

A NEW CURING AGENT FOR AQUEOUS-BASED PU DISPERSION

Shih-Chieh Wang*, Po-Cheng Chen, Kan-Nan Chen

Department of chemistry, Tamkang University,
Taipei, Taiwan

* e-mail: u5170327@tknet.tku.edu.tw

Introduction

Azetidine(AZ) was first synthesized by Gabriel and Weiner in 1888, and many similar methods have been developed since then. AZ and other N-substituted AZ were stable compounds with no pronounced tendency to deteriorate spontaneously, but those compounds would undergo ring opening reaction under a pH value below 7.0 with a nucleophilic agent (e.g. carboxylic acid).

Experimental

Preparation of curing agent (HDDAAZ)

A solution of aminopropanol was added into methyl acrylate (MA) and refluxed 6 hrs. Subsequent vacuum removed the excess MA, yielding 96.8% of (a). (a) was treated with SOCl_2 and reaction was maintained below 20°C about 6 hrs and then poured into $\text{NaHCO}_3(\text{aq})$. The organic layer dried over Na_2SO_4 and the solvent was removed under reduced pressure, yields 92.1% of product (b). Compound (b); Na_2CO_3 and pentaerythritol were placed in a 3-necked round-bottomed flask fitted with a vacuum-distillation head. The crude product was obtained by heating the suspension at 150°C /10~20 mmHg. The pure product was obtained by redistillation under reduced pressure, yielded 45.5% of (c). KOH and mineral oil were placed in a 3-necked round-bottomed flask fitted, a vacuum-distillation head and an addition funnel

containing compound (c). The mixture was heated to 140°C then compound (c) was added dropwise and generated of MeOH by reduced pressure. (d) was obtained by distillation of the reaction mixture from 140°C to 230°C , yielded 30% of (d). HDDA was treated with (d) at ice bath then reaction was keep at 60°C about 6 hrs. The excess of (d) were removal by reduced pressure. The curing agent (HDDAAZ) was obtained and yielded about 97%.

Preparation of aqueous-based PU dispersion

PU-prepolymer was synthesized from IPDI; DMPA and PPG-2000 following prepolymer process. An aqueous-based PU dispersion was obtained from a high shear rate mixing of PU with aqueous solution of EDA and TEA. PU dispersion contains 30% solid contents with a pH value at 8.5 after acetone is removed under vacuum. (Scheme II)

Curing Reaction of HDDAAZ with PU

The various ratios of HDDAAZ in acetone were mixed with aqueous-based of PU and cast on the glass plate, and dried for testing.

Results and Discussions

The curing agent (HDDAAZ) was obtained from a series reactions of MA with aminopropanol via Michael addition reaction. The crude material was treated with SOCl_2 to chlorination of OH group. Subsequently, cyclization was processed in the base condition at high temperature and low pressure. A cyclized product was reacted with KOH to formation of AZ and HDDAAZ was resulted from reaction of AZ with HDDA via Michael addition. (Scheme I) The curing reaction of HDDAAZ with PU dispersion was initiated on drying. While the evaporation of TEA, proton was exchanged to the AZ group of HDDAAZ and carboxyl groups attacked the AZ ring to

result ring opening reaction and forming a high cross-linked of PU resin. (Scheme III)

Properties of PU Films

In table I, gel content of aqueous-based PU was 0%, it was ascribed lower average molecular weight and deficient in chemical resistance. As various dosages of HDDAAZ introduced into PU resin could patently find the gel content value intensively increasing. This could explain curing reaction was generation and result network structure of PU resin and improved the chemical resistance. Water-uptake and alcohol-swollen properties were the same trends with gel content. In table II, tensile stress of aqueous-based PU at 600% elongation was 33.2kgf/cm² and its value was increased with increasing the amount of HDDAAZ. While 5phr of HDDAAZ introduced, tensile stress at 600% was 142.3kgf/cm². According to this could confirm cross-linkage structure was forming as HDDA-AZ addition.

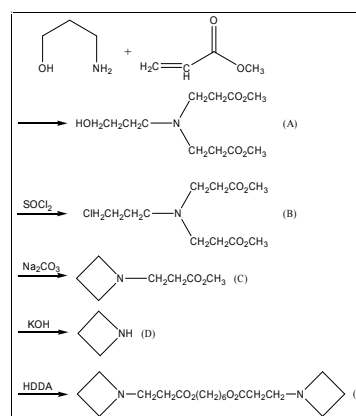
Conclusion

HDDA-AZ was prepared through a five-step process. HDDA-AZ served as a curing agent and reacted with aqueous-based PU dispersion on drying. It resulted in the formation of high network structure and demonstrated on their performance properties. This new curing agent offered an alternative choice.

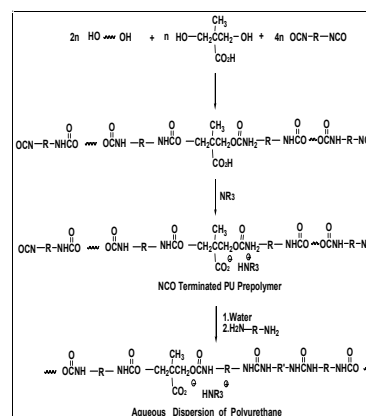
References

1. G. N. Chen and K. N. Chen, J. Appl. Polym. Sci., 63, 1609 (1997)
2. D. J. Wang and K. N. Chen, J. Appl. Polym. Sci., 74, 2499 (1999)
3. G. N. Chen and K. N. Chen, J. Appl. Polym. Sci., 71,903 (1999)

Scheme I Preparation of HDDAAZ



Scheme II Preparation of aqueous-based PU Dispersions



Scheme III Curing Reaction of HDDAAZ with Aqueous-based PU Dispersions

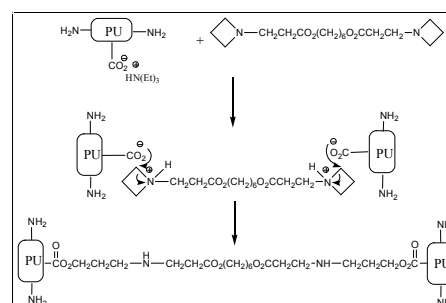


Table I Physical Properties of PU with Various HDDA-AZ Dosage

	Original	PU with HDDA-AZ(phr)				
	PU	1.0	2.0	3.0	4.0	5.0
Gel content (%) ^(b)	0	0	71.1	73.5	78.9	85.1
W _w (%)	23.9	23.7	23.1	22.3	21.4	19.5
W _x (%)	2.01	1.50	1.35	1.07	0.91	0.61
W _e (%)	-- ^(c)	-- ^(c)	3280	1473	1078	758
W _y (%)	100	100	26.5	20.9	17.2	13.4

W_w: amount of water-uptake by PU film

W_x: amounts of PU film dissolved into the water

W_e: amounts of ethanol absorption by PU film

W_y: amounts of PU film dissolved into the Ethanol solution

(a) Soxhelt extraction with THF

(b) PU Films 100% dissolved in ethanol

Table II Mechanical Strength of PU Cured Films with Curing Agent HDDA-AZ Series

Properties	PU with HDDA-AZ (phr)					
	Original	1.0	2.0	3.0	4.0	5.0

PU						
Elongation (%)	Tensile Strength (kg/cm ²)					
100	10.7	27.8	29.0	30.8	34.3	36.3
200	18.0	46.4	51.4	53.4	58.9	61.7
300	23.1	62.5	65.3	69.1	76.6	80.3
400	27.0	77.6	79.0	84.8	92.6	98.7
500	30.4	88.9	92.9	99.3	110.9	119.3
600	33.2	101.2	107.1	116.1	130.9	142.3
700	36.3	113.6	124.3	135.9	152.0	--
800	39.4	126.0	143.4	156.8	--	--
900	42.2	142.9	163.8	182.9	--	--
1000	45.0	159.7	--	--	--	--
1100	47.8	178.9	--	--	--	--
1200	50.6	--	--	--	--	--
Tensile strength (kg/cm ² / %)	50.8/ 1206	185.6/ 1136	171.3/ 930	182.9/ 900	173.7/ 786	166.5/ 685