Synthesis and Characterization of Aqueous Cationomeric Polyurethanes and Their Use as Adhesives*

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SYNOPSIS

Aqueous cationomeric polyurethanes (ACPU) were synthesized by a multistep reaction process. The alipathic diisocyanate, e.g., hexamethylene diisocyanate (HDI), was reacted with polyol, e.g., polypropylene glycol (PPG400) to form a prepolymer and it was chain-extended by reacting it with N-methyldiethanolamine (N-MDEA). Quarternization was then carried out by using dimethyl sulfate (DMS), acetic acid (HAc), or hydrochloric acid (HCl). The resultant cationomers were self-emulsified with deionized water. The effect of different percentages of N-MDEA in the polymer backbone on the structure and properties of ACPU were studied. Viscosity, thermal properties, electrolytic stability, and pH stability of the cationomeric polyurethanes were also studied along with the adhesion strengths between flexible and rigid surfaces. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Presently, the world over, there has been a trend to reduce the usage of solvents in adhesive or coating compositions, due to the environment protection act that came into force in 1992. In the light of this, water-based systems are gaining more importance. Extensive work has been done in the development of water-based anionomeric polyurethanes[1-8] and cationomeric polyurethanes[8-10] which contain a very small amount of solvent. Most of the work reported on cationomeric polyurethanes is in the form of patents which contained no systematic study on their stability toward heat and pH, the film-forming ability, the effect of ionic center concentration, the effect of different quarternizing agents (QA) in the polymeric backbone, and the adhesion properties. Synthesis of cationomeric polyurethanes[8-18] were carried out in different ways and with a wide variety of reactants. The effect of the addition of deionized water to the cationomers on the viscosity behavior was reported.[9,10,12] Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) studies

on aqueous cationomeric polyurethane systems were reported in specific cases.[12]

Therefore, in the present study, we are reporting in detail the synthesis of aqueous cationomeric polyurethanes (ACPU) with varying percentages of N-methyldiethanolamine (N-MDEA) (i.e., hard segment) and the ionic strengths. Cost-effective QAs like dimethyl sulfate (DMS), acetic acid (HAc), and hydrochloric acid (HCl) were used for quarternization instead of costlier glycolic acid.[15-17] The viscosity, thermogravimetric analysis (TGA), and differential scanning calorimetric studies (DSC) and the electrolytic and pH stability of ACPU systems were also studied. The film homogeneity and the adhesion strengths of the films between different surfaces, with varying percentages of ionic content, were also studied.

EXPERIMENTAL

Materials

Hexamethylene diisocyanate (HDI), di-n-butylamine, and cumene (Fluka); N-methyldiethanolamine (N-MDEA; Aldrich); bromocresol green and glacial acetic acid (Glaxo, India); and malachite green, paraffin oil, and HCl (Loba Chemicals, India) were used as received. Pyridine, n-Butylamine and tetrahy-

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Table I Recipe for Aqueous Cationomeric Polyurethanes (ACPU)

Designation	HDI g	HDI mol	PPG g	PPG mol	N-MDEA g	N-MDEA Wt %	DMS (g)	HAc (g)	HCl (g)
ACPU-1	25.2	0.15	40.6	0.102	1.36	2.0	1.39	—	—
ACPU-2	25.2	0.15	38.6	0.096	2.04	3.1	2.20	—	—
ACPU-3	25.2	0.15	35.7	0.089	2.69	4.7	2.72	—	—
ACPU-4	25.2	0.15	32.2	0.080	5.05	8.0	5.20	—	—
ACPU-5	25.2	0.15	30.0	0.075	6.00	9.9	6.20	—	—
ACPU-6	25.2	0.15	27.5	0.060	7.40	12.3	7.60	—	—
ACPU-7	25.2	0.15	22.0	0.055	9.80	17.1	10.40	—	—
ACPU-8	25.2	0.15	30.0	0.075	6.05	9.9	—	—	5.0
ACPU-9	25.2	0.15	35.2	0.084	4.00	6.2	—	2.01	—
ACPU-10	25.2	0.15	30.2	0.075	6.00	9.9	—	3.01	—
ACPU-11	25.2	0.15	26.1	0.065	9.09	15.0	—	4.54	—

Wt % = weight percentage. N-MDEA percentages were calculated on the basis of the total weights of HDI, PPG, and N-MDEA.

drofuran (Loba Chemicals) were distilled over KOH. Dimethyl sulfate (DMS), (s.d. Fine Chemicals, India) was distilled over K_2CO_3(anhydrous). Methyl ethyl ketone (MEK) was dried by distillation over P_2O_5 and then stored over 4 Å° molecular sieves. Linear poly(propylene glycol) (PPG400; M_n = 400, hydroxyl value [OHv 268], Fluka) was dried at 70°C under reduced pressure of 0.1 mmHg for 16 h.

Synthesis of Cationomeric Polyurethanes

The total synthesis of aqueous cationomeric polyurethanes (ACPU) was carried out in a four-necked, moisture-free resin kettle in four steps. A small amount of anhydrous MEK was taken into this hot (70–75°C) kettle and subsequently flushed with moisture-free nitrogen to create an inert and dry atmosphere in the kettle. The kettle was fitted with a mechanical stirrer, nitrogen gas inlet, and a condenser with a calcium chloride guard tube. The fourth neck was used for the addition of the reactants. The measured quantities of HDI, PPG400, N-MDEA, DMS, HAc, and HCl used in these reactions are given in (Table I).

In Step 1 of the reaction, a prepolymer was prepared by reacting HDI with PPG400 at 70–75°C for 3–4 h. The reaction was continued until the theoretical free NCO content (%) was reached as determined by the di-n-butylamine method[18,20] (Table II).

In Step 2, this prepolymer was chain-extended by reacting it with N-MDEA at 65°C for 1–2 h. The reaction was stopped when the theoretical free NCO
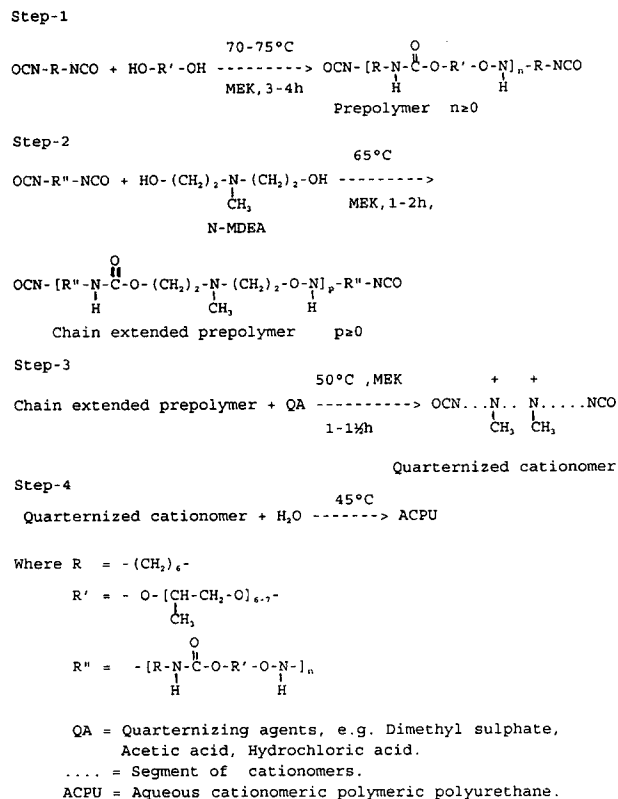
Table II Percent of Free Isocyanate and GPC Analysis of Chain-extended Prepolymer

Prepolymer Free NCO (%)[a] Theor.	Prepolymer Free NCO (%)[a] Obs.	Chain Extender N-MDEA (%)	Chain-extended Prepolymer Free NCO (%)[b] Theor.	Chain-extended Prepolymer Free NCO (%)[b] Obs.	MW	Dispersity
6.8	6.7	2.0	5.12	5.01	8101	1.4
7.5	7.3	3.1	4.82	4.62	7500	1.5
8.9	8.5	4.7	4.80	4.60	6371	1.2
10.6	10.7	8.1	4.10	3.90	4694	1.2
11.9	11.4	9.9	3.40	3.20	3286	1.7
—	—	9.9	—	—	4409[c]	1.8
13.4	12.9	12.3	2.40	2.32	3840	1.3
17.3	16.2	17.2	1.20	1.15	6892	1.4

[a] Di-n-butylamine method.
[b] n-Butylamine method.
[c] For "one-shot" process, Theor. = theoretical, Obs. = observed, MW = molecular weight.

Step-1

```
                    70-75°C                 O
OCN-R-NCO  +  HO-R'-OH ---------> OCN-[R-N-C-O-R'-O-N]_n-R-NCO
                    MEK,3-4h                 H                H
                                   Prepolymer   n≥0
```

Step-2

```
                                   65°C
OCN-R"-NCO  +  HO-(CH₂)₂-N-(CH₂)₂-OH --------->
                        |
                        CH₃        MEK,1-2h,
                      N-MDEA
```

```
           O
           ||
OCN-[R"-N-C-O-(CH₂)₂-N-(CH₂)₂-O-N]_p-R"-NCO
       |                |             |
       H                CH₃           H
       Chain extended prepolymer    p≥0
```

Step-3

```
                              50°C ,MEK          +      +
Chain extended prepolymer + QA ----------> OCN...N.. N.....NCO
                              1-1½h              |    |
                                                 CH₃  CH₃
                                        Quarternized cationomer
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Step-4

```
                              45°C
Quarternized cationomer + H₂O -------> ACPU
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```
Where R   = -(CH₂)₄-

      R'  = - O-[CH-CH₂-O]₆.₇-
               |
               CH₃
                    O
                    ||
      R"  = -[R-N-C-O-R'-O-N-]ₙ
               |             |
               H             H
```

QA = Quarternizing agents, e.g. Dimethyl sulphate,
     Acetic acid, Hydrochloric acid.
.... = Segment of cationomers.
ACPU = Aqueous cationomeric polymeric polyurethane.

Scheme I

content (%) was reached as determined by the n-butylamine method[21] (Table II). In these experiments, different weight ratios of N-MDEA on the weight of the total reactants (before quarternization) were used to vary the percent ionic content.

In Step 3, the chain-extended prepolymer was quarternized at tertiary nitrogen centers using DMS, HAC, or HCl at 50°C for 1–1.5 h. The quantities of the quarternizing agent depended upon the amount of the chain extender N-MDEA used in Step 2. Usually, it was maintained in the order of a 1 : 1 mol ratio.

In Step 4, the above NCO-terminated quarternized cationomers were self-emulsified with deionized water at 40–45°C under vigorous stirring. The amount of deionized water added depended on the total percentage of solids required in the ACPU systems. In most of the experiments, the percentage solids of around 35 was maintained. All these four steps are illustrated in Scheme 1.

All the above reactions belong to the "two-shot" process. But in the "one-shot" process, HDI, PPG-400, and a calculated amount of the chain-extending agent (N-MDEA) were allowed to react together. Quarternization and self-emulsification, i.e., Steps 3 and 4, are same for both systems.

Characterization

Infrared (IR) spectra of dried films were taken using a Nicolet FTIR 740 infrared spectrophotometer. Viscosity studies during self-emulsification at Step 4 of the ACPU systems were conducted by using a Brookfield Synchrolectric viscometer.

GPC analysis of chain-extended prepolymer film in tetrahydrofuran (THF) solution was carried out using poly(ethylene glycol) (PEG) as a standard using a Shimadzu GPC analyzer. THF was used as the eluant.

The ACPU film samples were prepared after drying the films at 100°C and at 5.0 mmHg for 5 h for thermogravimetric analysis (TGA), differential thermogravimetry (DTG), and differential scanning calorimetric (DSC) studies.

TGA and DTG were conducted by using a Linseis Westgerman thermobalance L80 Model instrument over a temperature range 25–350°C, at a heating rate of 10°C/min, and with sample weight 30 ± 1.0 mg under air. DSC analysis of ACPU samples was conducted by using Perkin-Elmer DSC 7 unit. Indium was taken as internal standard for analysis. DSC was run over a temperature range of 50–250°C,

Table III Downward Shift of N—H(str) Band (3337 cm⁻¹) with Increase in Percentage of N-MDEA in ACPU

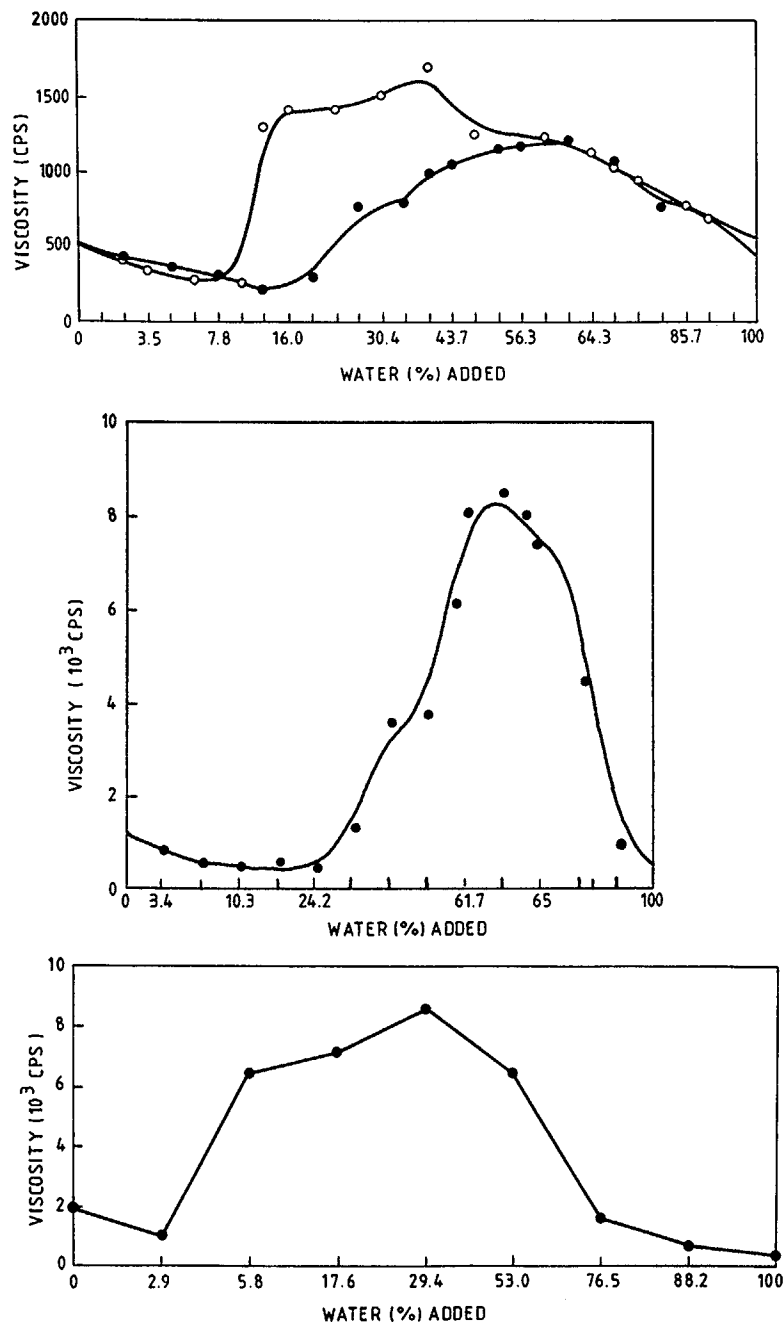| N-MDEA Percentage (From Table I)	Shift of N—H(str) Band (cm⁻¹)			Remarks
	From	To	Shift	
3.1	3337	3330	07	Shifts values increasing with increase in percentage of hard segment and ionomer content
8.0	3337	3324	13	
12.3	3337	3320	17	
17.2	3337	3314	23	

Figure 1 (a) Viscosity of (●) ACPU-5 and (○) ACPU-5* systems during the gradual addition of deionized water. (b) Viscosity of ACPU-8 system during the gradual addition of deionized water. (c) Viscosity of ACPU-10 system during the gradual addition of deionized water.

at a scanning rate of 10°C/min under N₂ atmosphere. The sample sizes were 4.5 ± 0.05 mg.

The homogeneity of the films was observed using a Hitachi S 520 Model scanning electron microscope. The films were dried in air and kept at 60°C under 5.0 mmHg in a vacuum oven before use.

Electrolytic stability of ACPU systems was observed for any phase separation by mixing a measured amount of a prepared standard aqueous potassium bromide (KBr) solution with a known amount of the ACPU system. The pH stability of ACPU system was carried out using standard pH solutions.
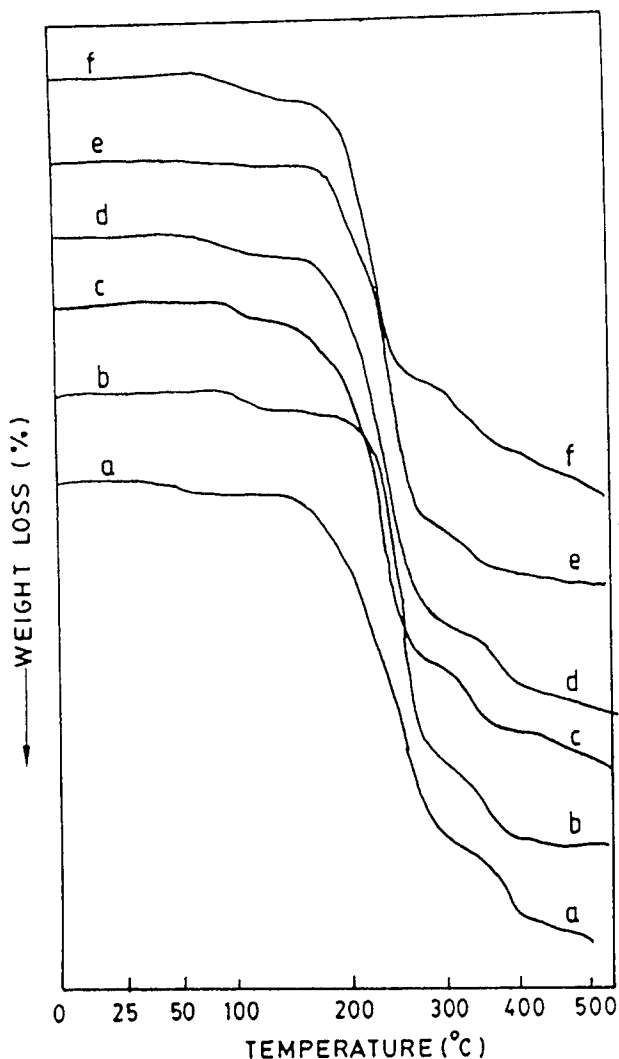
Figure 2 TGA curves of different ACPU systems: (a) ACPU-3; (b) ACPU-5; (c) ACPU-5*; (d) ACPU-7; (e) ACPU-8; (f) ACPU-10.

The adhesion bond strengths, i.e., tensile shear (TS) [ASTM D-1002-72] and peel [ASTM D-1876-72] strengths were determined using an Instron tensile testing instrument Model 1026, between various flexible and rigid surfaces.

RESULTS AND DISCUSSION

Infrared Spectroscopy

The course of the reaction from Step 1 to Step 3 [Scheme 1] was followed by IR spectroscopy. The progress of the reaction was indicated by the gradual disappearance of a broad O — H peak (3600–3200 cm^{-1}) with the simultaneous increase in the intensity of sharp N — H (3337 cm^{-1}) and carbonyl (1772

cm^{-1}) peaks of the urethane. The intensity of free NCO peak (2270 cm^{-1}) was reduced gradually from Step 1 to Step 3, but it was almost identical for Steps 3 and 4. The presence of a sharp and strong peak at 3337 cm^{-1} indicated that this N — H was hydrogen-bonded with oxygen of urethane carbonyl and oxygen of PPG.[22]

The IR spectrum of dried aqueous casted film showed no peak at 2270 cm^{-1} (absence of free NCO). A broad peak at ~3415 cm^{-1} was noticed instead of a sharp peak at 3337 cm^{-1} which is believed to be due to the overlap of N — H (str) with H — OH (str) of lattice water present in the film.

With increase in the percentage of N-MDEA and DMS, in ACPU, a gradual downward shift of the N — H (str) band at 3337 cm^{-1} was observed, the results of which are given in Table III. This observation is in agreement with the data reported in the literature.[23,24]

Viscosity

Increase in the viscosity (η) of the products of Steps 1 and 2 was due to the formation of higher molecular weight polyurethane. In Step 3, the sudden and manyfold increase in viscosity was due to the mutually strong Coulombic forces of attraction between the ionomers formed after quarternization. It was believed that due to the strong Coulombic forces of attraction between the polymeric chains there was an aggregation which led to the formation of a microionic lattice.[9,10] These microionic lattices had a very high effective molecular weight, due to which the viscosity of their solutions was very high.

The effect of dilution of cationomers with the addition of deionized water on the viscosity behavior during Step 4 was of special interest. It is known that the Coulombic force (F) is inversely proportional to the dielectric constant (e) of the medium. Since water has a very high e value ($e = 78.2$), it decreases the force (F). During the slow addition of deionized water under vigorous stirring, the water slowly entered into the core of the microionic lattice and it decreased the force (F) between the ionomers. Finally, when a particular amount (a few milliliters) of water was added, the microionic lattice literally diminished. This caused a sudden fall in viscosity. This was observed for all the ACPU systems [Fig. 1(a), (b), and (c)]. Further addition of water resulted in an increase in the viscosity of the system due to a lesser solvation of hydrophobic segments in the aqueous medium. Alignment of hydrophobic parts of the polymeric chains with increase in the amount of deionized water added

Table IV Characteristic Values of TGA and DTG Analysis of Different ACPU Systems

ACPU Systems	N-MDEA (%)	Temperature (°C) Stages			Weight Loss (%) Stages		
		I	II	III	I	II	III
ACPU-3	4.7	30–80	150–250	250–300	3.0	73.0	16.0
ACPU-5	9.9	80–120	180–260	260–300	4.0	66.0	10.0
ACPU-5*	9.9	80–120	170–250	250–300	4.0	67.0	15.0
ACPU-7	17.2	80–120	180–250	250–300	4.0	59.0	20.0
ACPU-8	9.9	50–120	180–270	250–300	6.0	68.0	17.0
ACPU-10	6.2	80–110	160–250	250–300	2.0	69.0	19.0
ACPU-11	15.0	80–120	180–250	250–300	6.0	62.0	18.0

caused a rapid increase in the viscosity to the highest value. With the further addition of water, the viscosity was reduced due to ionomeric chains forming microspheres where the ions remain on the outer side of the coiled backbone of the ACPU system.[28] The effect of dilution of cationomers with deionized water was found to be similar [Fig. 1(a), (b), and (c)], irrespective of the type of the QA, e.g., DMS, HAc, or HCl, used. Therefore, the viscosity of each system was rather dependent on the polymer backbone.

The viscosity of ACPU systems was studied for both "one-shot" (ACPU-5*) and "two-shot" (ACPU-5) processes. In both processes, DMS was used as the QA. The viscosity of the "one-shot" process was found to be higher than that of the same synthesized by the "two-shot" process. From GPC analysis of the molecular weight (Table II), it was observed that the molecular weight of the chain-extended prepolymer prepared from the "one-shot" process (MW = 4409) was higher than

that of the "two-shot" process (MW = 3268). Quarternization had no significant effect on the molecular weight of the chain-extended prepolymer. The higher molecular weight of ACPU-5* was responsible for its higher viscosity than that of ACPU-5. HAc- and HCl-quarternized ACPU showed a higher viscosity than did those with DMS, due to the presence of more and stronger H-bonding between the ionomeric chains.

Thermal Analysis

Thermogravimetric Analysis (TGA)

The percentage of weight loss at the corresponding temperatures from the TGA curves (Fig. 2) are given in Table IV. The weight loss was mainly in three stages at three different temperatures ranges. For all samples, a weight loss of 3–6% was observed in the first stage at 80–120°C which was due to the residual water present in the sample. In the second stage, a major weight loss of 60–75% for all samples was observed, at 180–250°C, which was due to the
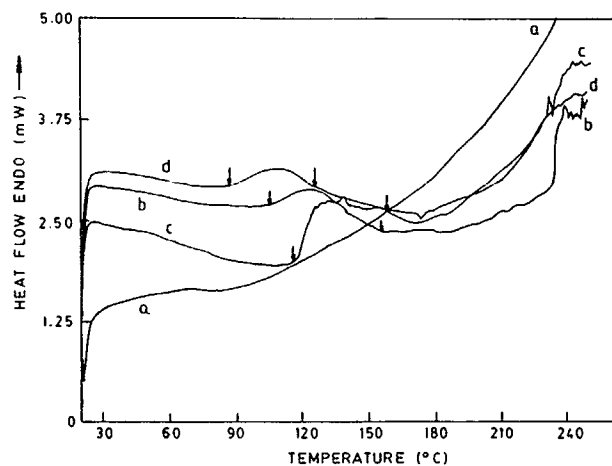

Figure 3 DSC curves of different ACPU systems: (a) ACPU-3; (b) ACPU-5; (c) ACPU-7; (d) ACPU-10.

Table V Characteristic Peaks from DSC Curves of Different ACPU Films

Samples	N-MDEA (%)	Endothermic Peak Temperature (°C)		ΔH (J/g)
		Lower	Higher	
ACPU-3	4.7	N	N	Nil
ACPU-5	9.9	119	170	6.67
ACPU-6	12.3	118	169	16.50
ACPU-7	17.2	121	172	64.60
ACPU-10	9.9	110	156	3.16

N = no peak and ΔH = energy absorbed by the corresponding system (J/g).

Table VI Physical Appearance of the ACPU Systems Before and After Film Formation

ACPU Systems	N-MDEA (%)	Appearance Before Film Formation	Film Appearance
ACPU-1	2.0	White coarse dispersion	Opaque, white, and coarse
ACPU-2	3.1	White finer dispersion	Matt-type nontacky transparent
ACPU-3	4.7	White dispersion	Matt-type, nontacky transparent
ACPU-4	8.0	White dispersion	Transparent, glossy, flexible, nontacky
ACPU-5	9.9	Colorless, transparent liquid	Glossy, transparent nontacky, and flexible
ACPU-6	12.3	Colorless transparent liquid	Glossy, transparent, tacky, and flexible
ACPU-7	17.2	Colorless transparent liquid	Glossy, transparent, tacky, and flexible
ACPU-9	6.2	Milky white dispersin	Glossy, transparent, tacky, and flexible
ACPU-10	9.9	Milky white dispersion	Glossy, transparent, tacky, and flexible
ACPU-11	15.0	Yellowish transparent liquid	Glossy transparent, tacky, and flexible

initial stage of the decomposition of the polymer. A later stage of decomposition at 250–350°C resulted in a weight loss of $\sim$ 20%. The percentage weight loss of ACPU systems having a lower percentage of N-MDEA (4.7%) was found to be high (73%). The ACPU system having a higher percentage of N-MDEA (17.2%) exhibited less weight loss (59%).

Differential Scanning Calorimetric (DSC) Analysis

DSC curves of the ACPU systems are shown in Figure 3. The analysis of the peaks of different ACPU systems are given in Table V. It was observed that except for ACPU-3 all systems showed an endotherm between $\sim$ 115–170°C. However, in this range of temperature, no weight loss was observed in the TGA (Table V). This endotherm was due to the breakage of electrostatic forces of ordered hard segment (N-MDEA) at higher temperature.[12,26–30] It can be concluded that with the increase in the percentages of ionic sites there was gradual increase in the corresponding ΔH (J/g) (Table V) values. This increase in ΔH can be explained on the basis of an increase in the Coulombic forces of attraction between the polymeric chains as the percentage of ionic sites increased. Therefore, the amount of energy required was high enough to break the Coulombic forces of the ordered hard segments. Hence, ΔH (J/g) values increased (Table V).

Both ACPU-5 and ACPU-10, having the same amount of N-MDEA, showed different ΔH values in the DSC analysis. This was due to the difference in the magnitude of electrostatic forces present in the system.[29]

Scanning Electron Microscope Analysis

The increase in hydrophilicity of the ACPU system with increase in the ionic center concentration

in the polymeric backbone was found true in our experiments from their physical appearance before and after film formation (Table VI). Scanning electron microscope (SEM) analysis of the casted films of different ACPU systems showed the extent of film homogeneity [Fig. 4]. From Figure 4, it is clear that although the films were essentially dry well-defined particle contours were found for ACPU systems having low percentages of N-MDEA (2–3%). A lower ionic content ACPU systems contain a fewer number of hydrophilic quarternized ammonium groups. They tend to locate on the particle surface by migrating toward the aqueous phase during the formation of particles.[31] But at higher percentages of N-MDEA (9.9–17.2) in the ACPU system, the films showed a significant increase in homogeneity among particles and, hence, they were more uniform.

Electrolytic Stability

ACPU contains cationomeric polymeric backbone and anionic counterions. Thus, ACPU systems have a definite ionic strength. So, when a certain amount of a stronger electrolyte having a higher ionic strength was added to ACPU, it resulted in phase separation or coagulation of the system. As the percentage of ionomeric centers increased from 3.1 to 17.2%, the ionic strength also increased, and as a result, the stability of ACPU dispersions toward electrolytes increased. Therefore, an increase in the strength and amount of electrolyte solution was required for the coagulation of different ACPU dispersions (Fig. 5).

pH Stability

The standard pH solutions were prepared to test the stability of ACPU systems toward pH as shown
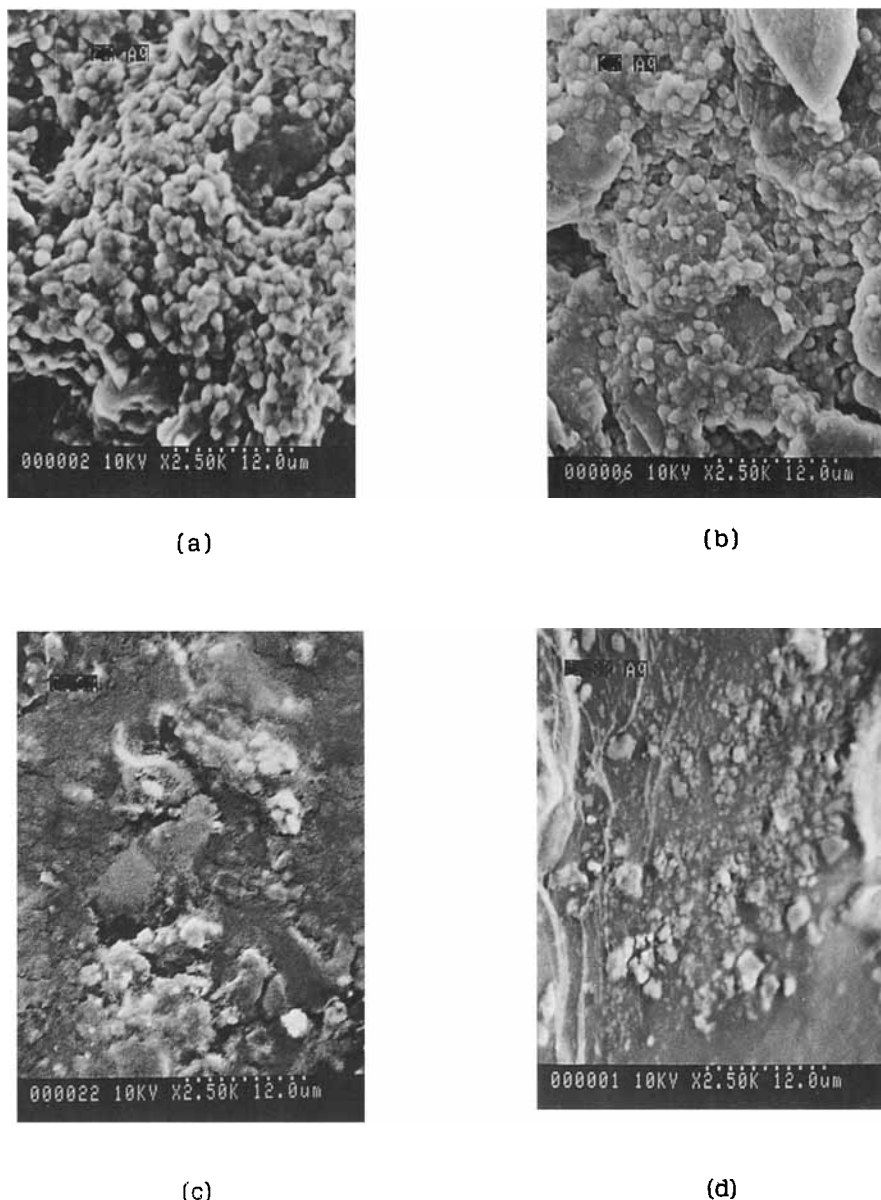
(a)

(b)

(c)

(d)

Figure 4 Scanning electron microscope photograph showing a progressive increase in homogeneity of different ACPU films: (a) ACPU-1; (b) ACPU-2; (c) ACPU-5; (d) ACPU-7.

in Table VII. The pH of all ACPU systems was between 7 and 8, and these ACPU systems were found to be stable between pH 1.10 and 13.10.

Evaluation as an Adhesive: Tensile Shear (TS) Strength

ACPU systems were evaluated as prospective adhesives by studying the TS bond strength between various flexible porous and rigid nonporous surfaces.

The flexible porous surfaces chosen were leather, poly(vinyl chloride) (PVC), and natural rubber. The rigid nonporous surfaces chosen were aluminum, brass, and glass. The TS strength of adhesive bonds obtained from various ACPU formulations are given in Table VIII.

The TS bond strengths were very low in the ACPU systems containing 2–4.7% of N-MDEA. At these lower ionic center concentrations, the effective Coulombic forces and H-bonding between hard seg-
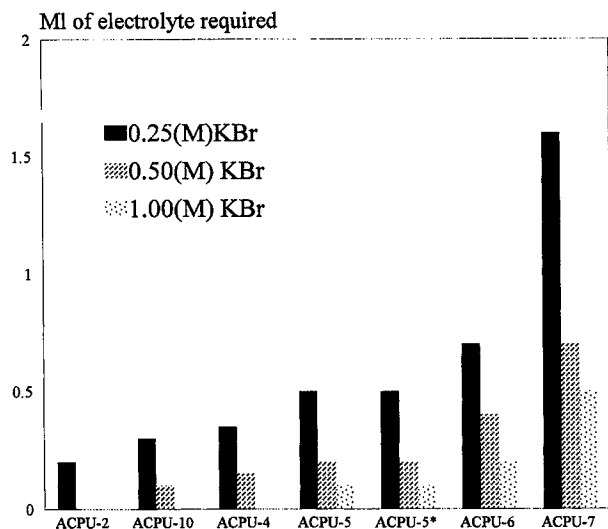
MI of electrolyte required

Figure 5 Electrolytic stability of different ACPU systems.

Table VIII Tensile Shear (TS) Strength (kg/cm²) of Different ACPU Systems on Different Surfaces

ACPU Systems	Tensile Shear Strengths (kg/cm²)			Remarks
	L–L	PVC–PVC	R–R	
ACPU-1	—	—	—	No adhesion
ACPU-2	—	—	—	No adhesion
ACPU-3	—	—	—	No adhesion
ACPU-4	2.50	1.10	2.34	Dry surface
ACPU-5	6.25	3.82	5.54	Dry surface
ACPU-5*	4.68	2.25	4.60	Dry surface
ACPU-6	2.81	1.15	2.56	Tacky surface
ACPU-7	1.37	0.88	1.15	Tacky surface*
ACPU-9	1.32	1.08	1.24	Tacky surface*
ACPU-10	1.65	1.25	1.58	Tacky surface*
ACPU-11	1.01	0.75	0.88	Tacky surface*

L = leather; PVC = poly(vinyl chloride); R = rubber; "—" = no value because of no adhesion; "*" = more tacky.

ments (N-MDEA) are much less for bonding two surfaces together. The bond strengths increased with increase in the percentage of ionic centers (4.7–9.9%), as was observed in ACPU-3, ACPU-4,and ACPU-5. This is because better adhesion was achieved when more Coulombic attraction forces were available between the ionic center sites in these cases.

However, lower adhesion strengths were obtained again with a further increase in the ionic center sites (N-MDEA 12.3–17.2%). It is believed that even at a higher percentage of ionic sites in the polymeric backbone the ionomeric chain might prefer to be in a ionic cluster structure. Moreover, with the increase in the ionic centers, the hydrophilicity of the polymer increased significantly, which, in turn, increased plasticization and the tackiness. Thus, it resulted in a lower bond strength.

The "one-shot" system (ACPU-5*) also gave moderately good bond strengths between various surfaces. However, it performed slightly inferior to "two-shot" system (ACPU-5). The higher TS bond strengths obtained from ACPU-5 was believed to be due to the presence of a regular block-type ionomeric backbone. The lower TS bond strengths obtained from ACPU-5* might be due to the random distribution of ionomeric segments in its polymeric backbone.

The TS adhesive bond strengths were determined between various flexible and rigid surfaces, using this ACPU-5 system (Table IX). The ACPU-5 system gave high TS bond strengths, as expected.

The peel strength of adhesive bonds was also determined (Tables X and XI). The trend observed

Table VII pH of Standard Aqueous Solutions at 25°C

Aqueous pH Solutions	pH
0.1M HCl solution	1.10
Saturated tartrate solution	3.55
Potassium hydrogen phthalate 0.05M solution	4.01
Standard neutral phosphate 0.025M solution	6.98
Borax 0.01M solution	9.14
Alkaline phosphate 0.01M solution	11.72
0.1M NaOH solution	13.10

Table IX Tensile Shear Strengths (kg/cm²) of ACPU-5 System on Different Flexible and Rigid Surfaces

Surfaces	Tensile Shear Strength (kg/cm²)		
	A	B	G
L	4.87	2.90	3.86
PVC	3.08	2.12	3.03
R	4.17	2.66	3.63

A = aluminum; B = brass; G = glass; L = leather; PVC = poly(vinyl chloride); R = rubber.

was the same as that of TS bond strengths for different ACPU systems (Tables VIII and IX).

Comparing the two series of the ACPU systems using DMS and HAc as the QA, it was observed that the systems using DMS are superior in performance as an adhesive to that of HAc—based systems (ACPU-4,5,6,7 vs. ACPU-9,10,11, Tables VIII and X) because the methyl-substituted counterion of DMS, i.e., $CH_3SO_4^-$, imparts a stronger Columbic attraction force than does the acetate counterion, i.e., $CH_3CO_2^-$, of acetic acid (HAc).[29]

CONCLUSIONS

Aqueous cationomeric polyurethane (ACPU) systems play a major role due to their better adhesion on a wide range of porous substrates in the field of waterborne adhesives. Especially, leather, PVC, and rubber were found to be the most suitable surfaces for the ACPU systems. These adhesives are also useful in bonding flexible surfaces with rigid surfaces, e.g., aluminum, brass, and glass. They gave overall better bond strengths and may prove to be potential adhesives in various applications, replacing those based on solvents. DMS was found to be a better quarternizing agent, giving better bond strengths. Although DSC results showed an increasing trend of ΔH (J/g) values, the bond strengths were found to be increasing initially up to 9.9% of N-MDEA and then decreasing thereafter. The probable formation of chain coiling above this percentage (9.9%) reduced the amount of exposed ionic sites for Coulombic forces and thus resulted in a lower bond strength. Free NCO (%) in Step 3

Table X   Peel Strengths (g/cm) of Different ACPU Systems on Different Surfaces

ACPU Systems	Peel Strength (g/cm)			
	L–L	PVC–PVC	R–R	Remarks
ACPU-4	383.5	221.0	334.0	Dry surface
ACPU-5	2135.0	950.0	1450.0	Dry surface
ACPU-5*	1125.0	725.0	920.0	Dry surface
ACPU-6	578.0	340.0	540.0	Tacky surface
ACPU-7	125.0	88.0	101.0	Tacky surface*
ACPU-9	121.0	98.0	118.0	Tacky surface*
ACPU-10	393.0	177.0	367.0	Tacky surface*
ACPU-11	98.0	78.0	92.0	Tacky surface*

L = leather; PVC = poly(vinyl chloride); R = rubber; "*" = more tacky.

Table XI   Peel Strengths (g/cm) of Different Flexible and Rigid Surfaces Using ACPU-5 System

Surfaces	Peel Strength (g/cm)		
	A	B	G
L	1708.7	1454.0	1529.0
PVC	921.5	996.0	992.0
R	1630.2	1441.0	1512.0

A = aluminum; B = brass; G = glass; L = leather; PVC = poly(vinyl chloride); R = rubber.

could not be determined due to formation of ionomers. IR, TGA, DTG, and SEM were found to be good analytical tools for the characterization of these ACPU systems.

REFERENCES

1. P. B. Jacobs and P. C. Yu, *J. Coat. Tech.*, **65**, 222 (1993).
2. Y. Chen and Y. L. Chen, *J. Appl. Polym. Sci.*, **46**, 435 (1992).
3. B. K. Kim and L. Y. Min, *J. Appl. Polym. Sci.*, **54**, 1809 (1994).
4. S. Ramesh and G. Radhakrishna, *Polym. Sci.*, **1**, 418 (1994).
5. C. K. Kim and B. K. Kim, *J. Appl. Polym. Sci.*, **43**, 2295 (1991).
6. K. Shinya, T. Tamaki, N. Shigeyoshi, and P. Nobuhiko, Jpn. Pat. JP 05,239,430 (1993).
7. M. Takeshi, Jpn. Pat. JP 0,431,425 (1992).
8. P. Markush, UK Pat. GB 2,104,085 (1983).
9. D. Dieterich, W. Keberle, and H. Witt, *Angew. Chem. Int. Ed.*, **9**, 40 (1970).
10. D. Dieterich, *Prog. Org. Coat.*, **9**, 281 (1970).
11. D. Dieterich, W. Keberle, and R. Wuest, *J. Oil Col. Chem. Assoc.*, **53**, 373 (1970).
12. S. A. Chen and W. C. Chan, *J. Polym. Sci. Part B Polym. Phys. Ed.*, **28**, **1499**, 1515 (1990).
13. S. L. Hsu, H. X. Xiao, H. H. Szmet, and K. C. Frisch, *J. Appl. Polym. Sci.*, **29**, 2467 (1984).
14. S. Saikumari and S. Rajduari, *J. Col. Soc.*, **24**(2), 19 (1985).
15. P. Markush, K. Noll, and D. Dieterich, Ger. Off. 2,651,505 (1978).

16. D. Dieterich, Br. Pat. 1,080,590 (1967).

17. H. Ohmura and T. Sakai, Ger. Off., 2,632,708 (1977).

18. J. S. Lee and B. K. Kim, *Prog. Org. Coat.*, **25(4)**, 311 (1995).

19. E. J. Malec and D. J. David, in *Analytical Chemistry of Polyurethane*, D. J. David and H. B. Staley, Eds., Wiley, New York, 1969.

20. G. Ortel, Ed., *Polyurethane Handbook,* Carl Hanser Verlag, Munich, 1985.

21. K. A. Kubitz, *Anal. Chem.*, **29**, 814 (1957).

22. R. W. Seymour, G. M. Estes, and S. L. Copper, *Macromolecules,* **3(5)**, 579 (1970).

23. R. K. Agrawal and L. T. Drzal, *J. Adhes. Sci. Tech.*, **9(10)**, 1381 (1995).

24. G. Spathis, M. Niaounakis, L. Apekis, P. Pissis, and C. Chritodoulides, *J. Appl. Polym. Sci.*, **54**, 831 (1994).

25. A. V. Dobrynin, R. H. Colby, and M. Rubenstein, *Macromolecules,* **28**, 1859 (1995).

26. R. W. Seymour and S. L. Cooper, *Macromolecules,* **6**, 48 (1973).

27. L. M. Leung and J. T. Kobestein, *Macromolecules,* **19**, 706 (1986).

28. J. T. Kobestein and T. P. Russel, *Macromolecules,* **19**, 714 (1986).

29. M. Fujimura, T. Hashimoto, and H. Kawi, *Macromolecules,* **14**, 1309 (1981).

30. K. Tadano, E. Hirasawa, H. Yamaoto, and S. Yano, *Macromolecules,* **22**, 226 (1989).

31. R. Y. M. Huang and Y. Wei, *J. Membr. Sci.*, **87**, 257 (1994).