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NOVEL FLUORINE-CONTAINING ANIONIC AQUEOUS POLYURETHANES

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ABSTRACT

Various amounts of fluorine-containing polyol (F-diol, MW = 3700) were introduced into the soft segment of anionic aqueous polyurethanes (PUs) to examine the effect of the F-diol on the properties of the anionic aqueous PUs. The hard segments in the anionic aqueous PUs consisted of 4,4′-methylene bis(cyclohexylisocyanate), dimethylolpropionic acid, and 1,4-cyclohexanediamine (cis/trans = 80/20). Both the mechanical and water resistance properties of the anionic aqueous PUs were improved after introducing small amounts of the F-diol in the soft segment of the aqueous PUs. This is due to the increased intermolecular forces and crystallinity as well as the hydrophobic characteristic of the F-diol. Thermal analysis of the F-diol modified anionic aqueous PUs by differential scanning calorimetry and dynamic mechanical analysis indicated that both intermolecular forces and crystallinity increased with increasing concentration of the F-diol. However, both the increased intermolecular forces and crystallinity could have an adverse effect on the interface adhesion.

INTRODUCTION

Aqueous polyurethanes (PUs) have been known for a long time. They are of increasing interest for coatings and adhesive applications due to environmental and safety restrictions and the cost of solvent recovery. Generally, aqueous PUs are prepared with the aid of suitable dispersants or from PU ionomers which contain either negative charge groups, such as carboxylic or sulfonic acid groups (anionomers), or positive charge groups, such as quaternary ammonium groups (cationomers), as shown in Scheme 1.

In general, dispersions of PU anionomers are prepared by introducing dimethylolpropionic acid (DMPA) into the prepolymer backbone, and after neutralization, dispersing as well as chain extending the prepolymer in water to yield aqueous polyurethane-urea dispersions.

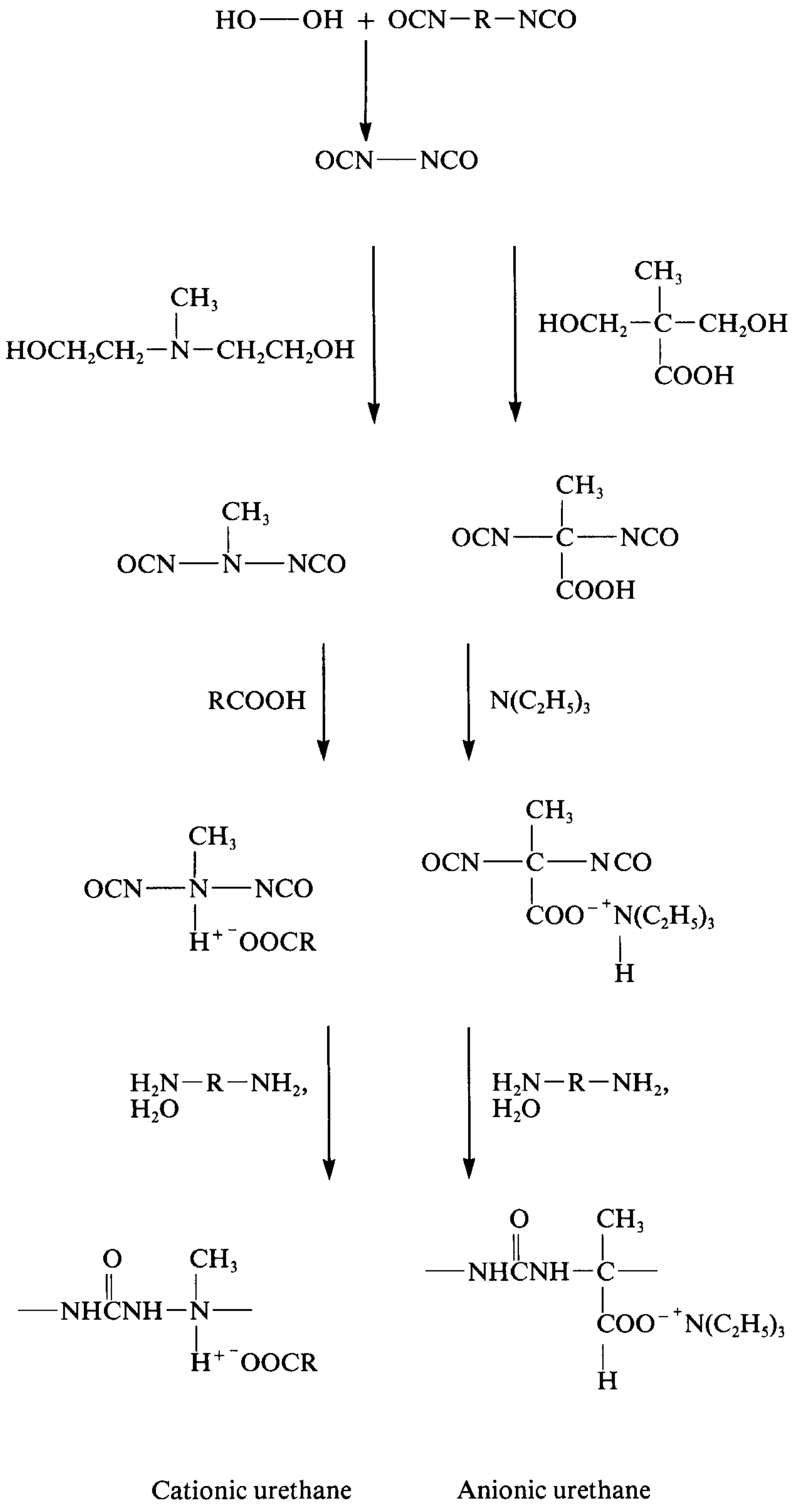
A great number of aqueous PUs have been developed, and more than 800 patents have been issued in the about forty years of their existence. Dieterich et al. [1-17] pioneered this field and made very important contributions. Rosthauser and Nachtkamp [18] listed the number of articles and patents in the field of aqueous PUs or PU dispersions regarding preparation, modification, and applications. However, no research has been reported regarding aqueous PU dispersions based on a fluorine-containing polyol which has a molecular weight of 3460 and the following structure:

$$H[-OCH_2(CF_2)_3CH_2OCF_2CHFOCF_2CF(CF_3)OCF_2CF_2CH_2O-]_nH$$

The present paper examines the effects of fluorine-containing polyol (supplied by E. I. du Pont de Nemours & Co., Inc.) on the properties of aqueous PUs for the first time.

EXPERIMENTAL

All raw materials are shown in Table 1. 4,4′-Methylene bis(cyclohexylisocyanate) ($H_{12}MDI$), fluorine-containing diol (F-diol), and DMPA as well as 1,4-cyclohexanediamine (CHDA) were used as received without further purification.


HO—OH + OCN—R—NCO
OCN—NCO
RCOOH
N(C2H5)3
H2N—R—NH2, H2O
H2N—R—NH2, H2O
Cationic urethane
Anionic urethane

SCHEME 1.

TABLE 1. Raw Materials

Designation	Chemical name	Supplier
$H_{12}MDI$	4,4′-Methylene bis(cyclohexylisocyanate)	Mobay Chemical Co.
CHDA	Cyclohexanediamine (cis/trans = 80/20)	DuPont
PTMEG-2000	Poly(oxytetramethylene) glycol (MW = 2000, $f = 2.0$)	DuPont
F-diol	Fluorine-containing glycol (MW = 3460, $f = 2.0$)	DuPont
DMPA	Dimethylolpropionic acid	IMC Corp.
TEA	Triethylamine	Eastman Chemical Co.
NMP	*N*-Methyl-2-pyrrolidone	BASF Co.

Triethylamine (TEA) and *N*-methyl-2-pyrrolidone (NMP) were dried by storing over 4 Å molecular sieves. Poly(oxytetramethylene) glycol (PTMEG-2000) was degassed at 70°C under vacuum overnight for removal of moisture before use.

The aqueous anionic PUs were prepared by the prepolymer method. PTMEG-2000 (prior to melting), F-diol, DMPA, $H_{12}MDI$, and 2% NMP (based on the total weight of the prepolymer) were charged, at a 1.4 equivalent ratio of NCO/OH and at 1.5 equivalent ratio of DMPA/(PTMEG + F-diol), into a reaction kettle which was equipped with a thermometer, stirrer, inlet and outlet of dry nitrogen, and a heating jacket. The reactants were heated by maintaining the reaction temperature at 80–85°C until the theoretical NCO value was reached as determined by the di-*n*-butylamine titration method. After the NCO content reached the theoretical value, neutralization was carried out by adding TEA at 40–50°C. Chain extension and dispersion were carried out at room temperature. The sample formulations are listed in Table 2.

Sample films were made by casting the aqueous PUs in a glass mold coated with a silicone release agent and dried at room temperature overnight, and then in an oven at 110°C for 4 hours. The stress-strain properties, peel strength (fabric/steel), and lap shear (steel/steel) were measured (ASTM D3196, D2630, and D1002) by means of an Instron-Tensile Tester at 5.0, 12, and 0.1 in./min of crosshead speeds, respectively. The water absorption was measured by measuring the weight

TABLE 2. Composition of Aqueous PUs Based on Various Amounts of F-diol

Designation	PTMEG-2000/ F-diol	NCO/OH	DMPA/ polyols	Salt groups, %	Hard segments, %
HTF-0	100/0	1.4	1.5	1.98	40.7
HTF-2	100/2	1.4	1.5	1.98	40.6
HTF-5	100.5	1.4	1.5	1.97	40.2
HTF-10	100/10	1.4	1.5	1.95	39.7

difference of the samples before and after immersing in deionized water at room temperature.

Differential scanning calorimetry (DSC) measurements were carried out at a 20°C/min heating rate by using a DuPont 910 differential scanning calorimeter module in a DuPont 9900 thermal analysis system. Temperature and enthalpy were calibrated by using indium as the standard. A thermomechanical analyzer (TMA) (DuPont 2100 Thermomechanical analyzer) was used to measure the softening temperatures, and the penetration mode was used for the measurements. The tray weight was 10 g and the heating rate was 10°C/min. A DuPont 983 dynamic mechanical analyzer (DMA) was used to measure the storage modulus (E'), loss modulus (E''), and tan δ at a 1-Hz frequency and a 5°C/min heating rate.

RESULTS AND DISCUSSIONS

The salt groups formed by neutralizing the carboxylic acid groups with tertiary amine groups impart to the PU a unique dispersion property in water. This is due to the fact that the salt groups play an important surfactant role. The viscosities of the dispersions, solids content, and pH values are listed in Table 3. The dispersions listed in Table 3 were kept at the same solids content, and the viscosities were measured at 25°C. The results indicate that there is a dramatic increase in the viscosity after introducing an F-diol in aqueous PUs, and it increases with increasing amounts of the F-diol. Sample HTF-5 shows a lower viscosity than sample HTF-2, presumably due to the low pH value. For aqueous anionic PUs, the viscosity increased with increasing pH value. The high viscosity resulting from the fluorine-containing aqueous PU could be due to the hydrophobic characteristic of the F-diol.

The results of the mechanical properties are shown in Table 4 and Fig. 1. Generally, both modulus and tensile strength of the polyurethanes depend upon the structure and concentration of the hard segments, the intermolecular forces, as well as the type of the soft segments. In the case of ionic polymers, they also depend on the type and concentration of the ionic groups. In order to investigate the influence of the F-diol on the properties of the aqueous PUs, all the polymers were prepared based on constant NCO/OH and DMPA/polyols ratios. Various amounts of F-diol were introduced into the polymer backbone. The distribution concentration of both the hard segments and salt groups decreased slightly with increasing F-diol content,

TABLE 3. Dispersion Properties of Aqueous PUs Containing Various Amounts of F-diol

Sample	HTF-0	HTF-2	HTF-5	HTF-10
Viscosity, cP[a]	77	1080	870	1920
pH	7.6	7.8	7.7	7.9
Solids, %	30	30	30	30

[a] Viscosity was measured by a Brookfield Viscometer (RVF) with a No. 1 spindel at 20 rpm and 25°C.

TABLE 4. Mechanical Properties of Aqueous PUs with Various Amounts of F-diol

Sample	HTF-0	HTF-2	HTF-5	HTF-10
Tensile strength, psi (MPa)	4745 (32.7)	5708 (39.3)	5997 (41.3)	6102 (42.1)
M_{100}, psi (MPa)	874 (6.02)	1054 (7.26)	1073 (7.39)	1084 (7.47)
M_{300}, psi (MPa)	1358 (.36)	1593 (10.98)	1690 (1.64)	1696 (11.69)
Elongation, %	934	1032	945	923
Hardness, Shore A	82	84	86	87
Peel strength, in·lb	8.0	6.5	5.5	5.5
Lap shear, psi (MPa)	170 (1.17)	180 (1.24)	157 (1.08)	121 (0.83)
Gardner Impact strength (−30°C), lb·in.	>160	>160	>160	>160

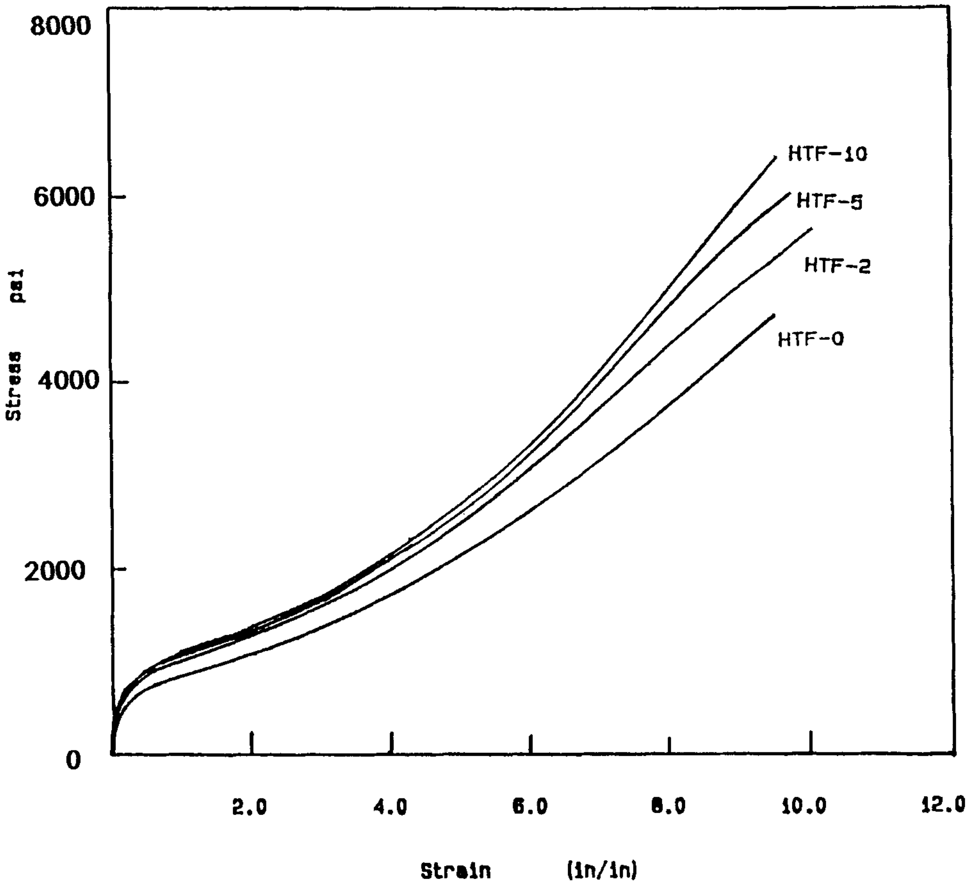


FIG. 1. Stress-strain properties of aqueous PUs films based on various amounts of F-diol.

as compared to that without any F-diol, because of the relatively high molecular weight of the F-diol (3700). The concentration of hard segments decreased from 40.7% in HTF-0 (without F-diol) to 39.7% in HTF-10 (with 10% of F-diol) as shown in Table 2, and the salt group concentrations also decreased from 1.98 in HTF-0 to 1.95 in HTF-10. Both modulus and tensile strength of the aqueous PU films increased with increasing amounts of F-diol. This implies that the F-diol plays an important role in the improvement of mechanical properties, presumably because of the intermolecular forces between the fluorine and other groups. As shown in Table 4, both peel strength and lap shear strength decreased and the hardness increased with increasing amounts of F-diol. This is presumably due to the fact that the intermolecular forces and hydrogen bonding resulting in the cohesive energy density (CED) of aqueous PUs increase with increasing amounts of F-diol [19-21]. As a result, this affects the interfacial adhesive strength between the PUs and the substrates. The low surface active energy or surface tension of fluorine-containing polymers could also affect the interfacial adhesive strength. However, the toughness or flexibility of aqueous PUs did not change, as shown in the results of elongation and impact strength. In particular, the impact strength of aqueous PU-based coatings at low temperature (−30°C) exhibited very good results (see Table 4).

The water resistance of aqueous PU-based coatings and adhesives is a very important property in different applications. As shown in Fig. 2, samples were saturated with water by 10 days immersion. The water absorption of aqueous PUs obviously decreased with increasing F-diol concentration. The mechanical properties of the sample films saturated by water are shown in Table 5. The results indicate that samples containing F-diol exhibited better retention of tensile strength. The better water resistance is presumably due to the hydrophobic characteristic of the F-diol compared to the polyether diol.

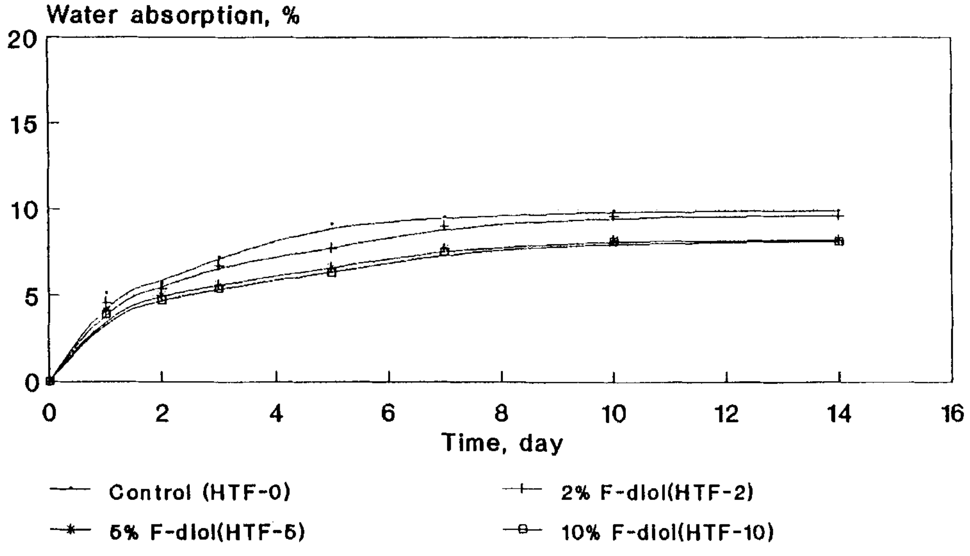


FIG. 2. Effect of various amounts of F-diol on the water absorption of aqueous PUs at room temperature.

TABLE 5. Effect of Water Immersion on the Properties of Aqueous PUs With and Without F-diol[a]

Sample	HTF-0	HTF-2	HTF-5	HTF-10
Tensile strength, psi (MPa)	2362 (16.27)	3033 (20.89)	3297 (22.72)	3376 (23.26)
M_{100}, psi (MPa)	396 (2.73)	492 (3.39)	547 (3.77)	594 (4.09)
M_{300}, psi (MPa)	587 (4.04)	696 (4.79	746 (5.14)	796 (5.48)
Elongation, %	1334	1314	1237	1195

[a] Room temperature × 10 days.

The glass transition temperatures of the soft segments and melting temperatures of the hard segments as well as the enthalpies are given in Table 6 and Figs. 3 and 4. As shown in Table 6 and Fig. 3, the melting temperature (T_m), softening temperature, and enthalpy of aqueous PUs increased with increasing amounts of the F-diol, presumably due to the increasing intermolecular forces. The results in Fig. 4 (by TMA) exhibit an increase in expansion with increasing F-diol concentration before the temperature reaches the softening point of the sample, and the curves shift upward. However, it is very interesting to observe that the glass transition temperature does not show any change except for sample HTF-5, which could be a small error in the measurement. There are some factors responsible for lowering the glass transition temperatures such as the chain length of the soft segments and a side chain in the backbone, the urea group in the polymer backbone, the ionic interaction in the hard segments, and the pendant ionic groups. The influence of the side chain length on the glass transition temperature of ionomers has been reported [22, 23]. Endothermic peaks (see Fig. 3) were observed in all samples, and they are considered to be the dissociation of hard domains. The increase in the endothermic enthalpy could be due to the destruction of intermolecular forces and the melting of the crystalline phase in the hard domains. The enthalpies summarized in Table 6 imply that the degree of crystallinity in the hard domains and the intermolecular forces increased with increasing amounts of the F-diol. This is in agreement with the TMA results. It is known that the hard domains can act as physical crosslinks or reinforcement in the PUs to enhance the mechanical properties. As shown in Fig. 3, the endothermic peak shifts toward higher temperatures with increasing F-diol concentration, which implies increasing intermolecular forces and crystallinity.

TABLE 6. Thermomechanical Properties of Aqueous PU Films Containing Various Amounts of F-diol

Sample	T_g, °C	T_m, °C	ΔH, J/g	T_s, °C
HT-0	−74	184	2.3	159
HT-2	−74	181	2.5	162
HT-5	−73	205	2.9	164
HT-10	−74	205	3.6	166

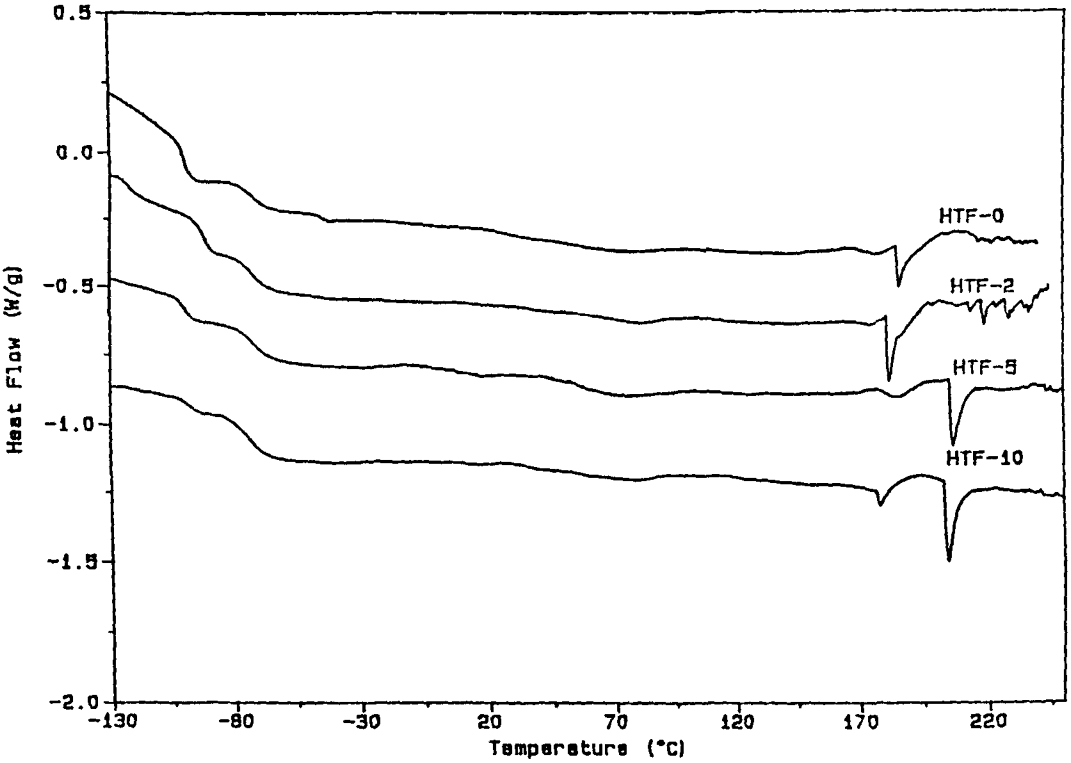


FIG. 3. DSC results of aqueous PUs based on various amounts of F-diol.

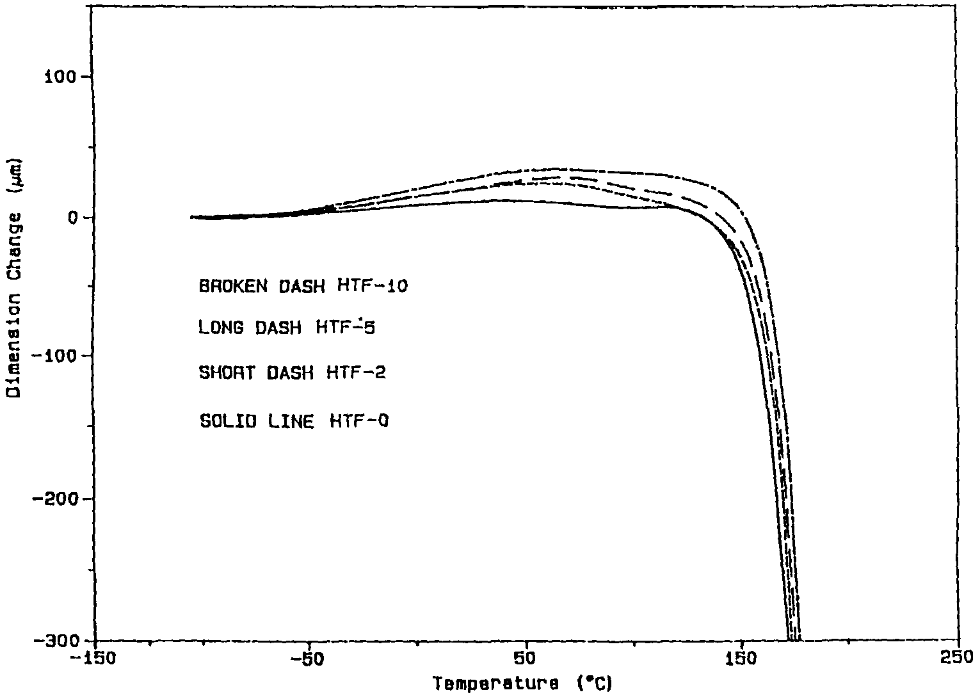


FIG. 4. TMA results of aqueous PUs based on various amounts of F-diol.

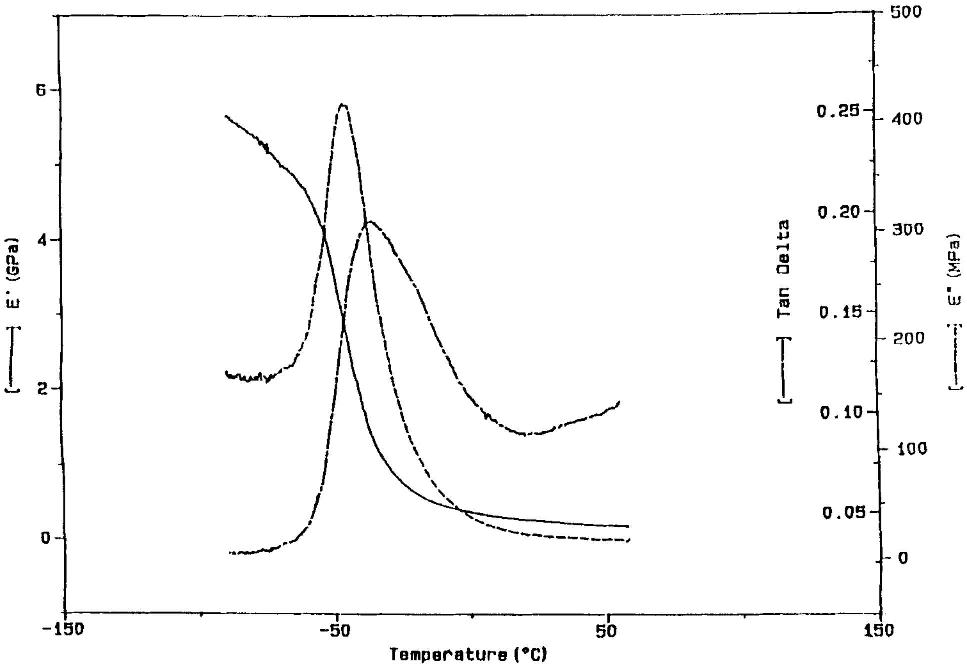


FIG. 5. DMA results of aqueous PU based on HTF-2.

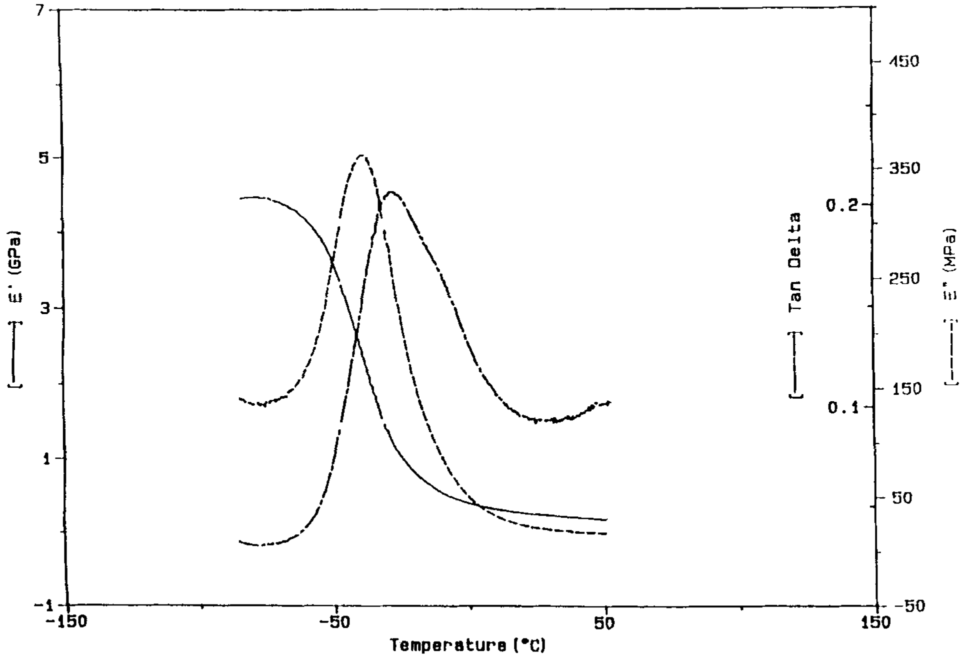


FIG. 6. DMA results of aqueous PU based on HTF-5.

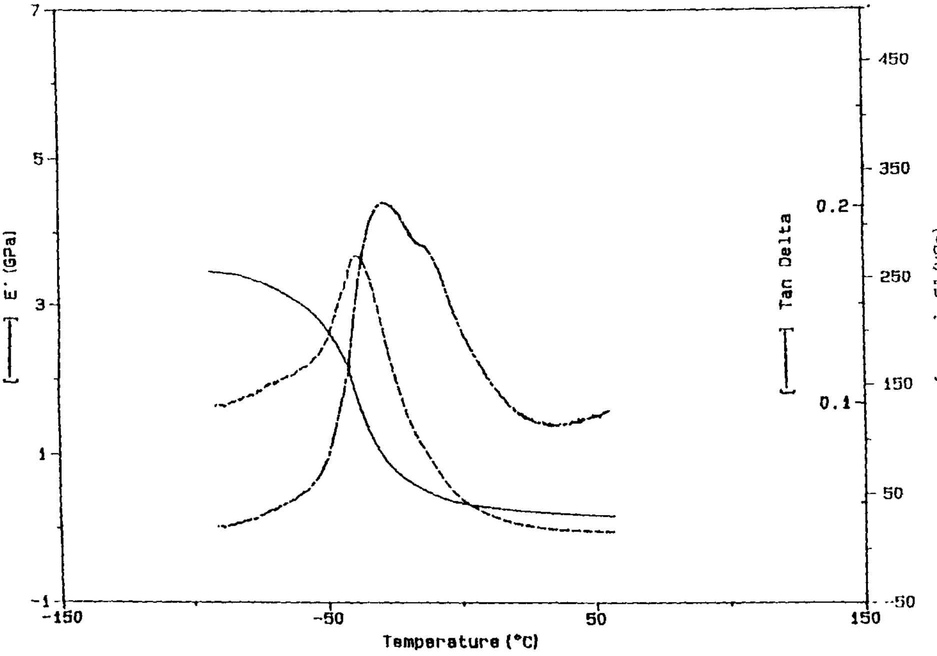


FIG. 7. DMA results of aqueous PU based on HTF-10.

Three F-diol-based aqueous PU films were investigated by using a DuPont DMA (Dynamic Mechanical Analyzer) to examine their morphology. As shown in Figs. 5–7, both peak temperatures of tan δ (tangent loss angle) and E'' (loss modulus) shifted slightly toward high temperatures with increasing F-diol concentration. The double peaks of tan δ curves are observed in both Figs. 6 and 7 with increasing amounts of F-diol in the soft segment of anionic PUs. This could be due to the presence of triphases in the F-diol-based anionic PUs. The structure and polarity of F-diol will affect the phase mixing between PTMG and F-diol in the soft segment as well as the phase mixing between hard and soft segments in the F-diol-based anionic PUs. The decrease in the loss modulus E'' with increasing F-diol concentration also indicated increased intermolecular forces and crystallinity.

CONCLUSION

Mechanical and water resistance properties of anionic aqueous polyurethanes based on PTMEG-2000 and CHDA as a chain extender were improved by introducing F-diol (MW = 3700) into the soft segment of polyurethanes. Thermal analysis of the F-diol-modified anionic aqueous polyurethanes by DSC and DMA indicated that the increased intermolecular forces and crystallinity, as well as the hydrophobic character of anionic aqueous polyurethanes, are due to using F-diol.

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