined by ^{1}H NMR and FTIR.

2.3.5. Synthesis of Normal Waterborne Polyurethane (WPU), Waterborne Polyurethane with Side Alkyne Groups (WPU-Al), and Waterborne Polyurethane with Side Azide Groups (WPU-N$_3$). The waterborne polyurethane polymers were synthesized according to Table 1 using the following procedure. First, isophorone diisocyanate (IPDI) and polypropylene glycol were charged into a 250 mL dried four-necked flask with a mechanical stirrer, thermometer, condenser, and nitrogen inlet/outlet. The mixture was homogenized with a stirrer for 10 min. The temperature was then increased to 85 °C, and the reaction was continued for 2 h. Then dimethylol propionic acid (DMPA) and 1,6-hexanediol (for WPU), propargyl 2,2-bis-(hydroxylmethyl)propionate (for WPU-Al), or 2,2-bis(azidomethyl)-propane-1,3-diol (for WPU-N$_3$) were added into the flask, and the reactions were continued for 3−4 h. The isocyanate (NCO) content was monitored during the reactions using the standard dibutylamine back-titration method. Upon reaching the theoretical NCO value, the temperature was decreased to 40 °C. If the viscosity of prepolymer was high, 10 mL of acetone could be added into the flask. Triethylamine was added, and the mixture was stirred for 20 min at 40 °C to neutralize the prepolymer. The reaction mixture was slowly added to a predetermined amount of ethylenediamine containing deionized water

Table 2. Reagent Amounts Employed for the Preparation of Polyester Dispersions (PED), PED-Al, and PED-N$_3$

	PED		PED-Al		PED-N$_3$	
	amount (g)	weight (%)	amount (g)	weight (%)	amount (g)	weight (%)
1,6-hexanediol	125.50	28.05	125.60	28.87	126.60	28.86
1,2-propylene glycol	35.50	8.26	0.00	0.00	0.00	0.00
M1	0.00	0.00	43.10	9.91	0.00	0.00
M2	0.00	0.00	0.00	0.00	43.30	8.11
phthalic anhydride	220.10	51.23	214.40	49.28	212.10	50.64
5-sulfoisophthalic acid sodium	53.50	12.45	51.95	11.94	52.25	12.40
total polymer	429.60	100.00	435.05	100.00	434.25	100.00
water	1000.00	—	1015.00	—	1010.00	—
solid content, wt %	30.05		30.00		30.07	
M_n (10^4 g/mol)	0.659		0.606		0.685	
M_w (10^4 g/mol)	2.10		2.20		2.04	
PDI	3.19		3.62		2.98	
average particle size (nm)	183.6		184.2		187.4	
particle size distribution (PDI)	0.066		0.083		0.079	

Table 3. Reagent Amounts Employed for the Preparation of Polyacrylate Emulsions (PAE), PAE-Al, and PAE-N$_3$

	PAE		PAE-Al		PAE-N$_3$	
	amount (g)	weight (%)	amount (g)	weight (%)	amount (g)	weight (%)
methyl methacrylate	115.00	44.32	90.00	34.68	90.00	34.68
butyl acrylate	135.70	52.29	135.70	52.29	135.70	52.29
acrylic acid	6.30	2.43	6.30	2.43	6.30	2.43
M3	0.00	0.00	25.00	9.63	0.00	0.00
M4	0.00	0.00	0.00	0.00	25.00	9.63
sodium laureth sulfate	0.50	0.19	0.50	0.19	0.50	0.19
octylphenoxy polyethoxyethanol	1.00	0.39	1.00	0.39	1.00	0.39
ammonium persulfate	1.00	0.39	1.00	0.39	1.00	0.39
total polymer	259.50	100.00	259.50	100.00	259.50	100.00
water	389.25	—	389.25	—	389.25	—
solid content, wt %		40.00		40.00		40.00
M_n (10^4 g/mol)		3.89		3.92		3.81
M_w (10^4 g/mol)		11.5		10.9		11.2
PDI		2.96		2.78		2.94
average particle size (nm)		138.3		132.2		130.8
particle size distribution (PDI)		0.126		0.133		0.154

under vigorous shearing (about 1500 rpm) for 15 min, and stable WPU, WPU-Al, or WPU-N$_3$ dispersions in water were obtained.
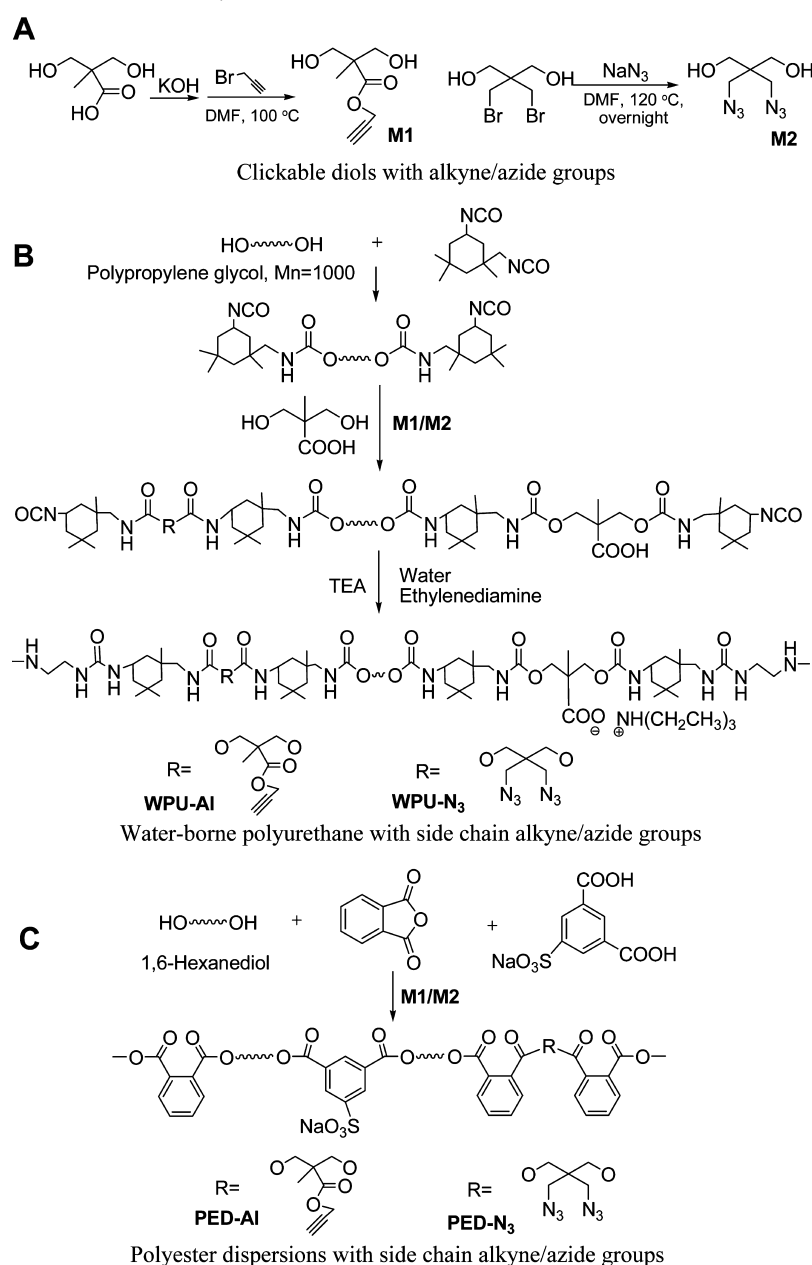
2.3.6. Synthesis of Normal Polyester Dispersions (PED), Polyester Dispersions with Side Alkyne Groups (PED-Al), and Polyester Dispersions with Side Azide Groups (PED-N$_3$). The polyester dispersion samples were prepared according to Table 2 using the following procedure. First, 1,6-hexanediol, 1,2-propylene glycol (for PED), or propargyl 2,2-bis(hydroxylmethyl)propionate (for PED-Al) or 2,2-bis(azidomethyl)propane-1,3-diol (for PED-N$_3$), phthalic anhydride, and 5-sulfoisophthalic acid sodium were charged into a 1000 mL dried four-necked flask with a mechanical stirrer, thermometer, condenser, and nitrogen inlet/outlet. Then the mixture was heated to 150 °C, and the reaction mixture was kept in molten state for 3 h. In order to further improve the extent of reaction, 50 mL of toluene was added to reflux at 200 °C for 10−12 h. The reaction temperature was reduced to 160 °C, and small molecules were removed from the mixture under vacuum (−0.05 to −0.1 MPa) for 2−3 h. The acid value was monitored during the reaction using the standard method of ASTM D974. Upon reaching a constant theoretical acid value, the temperature was reduced to 50 °C and deionized water was added to the reaction mixture. After 30 min of vigorous stirring (about 800−1000 rpm) using a high speed shear apparatus, PED, PED-Al, or PED-N$_3$ dispersions were obtained.

2.3.7. Synthesis of Normal Polyacrylate Emulsions (PAE), Polyacrylate Emulsions with Side Alkyne Groups (PAE-Al), and Polyacrylate Emulsions with Side Azide Groups (PAE-N$_3$). The

polyacrylate emulsions were prepared according to Table 3 using the following procedure. First, a solution comprising 40% of the total volume sodium laureth sulfate, octylphenoxy polyethoxyethanol, ammonium persulfate, and water was charged into a 1000 mL four-necked flask equipped with a reflux condenser, a nitrogen gas inlet tube, a poly(tetrafluoroethylene) stirrer, and a feeding tube for pre-emulsions. Meanwhile, the remaining 60% sodium laureth sulfate, octylphenoxy polyethoxyethanol, ammonium persulfate, and water were vigorously and homogeneously mixed with all of the methyl methacrylate, butyl acrylate, acrylic acid, and propargyl acrylate or 4-(azidomethyl)styrene to get a pre-emulsion according to the recipe for PAE, PAE-Al or PAE-N$_3$. The kettle solution was heated to 80 °C and the pre-emulsion was added to start the free-radical polymerization. The addition of pre-emulsion was completed in 4−5 h at a constant rate. The reaction was allowed to continue for another 2 h at 85 °C, the mixture was cooled to room temperature, and PAE, PAE-Al, or PAE-N$_3$ emulsions were obtained.

2.3.8. Particle Characterization and Molecular Weights of WPU/PED/PAE and Click-Suitable WPU/PED/PAE. Particle size and particle size distribution of normal and click-suitable WPU/PED/PAE in suspensions/emulsions were determined by dynamic light scattering (Malvern Nano-ZS 90) using diluted samples (1.00g/L). Molecular weights and polydispersity index (PDI) of polymers were measured by gel permeation chromatography (GPC) using a Thermo Scientific chromatograph equipped with an isocratic Dionex UltiMate 3000 pump and a RefractoMax 521 refractive index detector. Tetrahy-

Scheme 1. Schematic Representation of Click Monomers and WPU and PED Click Cross-Linking. (A) Synthesis of Click-Suitable Diol Monomers (M1, M2); (B) Polymerization of WPU-N$_3$ or WPU-Al, (C) PED-N$_3$ or PED-Al

A

Clickable diols with alkyne/azide groups

B

Water-borne polyurethane with side chain alkyne/azide groups

C

Polyester dispersions with side chain alkyne/azide groups

drofuran (THF) at a flow rate of 1 mL min^{-1} was chosen as the mobile phase. Samples were prepared by dissolving the obtained films in THF at 1 wt %. Monodisperse polystyrene was used as the standard.

2.3.9. Click Cross-Linking of WPU/PED/PAE. Click-cross-linking reaction was conducted between WPU/PED/PAE-Al and WPU/PED/PAE-N$_3$ as follows (Scheme 3): 15 g of WPU/PED/PAE-Al suspension (solid content: 30%, 30%, or 40%, respectively), 15 g of WPU/PED/PAE-N$_3$ suspension (solid content: 30%, 30%, or 40%, respectively), and a solution containing 0.05 g of copper sulfate (CuSO$_4$) in 1 mL of water were mixed together, and the mixture was stirred slowly for 5 min. Then a solution of 0.20 g of sodium L-ascorbate (NaLAc) in 1 mL of water was added into the mixture, and the click reaction was initiated. The mixture was stirred for an additional 2 min, and then 10 g of the mixture was poured into a 6 cm diameter Teflon disk to be dried at room temperature for 48 h. The resulting film was taken out for testing.

2.3.10. Preparation of a Normal WPU/PED/PAE Film. Ten grams of nonclick-suitable WPU/PED/PAE was poured into a 6 cm diameter

Teflon disk to be dried at room temperature for 48 h, and the film was then taken out for testing as reference.

2.3.11. Preparation of Physically Mixed Click-Suitable WPU/PED/ PAE (WPU/PED/PAE-N$_3$/Al). Five grams of a WPU/PED/PAE-Al suspension (solid content: 30%, 30%, or 40%, respectively) and 5 g of a WPU/PED/PAE-N$_3$ suspension (solid content: 30%, 30%, or 40%, respectively) were mixed together and poured into a 6 cm diameter Teflon disk to be dried at room temperature for 48 h. The film was then taken out for testing as reference.

2.4. Determination of Film Properties. The mechanical properties of fabricated films were measured using a universal testing machine (model 5966, Instron, Norwood, MA) at room temperature (23 °C). The tensile strength and elongation at break were recorded in the machine direction with a cross-head speed of 500 mm/min, according to ASTM D882. At least 10 dumbbell-shaped samples (115.0 × 6.0 × 2.0 mm) were tested for each film, and the results were averaged. The hardness of the film was tested by nanoindentation using an instrumented MTS Nanoindenter XP system. All indents

were performed using a Berkovich tip to a depth of 10 nm, and the radius of indent was about 100 nm. The adhesion strength was measured by a 180° peeling test using a universal testing machine (model 5966, Instron, Norwood, MA). Herein, SUS403 stainless steel plates (5 cm in length, 2 cm in width, and 1 mm in thickness) were treated by ultrasonication in acetone and ethanol for 10 min. Typically, polyacrylate emulsion samples (PAE, PAE-N$_3$/Al, and PAE-click) were applied to polypropylene (PP) films (100 μm thickness) by a Baker type film applicator (50 μm gap), respectively. The films were cut to 4 cm in length and 1 cm in width and heated for 2 min at 105 °C before being pressure-bonded on an SUS403 plate using a 2 kg hand roller for 10 min to obtain the test samples. Then the test samples were pulled at a speed of 300 mm/min.

The gel content of cross-linked film was determined by Soxhlet extraction for 24 h using tetrahydrofuran (THF) as a solvent. The extraction residue was transferred into a vacuum oven for drying. The ratio of insoluble remaining mass (dried to constant weight in a vacuum oven) to original mass was defined as the gel content G% (eq 1) for the sample.

$$G\% = \frac{M_r}{M_o} \times 100\% \tag{1}$$

where M_r = residual mass of the sample, and M_o = original mass of the sample.

For the water resistance test, polymer films (3 cm × 3 cm × 0.5 mm) were immersed in water for 72 h at 25 °C. The water absorption percentage was calculated from eq 2 as follows:

$$\text{absorption percentage} = \frac{W_2 - W_1}{W_1} \times 100\% \tag{2}$$

where W_1 = original weight of the sample, and W_2 = weight of the swollen sample.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization. The synthesis routes for click-suitable diols with alkyne or azide groups (Scheme 1) were suitable for preparing click-suitable waterborne polymers via step-growth polymerization. The click-suitable waterborne polymers with side alkyne groups (WPU-Al) or with side azide groups (WPU-N$_3$) were obtained according to various described routes (Scheme 1) and recipes (Table 1). PAE-Al and PAE-N$_3$ were synthesized as described in Scheme 2 and Table 2. Click-suitable vinyl monomers (M3, M4) with alkyne or azide groups were synthesized according to the routes shown in Scheme 2, which are amenable to preparing click-suitable waterborne polymers via free-radical polymerization. Click cross-linked WPU/PAE was simply and efficiently fabricated in the presence of CuSO$_4$ and NaLAc (Scheme 3). Click cross-linking mainly occurs on waterborne particle surfaces (Scheme 3A), while further click cross-linking can proceed along with the polymer diffusion process (Scheme 3B). It is possible that the neighboring "like" particles with the same click functional groups are unable to cross-link. But this phenomenon should be mitigated along with polymer interdiffusion process (Scheme 3B).

The FTIR and ^{1}H NMR spectra of click-suitable diols with alkyne or azide groups are shown in Figure 1. The successful synthesis of click-suitable diols with an alkyne group (M1) was verified by the characteristic infrared absorption peak[36] at around 2130 cm^{-1} (Figure 1A), and the presence of proton signals of CH_2C≡CH (δ 4.75 ppm, c in Figure 1C) and C≡CH (δ 2.49 ppm, d in Figure 1C) in the ^{1}H NMR spectrum. The structure of click-suitable diols with azide groups (M2) was confirmed by the appearance of the strong characteristic infrared absorption peak of the azide group[33] at around 2100

Scheme 2. Schematic Representation of Click Monomers and PAE Click Cross-Linking. (A) Synthesis of Click-Suitable Vinyl Monomers (M3, M4); B) Polymerization of PAE-Al and PAE-N$_3$
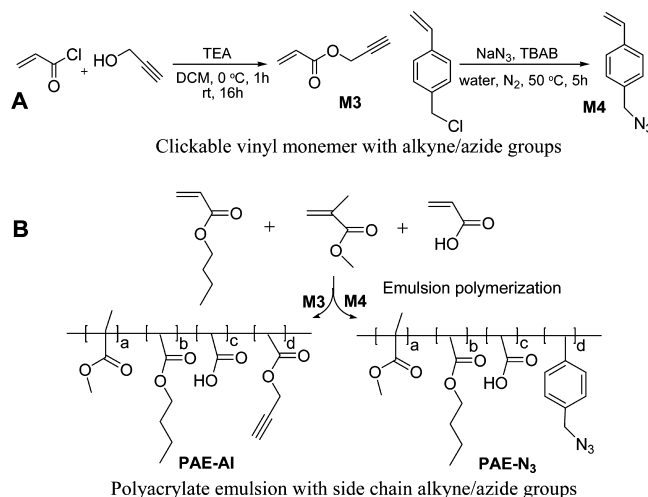
Scheme 3. Schematic Representation of Click Reaction and Water-Borne Polymer Film-Forming Mechanism. (A) A Typical CuAAC Click Cross-Linking of Waterborne Polymers; (B) Microparticle Interdiffusion and Film-Forming Mechanism of Clickable Waterborne Polymers
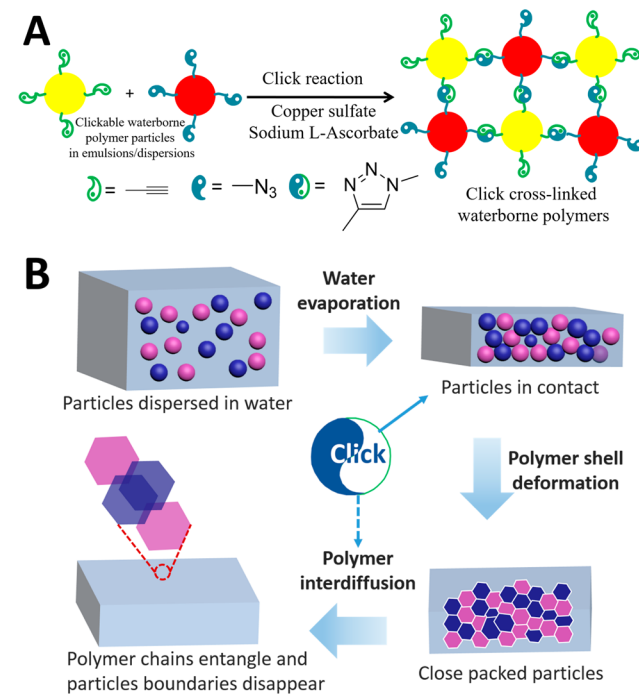
cm^{-1} (Figure 1B) and the downfield shifting of protons on CH_2 linked to the azide groups compared to the original reactant (b in Figure 1D, at 3.75 ppm). The FTIR and ^{1}H NMR spectra of click-suitable vinyl monomers with alkyne or azide groups (M3, M4) are shown in Figure 1. The appearance of the characteristic ^{1}H NMR peak of CH_2C≡CH (δ 4.73 ppm, d in Figure 1G) and C≡CH (δ 2.48 ppm, e in Figure 1G) of the propargyl group as well as the infrared absorption peak of the azide group at 2100 cm^{-1} (Figure 1F) indicated that M3 or M4 was successfully synthesized.
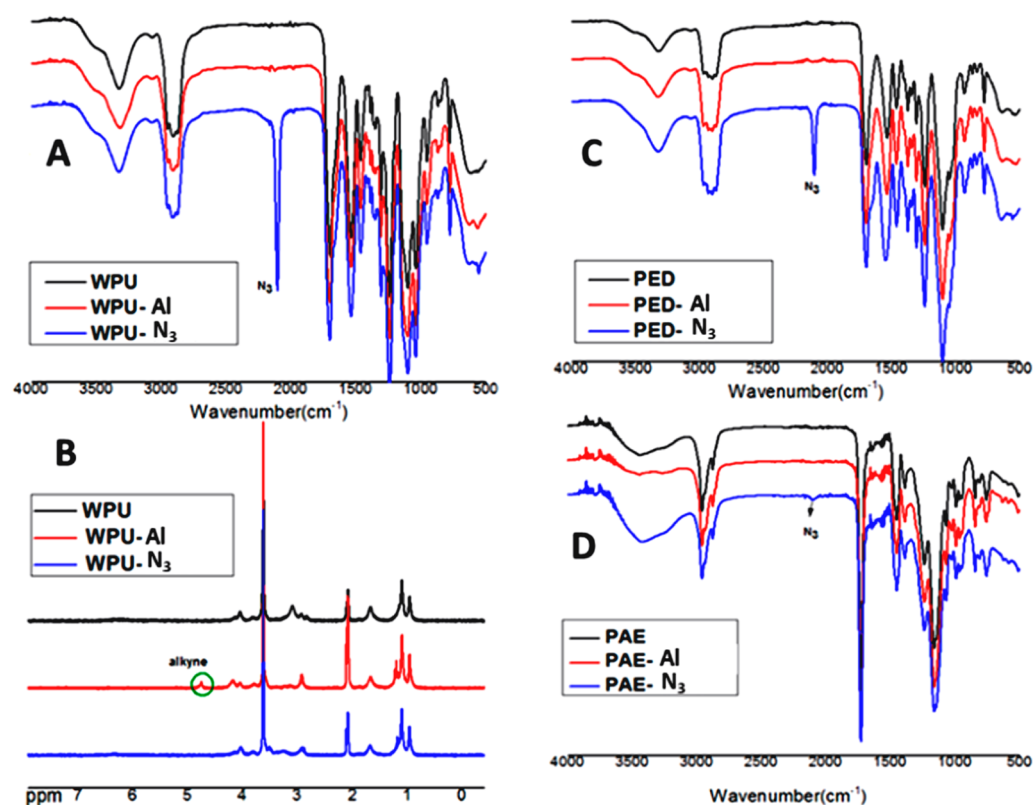
Figure 2. FTIR spectra (A) and ^{1}H NMR spectra (B) of nonclick waterborne polyurethane (WPU), waterborne polyurethane with side alkyne groups (WPU-Al), and waterborne polyurethane with side azide groups (WPU-N$_3$). FT-IR spectra of (C) PED, PED-Al, and PED-N$_3$ and (D) PAE, PAE-Al, and PAE-N$_3$.

The FTIR and ^{1}H NMR spectra of nonclick-suitable waterborne polyurethane (WPU), and click-suitable waterborne polyurethane with side alkyne (WPU-Al) and azide groups (WPU-N$_3$), which were synthesized according to Scheme 1, are shown in Figure 2. The successful introduction of azide or alkyne groups into waterborne polyurethanes was deduced by the appearance of the characteristic infrared absorption peak of the azide (N$_3$) group at 2100 cm^{-1} (Figure 2A) and peaks of the protons of CH_2C≡CH in the ^{1}HNMR spectrum (Figure 2B). The strong absorption peak at 2100 cm^{-1} in the FTIR spectra of modified PED and PAE polymers (Figure 2C and 2D) revealed that the azide groups were also successfully introduced to the PED-N$_3$ or PAE-N$_3$.

The particle sizes and size distributions, as well as the molecular weights and polydispersity indexes (PDI) of WPU/PED/PAE polymers and corresponding azide- or alkyne-modified WPU/PED/PAE polymers are shown in Figure 6A and Tables 1, 2 and 3 respectively. Azide- or alkyne-modified WPU/PED/PAE polymers possessed similar molecular weights and PDI as those of WPU/PED/PAE polymers, indicating that the addition of click monomers did not alter the sizes of the polymers significantly. Importantly, the suspensions or emulsions of WPU/PED/PAE and azide-/alkyne-modified WPU/PED/PAE are stable without obvious aggregation even after a full year of shelf-storage at room temperature.

Representatively, the FTIR spectra of nonclick-suitable WPU film, physically mixed click-suitable WPU film, and click cross-linked WPU film are shown in Figure 3. After CuAAC was applied, some azide groups were consumed by click reaction, which can be seen from the decrease of the intensity of the characteristic infrared peak of the azide group at 2100 cm^{-1} on
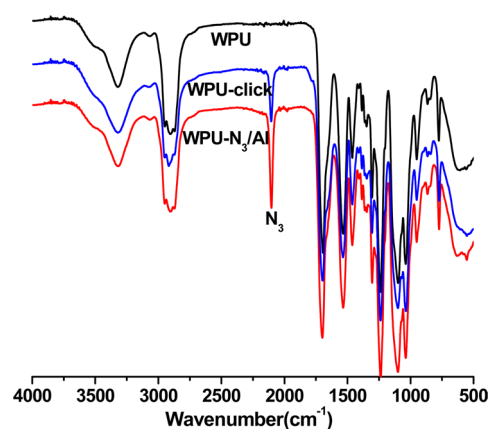
**Figure 3.** FTIR spectra of WPU, physically mixed click-suitable WPU (WPU-N$_3$/Al), and click cross-linked WPU (WPU-click).

click cross-linked WPU (WPU-click) compared with that of physically mixed WPU (WPU-N$_3$/Al). Some azide groups were preserved even after click cross-linking, because one azide monomer contains two azide groups, while one alkyne monomer contains only one alkyne group. With the same molar feeding ratio of azide/alkyne monomers, the amount of azide groups introduced was higher than that of alkyne groups.

3.2. Polymer Properties. The particle sizes of WPU, WPU-Al, and WPU-N$_3$ are all around 100 nm with narrow size distributions (Figure 4A). The tensile strengths, Young's moduli, stress−strain curves, hardness, and water resistance properties of click cross-linked WPU (WPU-click) and normal WPU films are shown in Figure 4B and 4C. They illustrate that
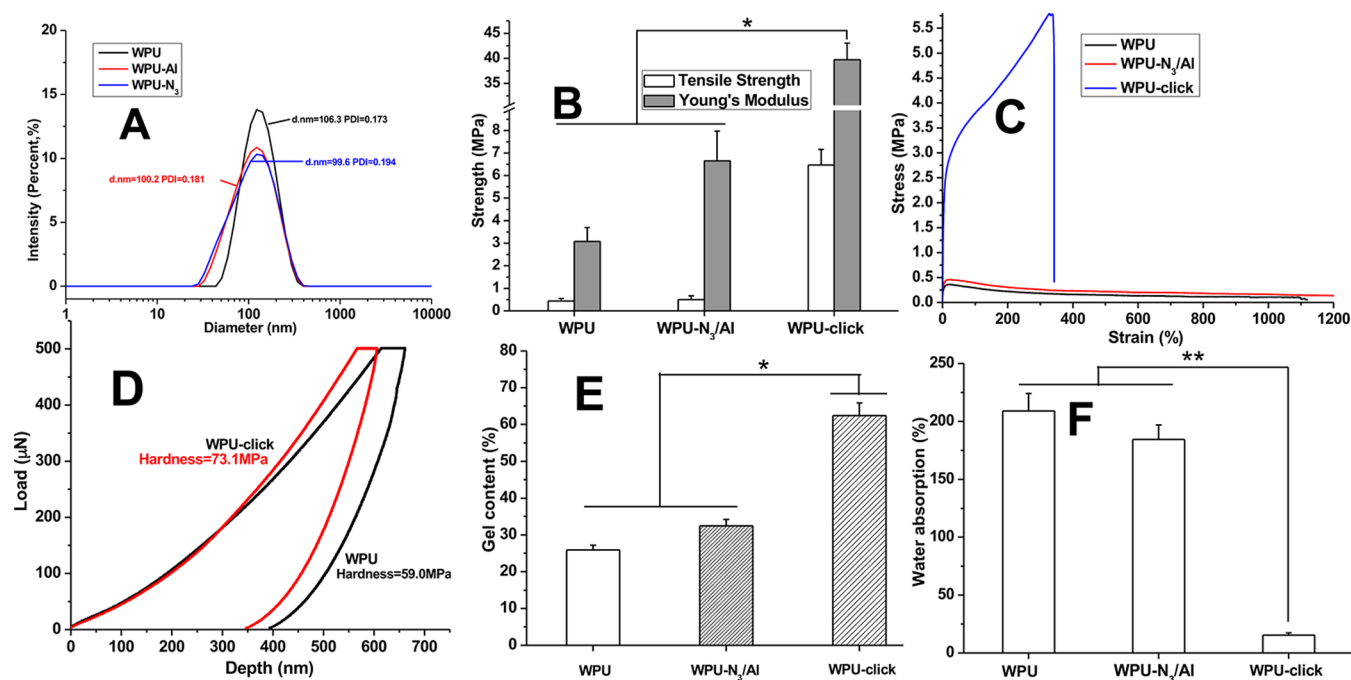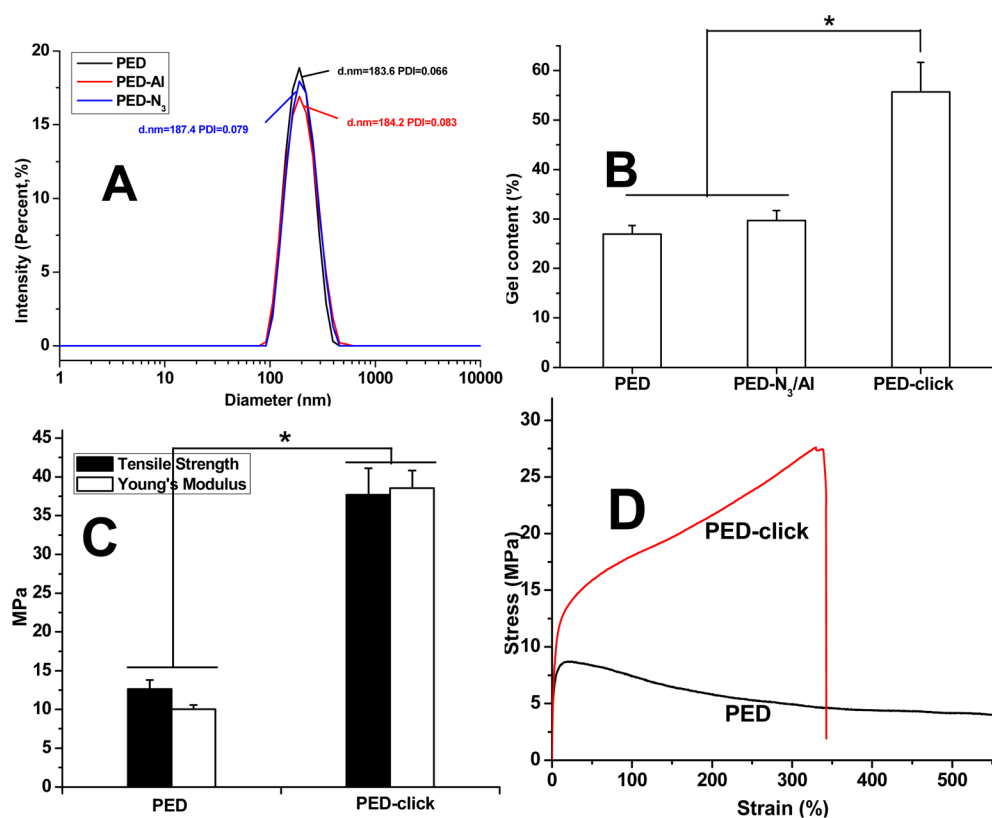
Figure 4. (A) Particle sizes and particle size distributions (PDI) of WPU, WPU-Al, and WPU-N$_3$ suspensions. (B) Tensile strength, Young's moduli, (C) stress−strain curves, (D) hardness (determined by nanoindentation test), (E) gel contents, and (F) water-resistance properties of WPU, physically mixed click-suitable WPU (WPU-N$_3$/Al), and click cross-linked WPU (WPU-click). *p < 0.05, **p < 0.01.
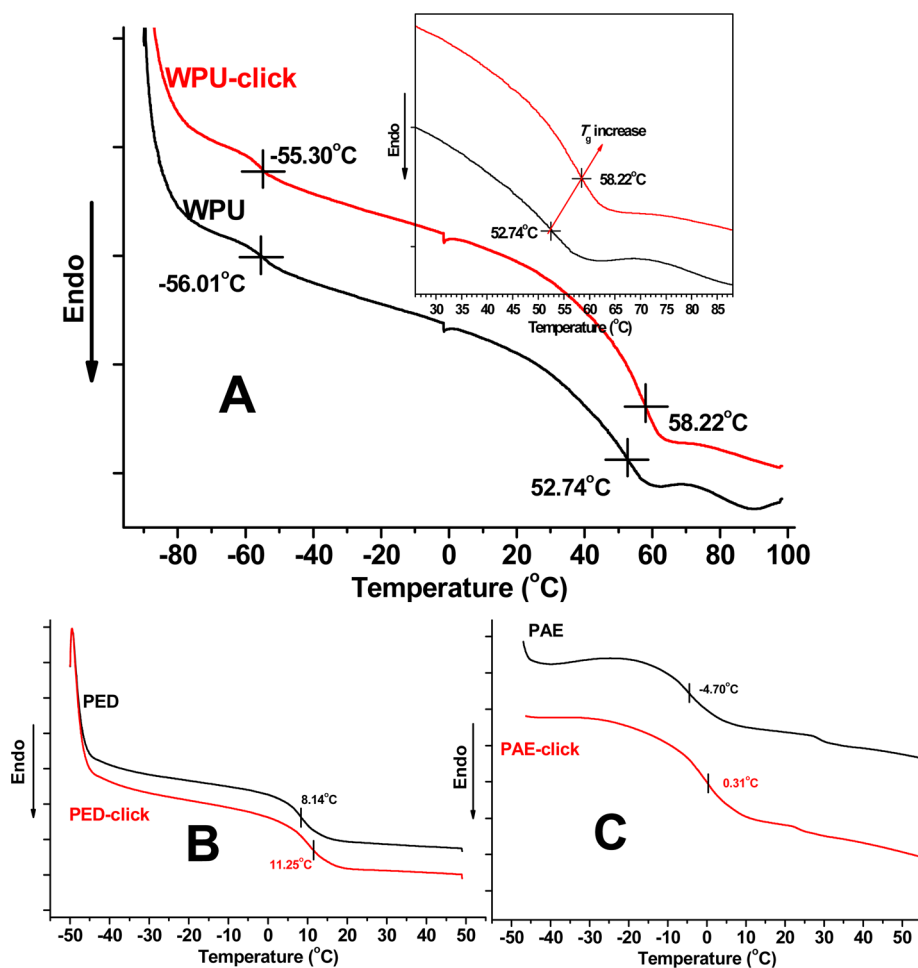

Figure 5. DSC curves of WPU and click cross-linked WPU (WPU-click) (A), PED and PED-click (B), and PAE and PAE-click (C).

Figure 6. (A) Particle sizes and particle size distributions (PDI) of PED, PED-Al, and PED-N_3 suspensions. (B) Gel contents of PED, physically mixed click-suitable PED (PED-N_3/Al), and click cross-linked PED (PED-click). (C) Tensile strengths, Young's moduli, and (D) stress−strain curves of PED and click cross-linked click-suitable PED (PED-click). *p < 0.05.
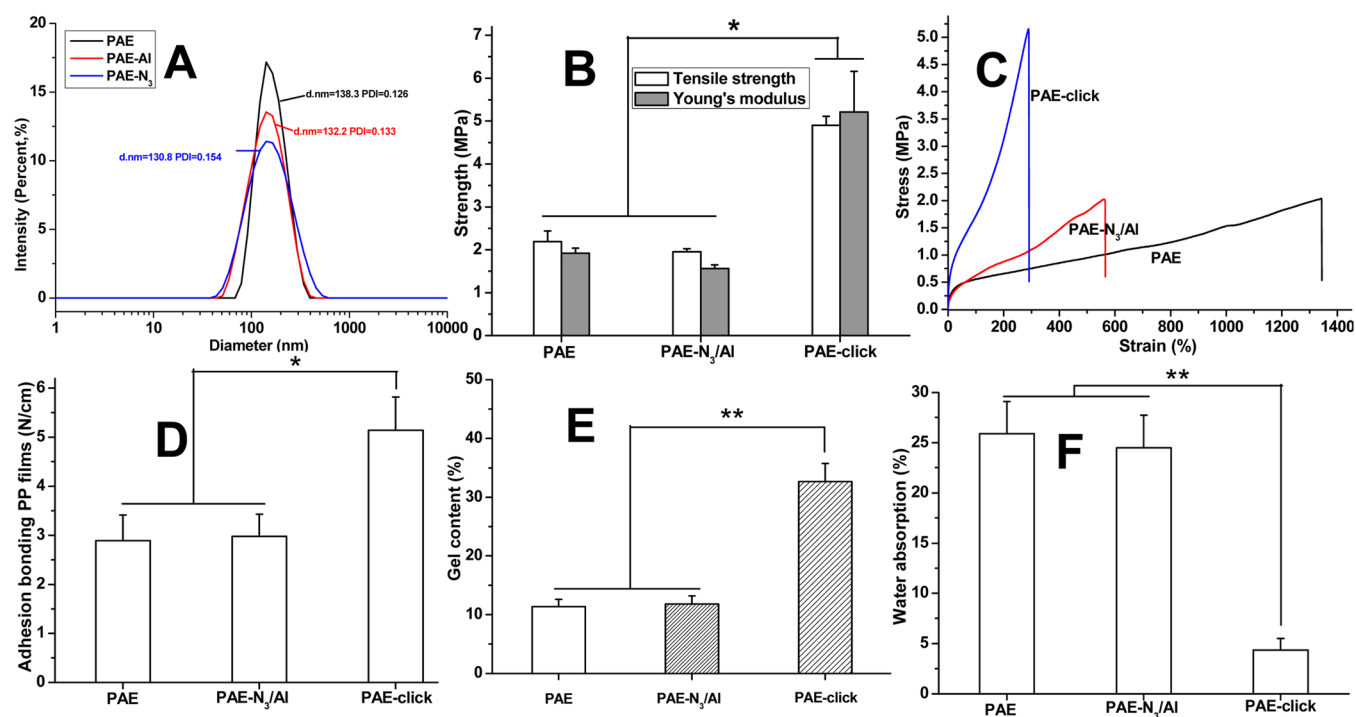
Figure 7. (A) Particle sizes and particle size distributions (PDI) of PAE, PAE-Al, and PAE-N_3 emulsions. (B) Tensile strengths, Young's moduli, (C) stress−strain curves, (D) adhesion properties, (E) gel contents, and (F) water-resistance properties of PAE, Physically mixed click-suitable PAE (PAE-N_3/Al), and click cross-linked PAE (PAE-click). *p < 0.05, **p < 0.01.

click cross-linking greatly enhanced both the tensile strength and Young's modulus of so-formed WPU film via cross-linking

and the restriction of the mobility of the polymer chains.[37] Specifically, the figures represent a 5-fold increase for tensile

strength and a 10-fold increase for the Young's modulus of WPU-click films, when compared to those of WPU films, while WPU-N$_3$/Al films did not bring significant improvement in mechanical strength (Figure 4B). Although the elongation rate at break of WPU-click film decreased compared to that of WPU and WPU-N$_3$/Al film, it was still higher than 300% (Figure 4C). A similar phenomenon of the decrease of elongation after cross-linking was found in epoxy cross-linked WPU reported by Wen et al.[38]

Click cross-linking also enhanced the hardness of the obtained films (Figure 4D), which is related to the increase in T_g (Figure 5A), gel content (Figure 4E), and water resistance of WPU (Figure 4F) after click cross-linking.[39] Usually the water transport is along the interfaces between particles. Therefore, the formation of cross-links between particles could be particularly effective in reducing water absorption. The water absorption was dramatically decreased from higher than (for WPU) or around (for WPU-N$_3$/Al) 200% to less than 20% when the films were immersed into water for 72 h, which is attributed to the prevention of water penetration into the polymeric bulk due to the cross-linking of the polymer particles.[39] These results demonstrate that high water resistance of coatings can be achieved by click cross-linking of WPU. It is well-known that microphase separation is a characteristic of most polyurethanes, including WPU.[40,41] Microphase separation was also found in our case, as the presence of two T_gs in WPU and WPU-click films confirms. Interestingly, click cross-linking only improved the second T_g of WPU (Figure 5), which is attributed to the restriction of the molecular motion via cross-linking.[42] The low temperature range T_g, which may be attributed to incorporated macromolecules, such as poly-(ethylene glycol) (PEG), did not change drastically (Figure 5), indicating that click cross-linking would not affect the low temperature brittleness of so-formed WPU. Click chemistry not only provided an efficient cross-linking route, but also imparted the cross-linked films with improved durability and water/solvent resistance due to the stability of resultant triazole rings.

The particle sizes of PED, PED-Al, and PED-N$_3$ are all around 180 nm with narrow size distributions (Figure 6A). Figure 6B also shows a dramatic increase of gel content of PED after click cross-linking. Figure 6C shows a 2-fold increase for the mechanical strength of polyester dispersion (PED) films after applying click cross-linking, while the elongation rate at break decreased but was still at a favorable level for coating applications (Figure 6D). Click cross-linking reaction also increases the T_g of PED. It can be seen from the DSC curves that the T_g of PED increased from 8.14 °C to 11.25 °C after click cross-linking (Figure 5B).

The particle sizes of PAE, PAE-Al, and PAE-N$_3$ are all around 180 nm with narrow size distributions (Figure 7A). As shown in Figure 7B and 7C, the tensile strength and Young's modulus of polyacrylate emulsions (PAE) films doubled after applying click cross-linking. Compared to those of normal PAE (PAE) films, the elongations of physical mixing click-suitable PAE (PAE-N$_3$/Al) and click cross-linked PAE (PAE-click) decreased resulting from the introduction of rigid alkyne or (azidomethyl) phenyl or/and triazole groups (Figure 7C). Meanwhile, we observed that the adhesion strength of PAE-click to polypropylene (PP) film (Figure 7D) increased 2 N/cm compared to that of PAE. Sardon[43] and Lei[44] revealed that along with the increase of cross-linking degree, adhesion strength of polymer first increased and then decreased after reaching its maximum value. This phenomenon was considered

primarily due to the improvement of cohesion strength brought by cross-linking[45] and the improved hydrophobic interactions between the click-cross-linked polymers and the substrate polypropylene. The occurrence of click cross-linking is also reflected by the increase of gel content of PAE-click film compared to that of PAE and PAE-N$_3$/Al films (Figure 7E). The degree of cross-linking in our experiment is in the suitable range, and the click cross-linked PAE film not only displayed decreased water absorption (5% compared to 25% in control films) (Figure 7F) but also increased adhesion strength (Figure 7D, from 3 to 5.5 N/cm). The T_g increasing effect was further proven in the case of PAE. The T_g of PAE was increased from −4.70 to 0.31 °C after click cross-linking (Figure 5C).

We further investigated the microstructure of WPU, PED, and PAE films (with or without cross-linking). The microstructure images of these films was observed by atomic force microscope (AFM), and the results are shown in Figure S1 (Supporting Information). From Figure S1, it can be seen that the films are formed by fused microparticles, which is in agreement with the film-forming theory as suggested in Scheme 3B.

It should be noted that click chemistry may also allow further improvement of performance of the click cross-linked coating/adhesives through click conjugation via the unreacted azide groups or alkyne groups (Figure 3). Additive modules, such as antibiotic agents, pigments, and antistatic agents can be conjugated to the polymers after or concurrent with click cross-linking.

4. CONCLUSION

For the first time, copper-catalyzed azide−alkyne cycloaddition (CuAAC) click chemistry was introduced in the syntheses of waterborne coating/adhesive polymers, including waterborne polyurethane (WPU), polyester dispersion (PED), and polyacrylate emulsion (PAE) as a cross-linking strategy to improve the performance of these polymers. Click cross-linked polymer films exhibited significantly improved mechanical strength, hardness, and water/solvent resistance. These click cross-linked films may help eliminate the need of using hardeners and thus potentially reduce costs when used in industrial coating applications. These results prove that click chemistry is an extremely efficient and "environment-friendly" cross-linking method to obtain high-performance waterborne coating/adhesive materials.

■ ASSOCIATED CONTENT

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Notes
The authors declare the following competing financial interest(s): Dr. Jian Yang and The Pennsylvania State University have financial interests in Aleo BME, Inc. These

interests have been reviewed by the University's Institutional and Individual Conflict of Interest Committees and are currently being managed by the University.

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