

# Synthesizing Self-Crosslinking Waterborne Polyurethane-Silanol Dispersion for Waterproofing Application

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## Abstract

Polyurethane dispersions (PUD) have diversified into a myriad of applications over the years. This has led to extensive research on both industrial and laboratory fronts as polyurethane dispersions provide liberty to interplay at the molecular level to diversify the properties of the product which has also led to the development of eco-friendly waterborne dispersions. Yet, waterborne PUDs are limited in their mechanical and physical properties as compared to solvent-based products. The incorporation of crosslinkers in the PUD further bolsters these properties thus improving water and solvent resistance. The incorporation of silanols increases solvent resistance and adhesion of the resultant PUD. In this work, a post crosslinking system based on the ketone-hydrazine mechanism was incorporated into the PUD thus providing the required structural reinforcement for construction application. The targeted application for this work is the use of PUDs for waterproofing.

## Keywords

Polyurethane, Dispersion, Waterborne, Crosslinking, Waterproofing

## 1. Introduction

Waterborne Polyurethane dispersions (WPUD) have found a myriad of applications on the account of being environmentally friendly while also possessing good mechanical properties. Apart from the major applications of sealants, adhesives, and wood/leather finishes, WPUDs have also found niche applications in waterproofing [1] [2], functional coatings [3], UV Curable coatings [4], breathable textile coatings [5] to name a few. Yet in some applications, the water resistance and weather resistance of WPUDs are deficient as compared to their

solvent-based counterparts. Introducing crosslinking in WPUDs can be a definite step towards improving the said properties.

There are two key techniques of inducing this crosslinking in the polymer backbone. The first involves the use of functionalized monomers or multi-functionality chain extenders which are introduced in the system earlier in the synthesis and are thus called pre-polymer crosslinking [6]. As all-encompassing as they may seem, the resultant of pre-polymer cross-linked dispersions have viscosities that are high and undesirable from an application perspective [7]. The other step is one of post-crosslinking where the crosslinking reaction is initiated while or shortly after the film formation process starts by the addition of a crosslinker [8]. The reaction is initiated by chemicals added during the dispersion step which target the carboxylate [9] [10] [11] or hydroxyl groups [12] [13] in the WPUD. This method comes with its drawback such as the requirement of external parameters like elevated temperatures to initiate the reaction or of limited pot life.

Another method of post-crosslinking involves the incorporation of functional monomers in the polyurethane backbone which could be then turned into crosslinking sites by the addition of external crosslinking agents. These functional monomers can react with the free isocyanate groups and thus their incorporation in the system is convenient and will not hinder the physical properties such as viscosity. Silanes have been incorporated for their ability to self-crosslink although they are not best suited for aqueous systems [14]-[19]. Thus, we require a crosslinker system that is stable in an aqueous medium and enables an ambient temperature curing reaction. Ketone-Hydrazine crosslinking reactions provide the above-mentioned pre-requisites. They have been studied in WPUDs which are acrylate modified [20] [21].

In this paper, we have synthesized N-[(1,1-dimethyl-2-acetyl)ethyl]- $\beta$ -dihydroxy ethylaminopropanamide (DDP) which consists of a carbonyl group terminated with hydroxyl structure based on previous work [22] [23]. This group is directly incorporated in the polyurethane backbone. The post addition of dihydrazine during the dispersion step results in the crosslinking reaction when the film formation process is initiated resulting in a crosslinked film. Silane groups with OH termination termed silanol (SiOH) have also been incorporated in the polymer backbone. The resultant film is targeted to waterproofing applications which can be used to replace fluorinated WPUDs for similar applications [24].

## 2. Experimental

### 2.1. Materials

Polypropylene Glycol (PPG; 1000 g/mol) and Isophorone Diisocyanate (IPDI) were obtained from Dow Chemicals, India, and stored in an airtight vessel before use to prevent contact from any possible moisture. 2,2-bis(hydroxymethyl)propionic acid (DMPA) was purchased from Sigma Aldrich, India. Trimethylolpropane (TMP), Triethylamine (TEA), 1,4-butanediol (BDO) and Diethanol Amine (DEA),

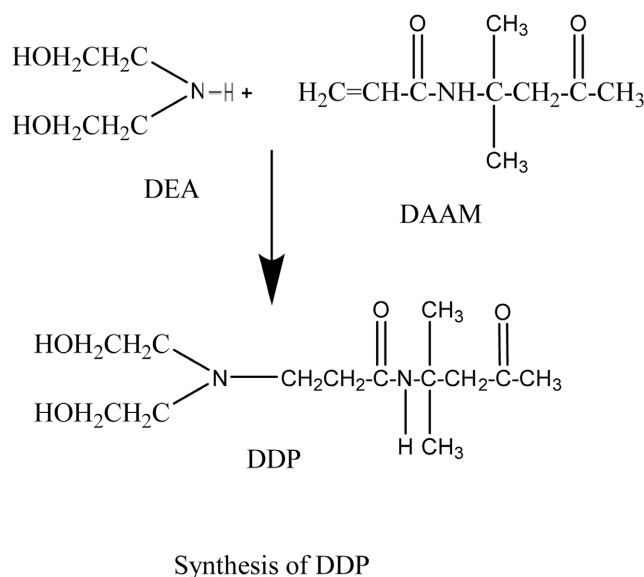
Dibutyl tin dilaurate (DBTDL) were procured from SD Fine Chemicals, India. PPG-1000 was dried at 85 °C for 4 hrs before use. DMPA and TMP were dried at 60 °C overnight in an oven. Adipic dihydrazide (ADH) and Diacetone Acrylamide (DAAM), industrial grades, were acquired from Ambani Organics Pvt. Ltd. Hydroxylated Silane, Silanol (SiOH) was procured from Supreme Silicones India. Apart from the mentioned, other chemicals were used as received.

## 2.2. Synthesis of N-[(1,1-dimethyl-2-acetyl)ethyl]- $\beta$ -dihydroxyethylaminoprop anamide (DDP)

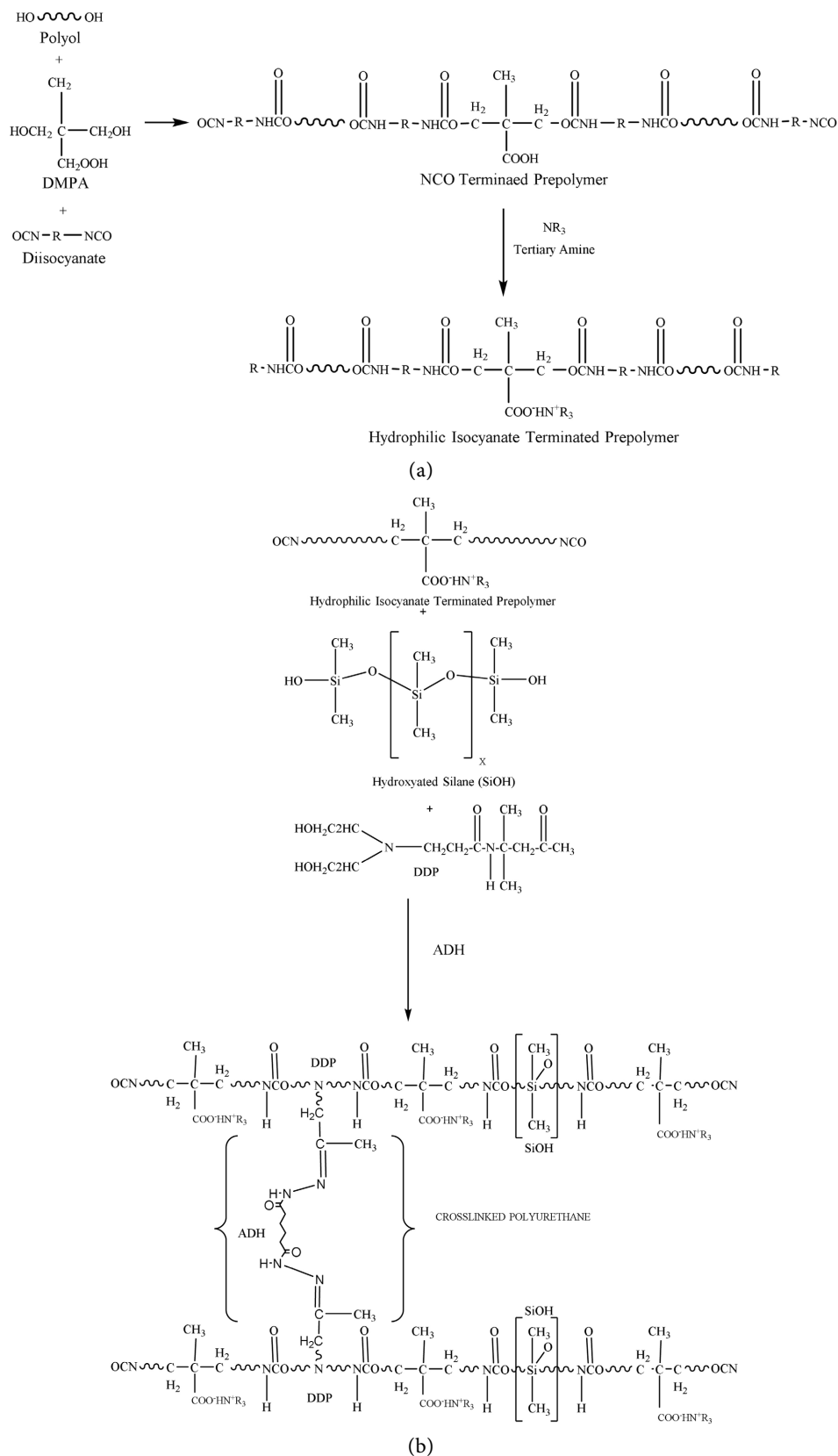
For the synthesis of DDP, equimolar amounts (0.4 mol) of both DEA and DAAM were reacted. DEA (42 g) was charged directly to the glass reactor whereas DAAM (67.6 g) was first dispersed in 25 ml Dimethyl Formamide (DMF) and then added dropwise to the reactor under at 90 °C under constant stirring. The synthesis takes place through Michael's addition reaction which was allowed to proceed for 12 h. The reaction is as shown in **Scheme 1**. After this, the solvent was removed by heating the reaction product under vacuum at 85 °C for 8 h. The resultant product was then directly used in the successive synthesis.

## 2.3. Preparation of Waterborne Polyurethane Dispersion (WPUD)

The acetone process was used to synthesize the WPUD as shown in **Scheme 2(a)** and **Scheme 2(b)**. Pre-dried PPG-1000 (polyol) was weighed and added to a 500 ml glass reactor with suitable attachments for mechanical agitation, thermocouple, a nitrogen inlet, and a condenser. The reactor was initially maintained at 60 °C using a water bath. Pre-dried DMPA and TMP (polyol) were then subsequently added to the reactor under constant stirring. The reactor was then flushed out using nitrogen gas which was followed by the addition of IPDI and



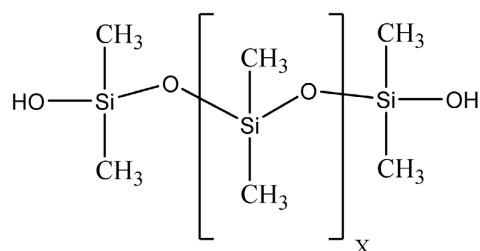
**Scheme 1.** Synthesis of DDP.



**Scheme 2.** (a). Hydrophilic isocyanate terminated prepolymer. (b). Synthesis of cross-linked WPUD.

DBTDL (catalyst). The reaction temperature was then raised to 85°C. The components were allowed to react for 2 h to obtain an NCO-terminated prepolymer. BDO and DDP were then introduced to the reactor. A measured quantity of acetone was added to the reactor to maintain a suitable viscosity. The reaction temperature was dropped down to 65°C and the reaction was allowed to continue for an additional 1.5 h.

The subsequent step was to neutralize the DMPA in the polyurethane for which TEA was added dropwise to the reaction mixture. The neutralization step was carried out for 1 h, following which the reaction mixture was allowed to stir for an additional 30 min until it reached ambient temperature. A mixture of ADH and distilled water was first thoroughly mixed separately and then added dropwise to the reaction mixture at a constant stirring rate of 1500 rpm. In the next formulation, the BDO was replaced with silanol (**Scheme 3**) and the properties of the resultant dispersions and films were compared. The compositions of both the dispersion are listed in **Table 1**. The silanol used is demethylated hydroxylated silanol. The molecular weight of the silanol was chosen to be moderate so as to participate in the chain extension step and not to participate as a crosslinker in the reaction.



Hydroxylated Silane (SiOH)

**Scheme 3.** Hydroxylated Silane (SiOH).

**Table 1.** Composition of WPUD.

Designation	PPG/g	IPDI/g	DMPA/g	TEA/g	TMP/g	BDO/g	DDP/g	ADH/g
PU-BDO-1	6.00	8.50	1.00	0.90	0.30	0.86	0	0
PU-BDO-2						0.75	0.345	0.132
PU-BDO-3						0.6	0.8	0.31
PU-BDO-4						0.45	1.25	0.48
						<b>SiOH/g</b>		
PU-SiOH-1	6.00	8.50	1.00	0.90	0.30	0.86	0	0
PU-SiOH-2						0.75	0.345	0.132
PU-SiOH-3						0.6	0.8	0.31
PU-SiOH-4						0.45	1.25	0.48

## 2.4. Preparation of WPUD Film

The films were cast on by pouring the emulsion on Teflon sheets and dried at room temperature for 5 days followed by drying them in an oven at 60°C for 24 h. The sheets were then stored in an air-tight desiccator. During the drying of the film, it undergoes the Keto-Hydrazine crosslinking mechanism which results in the crosslinked film, the mechanism of which is shown in **Scheme 2(b)**. The carbonyl group reacts with the hydrazine group of the ADH in acidic conditions. As the water in the dispersion evaporates during film formation, the WPUD hints toward a weakly acidic nature which enables the reaction to take place.

## 2.5. Characterization

Fourier transform infrared (FTIR) spectra of the samples were obtained by using a Bruker Tensor-27 FTIR spectrophotometer in transmittance mode at a scanning number of 25. The samples were used in the liquid form for the test. <sup>1</sup>H-NMR spectral analysis was carried out on ADVANCE 600 (Bruker) with Dimethyl Sulfoxide (DMSO) as solvent. Differential scanning calorimeter measurements were performed using a TA Q100 analyzer (T.A. Instruments, USA). Calibration was performed using Indium a reference (T<sub>m</sub> 156.6°C and heat flow -2.8 J/g). The weight of the sample was taken around 6 - 7 mg in standard aluminum pan temperature. The sample under a nitrogen atmosphere was heated from -60°C to 180°C at a rate of 20°C/min and again cooled to 35°C. Thermogravimetric Analysis (TGA) was performed on Perkin-Elmer Pyris 1 TGA in a temperature range of 25°C to 650°C.

## 2.6. General Coating Properties

### Determination of Water Absorption

The WPU films were cast on a Teflon sheet. The films were then dried at room temperature for 5 days before drying them at 50°C in an oven. The samples were then weighed and their dry weight ( $W_1$ ) was noted. The films were then completely immersed in water. The wet weights of the films were determined after 48 hrs. For this, the films were first wiped dry using a filter paper and then weighed to determine the wet weight ( $W_2$ ). The % water (%  $W$ ) absorbed was then calculated using the equation;

$$\%W = \left[ \frac{W_2 - W_1}{W_1} \right] \times 100$$

The crosslinking density of a film was quantified by extraction method (CSN EN ISO 6427) by placing dried film of weight ( $W_1$ ) in a Soxhlet extractor and extracted with tetrahydrofuran (THF) for 24 hours. After an extraction, the uncrosslinked film was dissolved away by THF, while the crosslinked film remained and was weighed ( $W_2$ ) after drying for 1 hr at 150°C. The crosslinking density was calculated by using the following formula:

$$\text{Crosslinking Density (\%)} = \left[ \frac{W_2}{W_1} \right] \times 100$$

The Particle size of the dispersions was determined using the Nanoplus Particle size and Zeta potential DLS analyzer. Adhesion was evaluated on a metal panel by Tape test (dolly) test according to ASTM D 3359. Pencil hardness on a metal panel was tested as per ASTM D 3363. The coatings with a wet thickness of 100  $\mu\text{m}$  were applied on glass panels and air-dried at room temperature for 24 hours. Applied coatings were evaluated for water whitening resistance according to ASTM D 870-02. The hydroxyl value was determined using ASTM D42740-16 and the free isocyanate content was determined using the Dibutyl Amine back titration process based on the procedure described in ASTM D 2572-97. Solvent resistance was quantified using the solvent resistance rub test as specified in ASTM D4 752.

### 3. Results and Discussion

#### 3.1. Raw Material Testing

The hydroxyl value of the polyol was determined to be 111.72 mg KOH/gm. The hydroxyl value reported in the TDS was 112 mg KOH/gm. The IPDI was also tested for NCO content. The NCO content was calculated using the ASTM D2572-19 standard and was determined to be 31% while the NCO content reported in the TDS was in the range of 30% - 32%. This concluded that the hydroxyl value and NCO content did not drop appreciably.

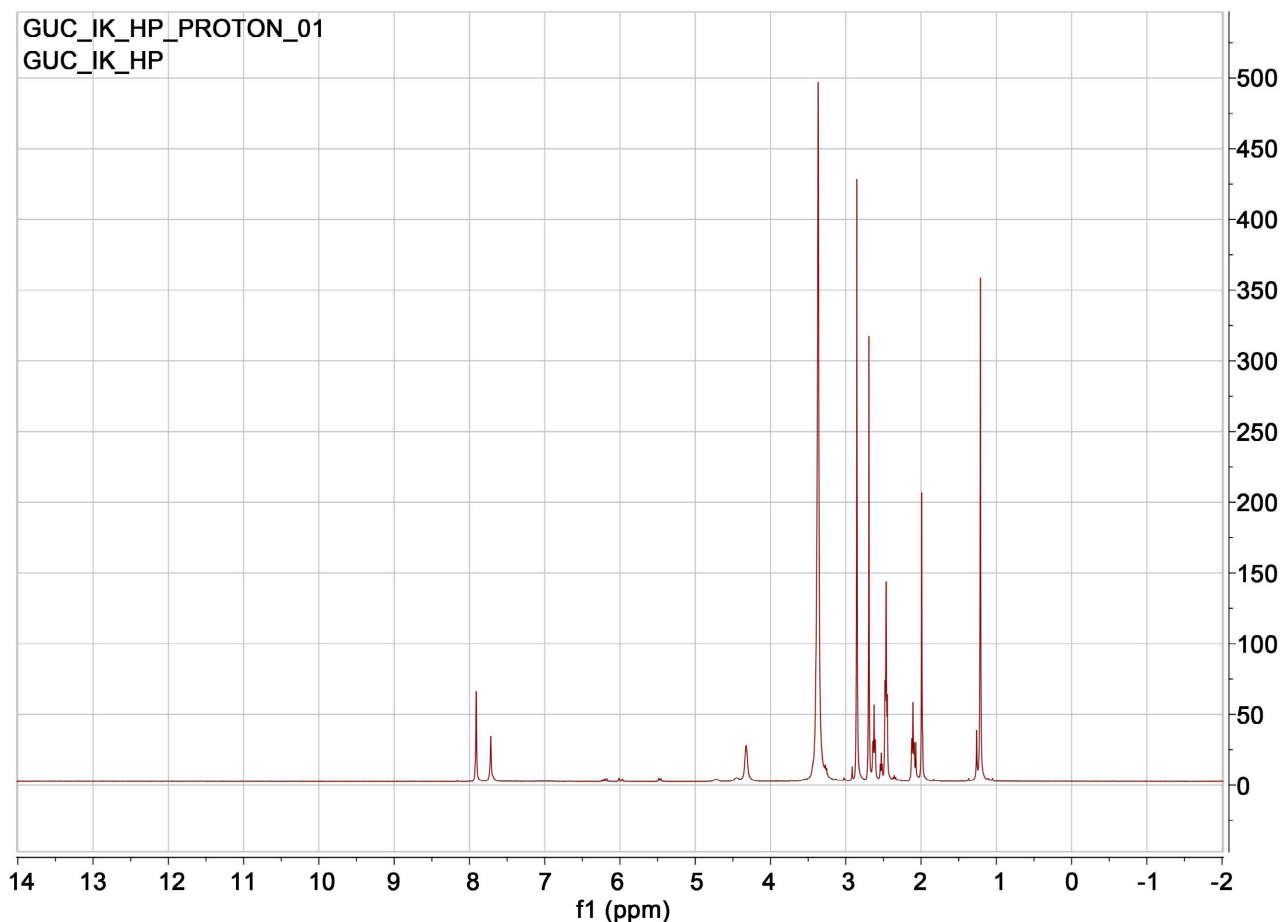
#### 3.2. $^1\text{H-NMR}$ Analysis

**Figure 1** shows the  $^1\text{H-NMR}$  analysis of the reaction to synthesize DDP. The peaks at  $\delta$ 2.17 and  $\delta$ 2.54 ppm indicated that the C=C in DAAM has reacted with diethanolamine and -CH<sub>2</sub>-CH<sub>2</sub>- exists in the synthetic product. The tertiary amine and -CH<sub>2</sub>-CH<sub>2</sub>- structure confirm that the DDP has been synthesized successfully.

#### 3.3. FTIR Spectra Analysis

The FTIR spectra of the WPUD were obtained as shown in **Figure 2(a)**. The strong peak at 3347  $\text{cm}^{-1}$  was due to the OH group present in water. The peak at 2955  $\text{cm}^{-1}$ , 1145  $\text{cm}^{-1}$ , and 1454  $\text{cm}^{-1}$  are due to C-H stretching, C-O-C bond, and COO of polyol. Peaks at 1729 and 1240  $\text{cm}^{-1}$  were representatives of the C=O stretching and N-CO-O + C-O-C asymmetric stretching of the urethane linkage. The peak at 1640  $\text{cm}^{-1}$  is due to the C-O group of urea. Peaks at 1542  $\text{cm}^{-1}$  and 1055  $\text{cm}^{-1}$  are due to the C-N, N-H, and N-CO-O groups of urethane and urea.

**Figure 2(b)** shows the FTIR spectra of the dried WPUD film. The peak at 3304  $\text{cm}^{-1}$  was due to the stretch vibration of the N-H in ADH which is present in the dispersion and due to the N-H present in the urethane linkage. The peaks at 2922  $\text{cm}^{-1}$  and 1301  $\text{cm}^{-1}$  are due to the C-H stretching and C-O-C linkage which are the characteristic of the polyol. The presence of urethane linkage can be determined by the peaks at 2858  $\text{cm}^{-1}$ , 1455  $\text{cm}^{-1}$ , and 1235  $\text{cm}^{-1}$  which are



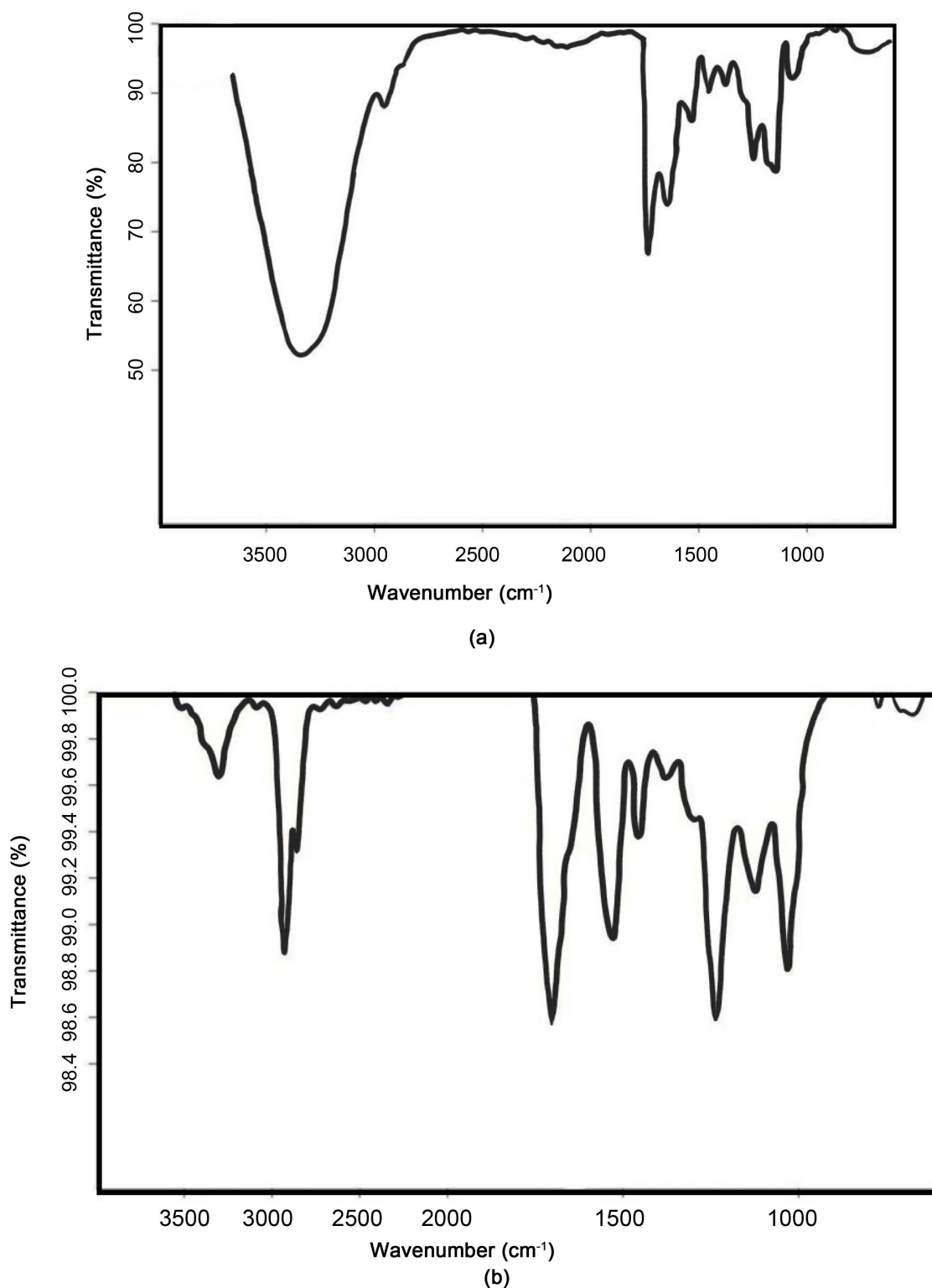
**Figure 1.**  $^1\text{H}$ -NMR spectra of DDP.

due to the  $\text{C}=\text{O}$  stretching,  $\text{N}-\text{CO}-\text{O} + \text{C}-\text{O}-\text{C}$  asymmetric stretching, and  $\text{N}-\text{CO}-\text{O}$  group of the urethane linkage. The peaks at  $1126\text{ cm}^{-1}$  and  $1029\text{ cm}^{-1}$  are indicative of the  $\text{C}-\text{O}$  stretching vibration. The crosslinked film showed the resulting groups of the keto-hydrazine reaction in peaks at  $1703\text{ cm}^{-1}$ ,  $1533\text{ cm}^{-1}$ , and  $1374\text{ cm}^{-1}$  which are due to the keto-carbonyl group, the amide linkage, and the tertiary amine group present in DDP respectively.

### 3.4. Particle Size Analysis

The particle size of the PU-BDO (WPUD with BDO as chain extender) and PU-SiOH (WPUD with SiOH as chain extender) schemes were compared. As the concentration of DMPA in the dispersions is constant, the increase in the particle size could only be attributed to the replacement of BDO by SiOH. The average particle size of the PU-BDO-4 system was determined to be 80.5 nm while the average particle size of the PU-SiOH-4 system was determined to be 351.7 nm. This increased particle size could be due to the polarity induced by the presence of the Si groups in the backbone of the PU. This could lead to the aggregation of water molecules near the polymer chain which could lead to an increase in the particle size.





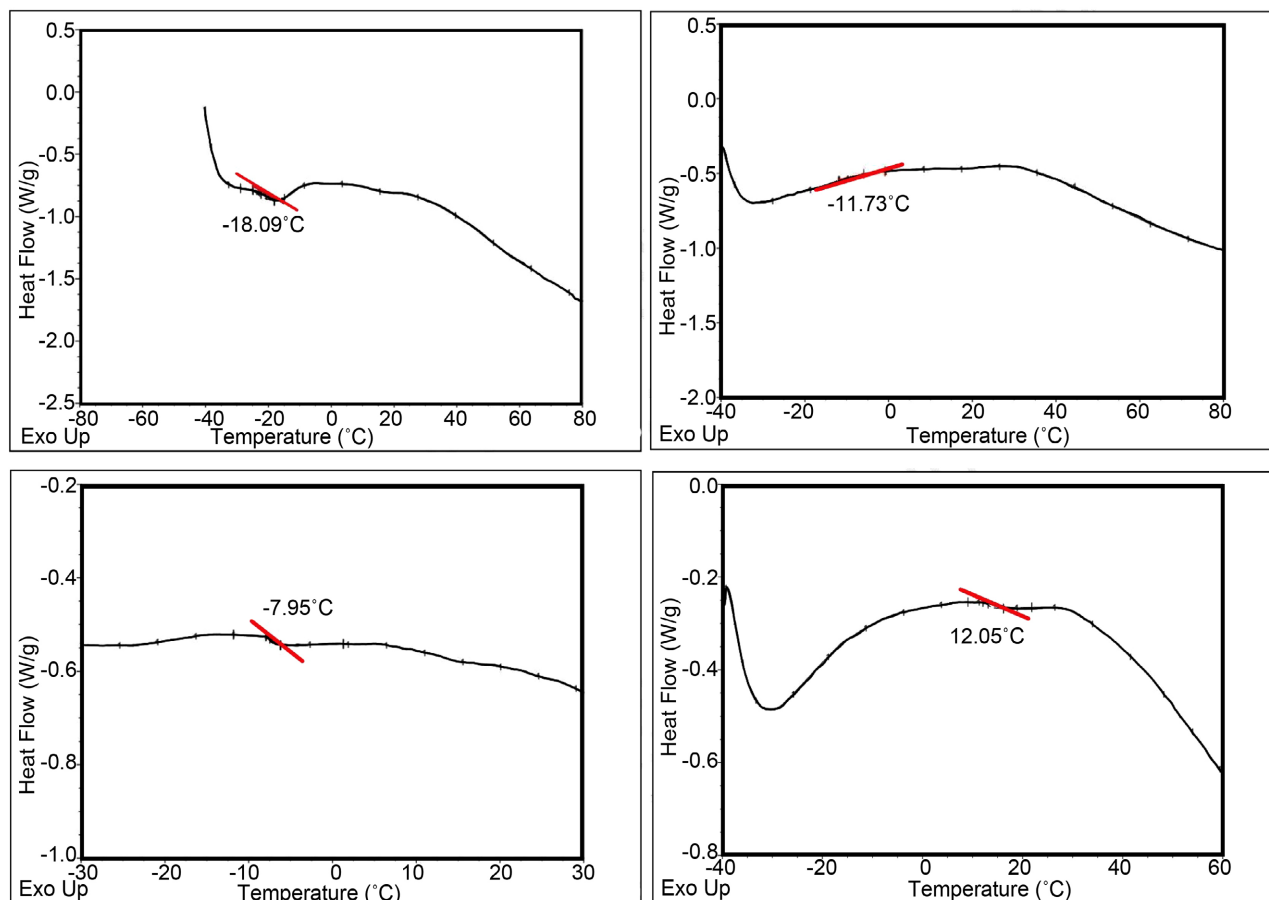
**Figure 2.** (a) FTIR Spectra of WPUD; (b) FTIR Spectra of WPUD film.

It is to be noted that the PU-SiOH-1 was synthesized but was found to be very unstable with the dispersion breaking overnight resulting in the polymer separating from the water phase. The batch was repeated several times with the same

result each time. The possible reasons for this anomaly have been discussed later. This anomaly was interpreted to be because of the hydrogen bonding resulting between the silanol groups and silanol and TEA groups. It has been observed that in the presence of high concentrations of hydroxyl-terminated silane, the OH groups in the silane form complexes with the amide group. As the PU-SiOH-1 group has the highest concentration of SiOH, this tendency to form a complex would be highest in this case. The formation of these complexes would mean that the TEA molecules would no longer be able to form quartered ammonium salts with the DMPA molecules and this would result in the drastic reduction of these hydrophilic groups and thus as a result would lead to the breaking of the dispersion.

### 3.5. DSC Analysis

The WPUD films of the PU-BDO system were subjected to DSC analysis as shown in **Figure 3**, to determine the effects of the increasing DDP concentration on the thermal properties. It was determined that as the DDP concentration increased, the glass transition temperature ( $T_g$ ) increased. The  $T_g$  increased from a value of  $-18.09^\circ\text{C}$  for PU-BDO-1 to  $12.05^\circ\text{C}$  for the PU-BDO-4 system. An



**Figure 3.** DSC analysis of PU-BDO system; (a)  $T_g$  of PU-BDO-1; (b)  $T_g$  of PU-BDO-2; (c)  $T_g$  of PU-BDO-3; (d)  $T_g$  of PU-BDO-4.

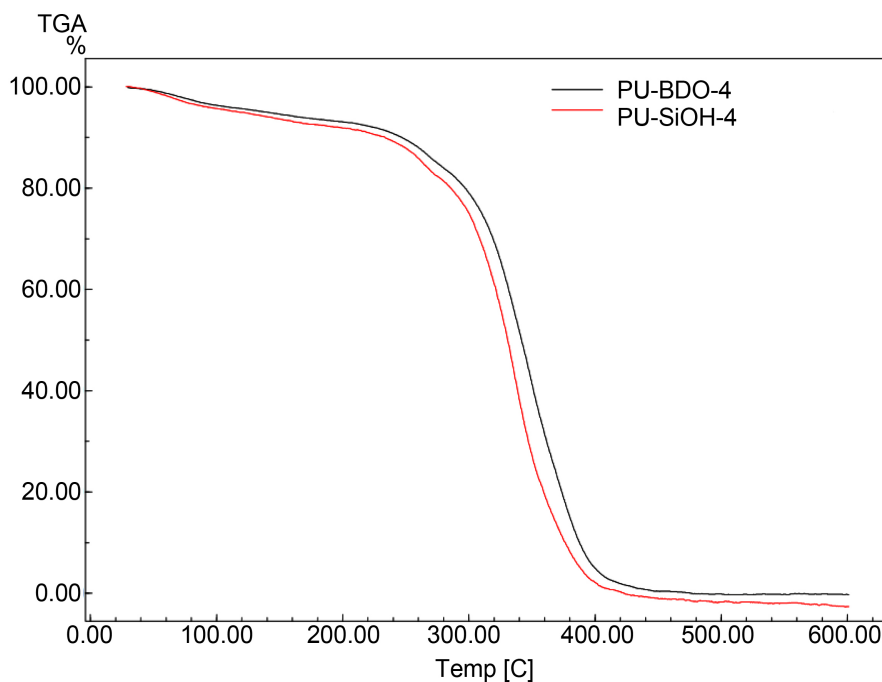
increase in the crosslinking of the WPUD film could lead to a dense network structure. These hard segments will restrict the chain motion and thus will increase the thermal energy required for the Brownian motion and the creation of free volume on the application of thermal energy which is reflected by the increase in the  $T_g$ .

### 3.6. TGA Analysis

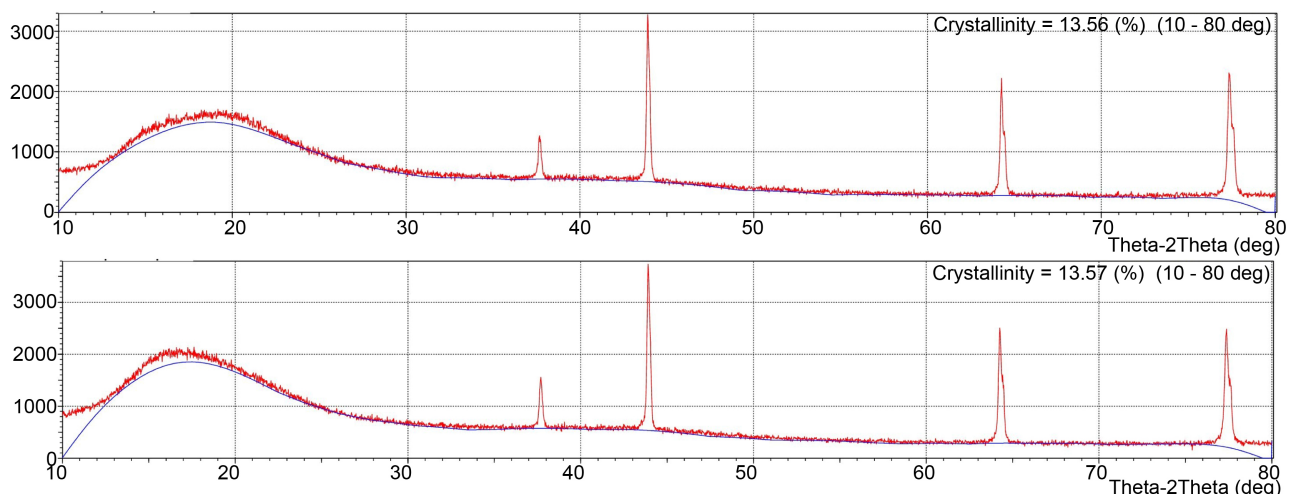
The PU-BDO-4 and PU-SiOH-4 batches were subjected to TGA analysis to determine if the addition of SiOH to the system has any noticeable effect on the degradation characteristics of the WPUD. The results obtained were as shown in **Figure 4**. The incorporation of Si in the backbone did not have any difference in the degradation temperature or the onset of degradation. Both the systems undergo similar degradation carving a similar trajectory as they completely degrade leaving no char behind. The degradation characteristics mainly depend on the concentration of crosslinker in the system and as the crosslinker concentration is the same for both the systems, the systems show a similar degradation curve with no substantial change due to the presence of Si in the backbone of the PU.

### 3.7. XRD Analysis

The PU-BDO-4 and PU-SiOH-4 Batches were subjected to XRD analysis to determine if the incorporation of Si in the PU backbone has any substantial changes in the crystallinity of the resultant PU film, the results of which are shown in **Figure 5**. The % crystallinity of both systems was 13.56% and no difference in the values was observed. The crystallinity of the PU film would be



**Figure 4.** TGA analysis of PU-BDO-4 and PU-SiOH-4.



**Figure 5.** XRD analysis; (a) PU-BDO-4; (b) PU-SiOH-4.

affected by the hard segment present in the system. In both cases, the amount of NCO groups and chain extender OH groups are the same, and thus the amount of hard segment in both the cases will be similar, thus exhibiting similar crystallinity.

### 3.8. General Coating Properties

The coating properties have been summarized in **Table 2**. The crosslinking density of the WPUDs was found to be increasing with an increase in the DDP concentration. The results ranged from 72.72% for PU-BDO-1 to 77.25% for PU-BDO-4 and 75.26% for PU-SiOH-2 to 79.43% for PU-SiOH-4. This result indicated a successful crosslinking reaction as the crosslinking density of the resultant films increased as expected.

Another visible result was the slight increase in the crosslinking density with Si present in the backbone of the PU. This increase could be attributed to superior phase segregation between the hard and soft segments of the PU due to the presence of the Si groups. The PU-SiOH series of batches showed superior adhesion properties as compared to the PU-BDO systems. The presence of Si groups would improve the surface activity of the PU and thus improve the adhesion of the PU to the metal substrate. Another inference of the test was the decreasing adhesion as the concentration of DDP increased. The increased hardness of the WPUD films resulted in a lowered adhesion strength.

The solvent resistance rub test showed results favoring the PU-SiOH system. The improved resistance of the PU-SiOH system was due to the presence of the Si groups. The PU-BDO-1 batch lasted 98 MEK rub cycles before the substrate was visible which increased to 160 cycles for PU-BDO-4. The PU-SiOH-2 batch lasted 140 MEK rub cycles before the substrate was visible which increased to 200 cycles for PU-SiOH-4. This increased solvent resistance was due to increased crosslinking density which improved the coating properties.

The water swelling test results showed a decreasing trend of 2.43% for

**Table 2.** Properties of WPUD films.

Designation	pH	Crosslinking Density (%)	Adhesion (%)	Solvent Resistance Rub Test (Cycles)	Pencil Hardness	Water Swelling (%)	Water resistance	Water Whitening
PU-BDO-1	7.78	72.72	100	98	H	2.43	10	No Whitening
PU-BDO-2	7.44	74.25	80	120	H	2.24	10	No Whitening
PU-BDO-3	7.24	76.33	70	150	2H	2.12	10	No Whitening
PU-BDO-4	7.64	77.25	70	160	2H	1.86	10	No Whitening
PU-SiOH-2	7.60	75.26	100	140	H	2.86	10	Slightly White
PU-SiOH-3	7.55	77.95	90	160	2H	2.75	10	No Whitening
PU-SiOH-4	7.67	79.43	80	200	3H	2.56	10	No Whitening

PU-BDO-1 to 1.86% for PU-BDO-4. These results were reciprocated in PU-SiOH systems where the % swelling dropped from 2.86% for PU-SiOH-1 to 2.56% for PU-SiOH-4. This decreasing trend indicated that as the DDP concentration in the system increased, the water swelling of the films decreased. The incorporation of SiOH in the system increased the water swelling tendency of the PU-SiOH films. These results reinforce the interpretation that the presence of Si in the PU backbone enhances the interactions with water, which as stated earlier led to an increase in the particle size. All the WPUD films passed the water-resistance test after 48 h with no visible blistering or delamination and no visible water whitening in the resultant films.

#### 4. Conclusion

Self-crosslinked waterborne PUD was synthesized in which DDP and SiOH were successfully incorporated in the backbone of the prepolymer which when mixed with the post crosslinker of ADH, was able to successfully undergo the crosslinking reaction by the Keto-Hydrazine mechanism. The increase in the crosslinker increased the Tg of the resultant film which is due to the increased restrictions in chain mobility. The incorporation of SiOH in the backbone increased the particle size of the dispersion which was interpreted to be because of the active Si groups present in the PU backbone which could lead to strong interaction with the water molecules. This effect was also responsible for a visibly higher water swelling tendency of the Si-modified systems. The incorporation of Si did not show any substantial difference in the TGA degradation curves and neither did it increase the crystallinity of the final crosslinked film. The Si however enhanced the adhesion to the substrate and improved the solvent resistance.

#### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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