

Anionomeric Waterborne Poly(urethane semicarbazide) Dispersions and Their Adhesive Properties

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ABSTRACT: Aqueous polyurethane dispersions were prepared from isocyanate-terminated ionic polyurethane prepolymers by chain extension with dihydrazides. These water-borne dispersions had excellent adhesive properties and were used to bond leather and canvas. The base polymers were varied with respect to (1) the ionic content with the same chain extender and (2) the nature of the chain extender with the ionic content kept constant. Studies on the particle size and viscosity revealed that the ionic content had an influence on the aforementioned properties: the particle size decreased and the viscosity increased with increasing ionic content. The polarity of the films cast from the dispersions were determined with contact-angle measurements: hydrophilic character was exhibited by all the compositions. X-ray studies revealed that the increase in the ionic content led to increasing intensities of the dif-

fraction peaks due to increased secondary forces of bonding. The tensile strength measurements showed that the films were highly elastomeric and had good mechanical strength, which varied with the composition. A shear strength and peel strength analysis of specimens obtained through the bonding of leather to leather, leather to canvas, and canvas to canvas revealed that the waterborne dispersions were excellent adhesives for bonding leather surfaces. Thus, a very efficient, ecofriendly waterborne dispersion of polyurethane that could find applications in bonding leather in the footwear industry was prepared successfully. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2833–2840, 2008

Key words: adhesion; dispersions; ionomers; particle size distribution; X-ray

INTRODUCTION

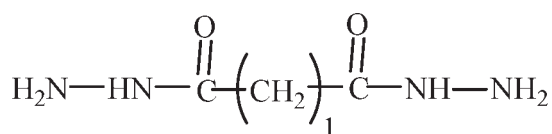
The evaporation of volatile organic compounds during the formulation of coatings, inks, and paints causes a wide variety of problems. To reduce or eliminate the organic solvents in this process, the solvents should be partially or completely replaced with environmentally friendly solvents such as water.^{1,2} Polyurethanes (PUs) are widely used in coatings and adhesives, and aqueous PU dispersions prepared with low levels of organic solvents see wider usage.^{3–6} Conventional PUs are insoluble in water, and to be dispersible, they should contain ionic and/or nonionic segments in their structure. The stabilizing effect of the ionic site is due to the formation of tiny spheres that contain a core of an aggregate hydrophobic segment and a boundary layer carrying ionic groups, which result in a stable dispersion in water.

PUs in general exhibit good adhesive properties because of their elastomeric properties, which are enhanced by soft segments of polyol and by the polar character of urethane groups. The applications of

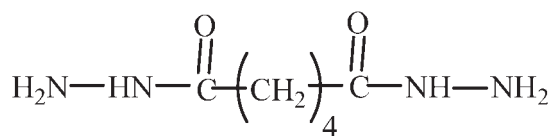
PU adhesives include substrates such as glass, wood, leather, plastics, rubber, metals, concrete, and ceramic.⁷ Adhesive bonding depends on adhesive selection, joint design, durability, bond making, and applications. PU adhesives are generally used for good, durable load-bearing joints with a shear strength of at least 15 MPa. Aqueous PU dispersions are efficient alternatives to solvent-based adhesives, a class of nonreactive adhesives that are commonly used in the footwear industry to bond uppers to soles. The viscosity of water-based adhesives is usually lower, and the solid content is higher, in comparison with solvent-based adhesives. There are already ionic water-borne PU adhesives, and the influence of chain extenders on the physical properties of dispersions, including their films, has been studied by several groups.^{8–11}

In the literature, chain extenders such as hydrazine hydrate, ethylene diamine, and hexamethylene diamine have been used to prepare PU dispersions exhibiting adhesive properties.^{11,12–15} In this investigation, some dihydrazides of various backbone natures and chain lengths were used as chain extenders to prepare anionomeric poly(urethane semicarbazide) dispersions with adhesive properties. Earlier, we reported the preparation of such poly(urethane semicarbazide)s with good film-forming properties that were basically nonionic in nature.^{16–19}

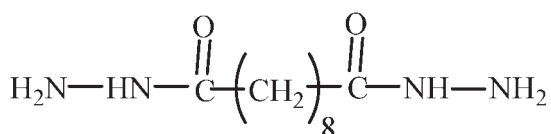
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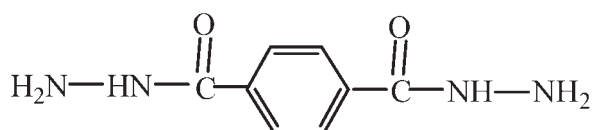
Malonic dihydrazide



adipoyl dihydrazide



sebacoyl dihydrazide



Terephthalic dihydrazide

Scheme 1

The objective of this study was to prepare different aqueous PU ionomer dispersions for the purpose of developing adhesives for the footwear industry. The structure–property relationship of dispersions of various compositions and their dispersion-cast films was studied extensively with particle size measurements, viscosity determination, X-ray diffraction studies, and static mechanical analysis. The influence of the ionic content and nature of the chain-extending dihydrazide on the dispersion and film properties of the PU ionomers were investigated.

EXPERIMENTAL

Reagents

Poly(propylene glycol) (PPG) 1000 (Manali Petrochemicals, Chennai, India), isophorone diisocyanate (IPDI) (Aldrich Chemie GmbH, Steinheim, Germany), and dimethylol propionic acid (DMPA, Milwaukee, MI) were used as received. Hydrazine hydrate (S.D. Fine Chemicals, Mumbai, India) and triethyl amine (TEA; Rankem, Delhi, India) were also used as received. The dihydrazides used as chain extenders were synthesized from the corresponding diesters by their reaction with hydrazine hydrate. The diesters were all procured from S.D. Fine Chemicals, except for diethyl sebacate, which was prepared from the diacid by esterification.

Preparation of the PU dispersions

Synthesis of the chain extender

The chain extenders (dihydrazides) were prepared from the corresponding diesters by their reaction with hydrazine hydrate in methanol. The procedure is available in the literature.²⁰ Variations were conducted with respect to the nature of the backbone (aliphatic chains of various chain lengths and aromatic rings) to study the influence of the chain extender on the solution and solid-state properties of the dispersion and dispersion-cast films. Four different chain extenders—malonic dihydrazide, adipoyl dihydrazide, sebacoyl dihydrazide, and terephthalic dihydrazide—were prepared. In one formulation, hydrazine hydrate was used as a chain extender for comparative studies. The structures of the chain extenders (dihydrazides) are shown in Scheme 1.

Prepolymer preparation and dispersion

The PU dispersions were prepared by a prepolymer process. The macroglycol (PPG 1000) was mixed

TABLE I
Sample Codes, Compositions, and Ionic Contents of the PUS Dispersions

Sample code	Molar ratio				
	Macroglycol (PPG 1000)	Isocyanate (IPDI)	Ionizer (DMPA)	Chain extender dihydrazide	Ionic content (%)
PUS-HH	1.0	2.5	0.55	HH-0.95	4.5
PUS-MDH	1.0	2.5	0.70	MDH-0.80	5.6
PUS-ADH1	1.0	2.5	0.50	ADH-1.00	4.1
PUS-ADH2	1.0	2.5	0.55	ADH-0.95	4.5
PUS-ADH3	1.0	2.5	0.60	ADH-0.90	4.9
PUS-ADH4	1.0	2.5	0.70	ADH-0.80	5.6
PUS-SBDH	1.0	2.5	0.70	SBDH-0.80	5.6
PUS-TDH	1.0	2.5	0.70	TDH-0.80	5.6

ADH, adipoyl dihydrazide; HH, hydrazine hydrate; MDH, malonic dihydrazide; PUS, poly(urethane semicarbazide); SBDH, sebacoyl dihydrazide; TDH, terephthaloyl dihydrazide.

with DMPA and IPDI in stoichiometric amounts (the ratios are listed in Table I). Dibutyltin dilaurate (0.01 wt % of isocyanate) was added, and the reaction mixture was heated at 120°C for 2 h. When the desired NCO content was reached, the prepolymer, obtained as a very viscous mass, was cooled and dissolved in a minimum amount of acetone. TEA (20% excess of the amount sufficient to ionize DMPA completely) was mixed with deionized water, and the mixture was added dropwise at a rate of 0.1 mL/min to the prepolymer stirred at a speed of 1000 rpm. The amount of water added was calculated on the basis of the solid content desired. When the addition of water was completed, the stirring speed was reduced, and the dihydrazide was added portionwise to the prepolymer dispersed in water. The chain-extension step was carried out at room temperature for about 4–5 h until the reaction was complete. The dispersions were transferred to air-tight containers to avoid skin formation. One composition was prepared with hydrazine hydrate as a chain extender for comparison. Scheme 2 presents the steps involved in the preparation of waterborne dispersions.

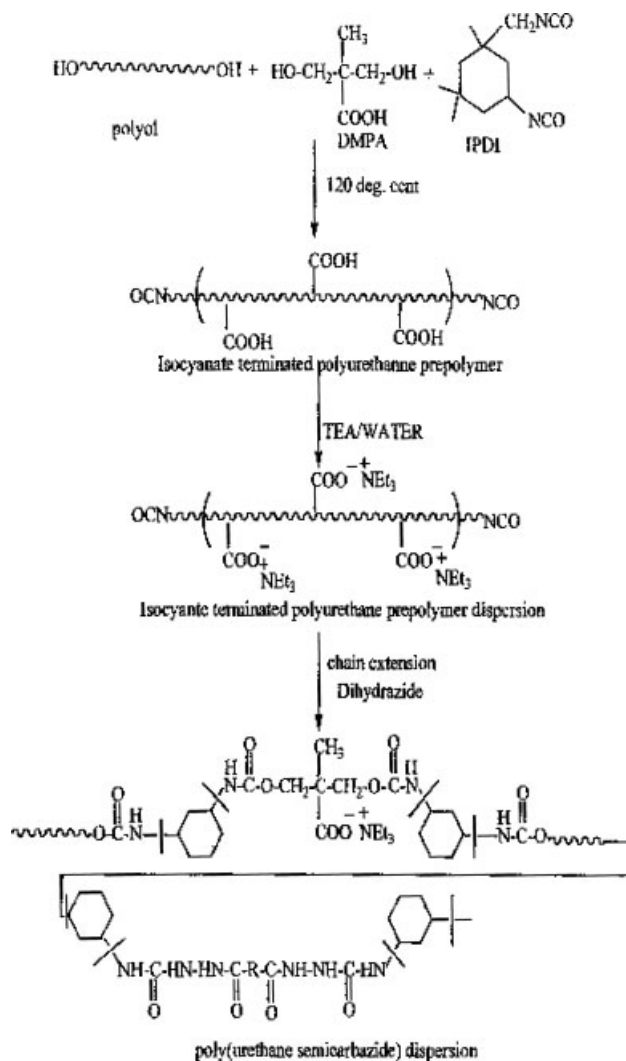
Table I presents the compositions of the dispersions and their ionic contents. All the ionomers had a hard segment content of ~ 40%. Compositions with NCO/OH ratios less than 2.5 did not form films, whereas those with ionic contents lower than 4% were not dispersible. A minimum ionic content is essential for the formation of a stable dispersion. The dispersibility is governed by the hydrophilicity of the chains and hydration of the neutralizing cations. Only those compositions that could be dispersed in water are listed in the table.

Preparation of the films

The water-borne dispersions with 20% solid content were cast into films by measured amounts of the dispersions being poured into polytetrafluoroethylene molds and allowed to dry at room temperature for 2–3 days. They were then dried in a vacuum oven at 50°C for 24 h. The films thus obtained were stored in a vacuum desiccator before testing.

Characterization techniques

The $^1\text{H-NMR}$ spectrum was recorded with a Gemini (Fallanden, Switzerland) 200 spectrometer with CDCl_3 as the solvent and tetramethylsilane as the internal standard. The IR spectrum was recorded with a PerkinElmer (Bucks, UK) Spectrum BX Fourier transform infrared system in the $4000\text{--}400\text{-cm}^{-1}$ range. The viscosity of the dispersions was determined with an Anton Paar Physica MCR 51 rheometer (Graz, Australia) at a shear rate of 50 s^{-1} at 30°C.



Scheme 2 Steps involved in the preparation of waterborne poly(urethane semicarbazide) dispersions by the prepolymer process.

A Malvern zeta sizer (Malvern Instruments, Ltd., Worcs, UK) was used to determine the particle size of the dispersions diluted to 0.1%. The pH of the dispersions was determined with a pH meter manufactured by Global Instruments (Hyderabad, India). X-ray diffraction studies were performed with wide-angle X-ray diffraction spectra of powder samples obtained with a Bruker (Karlsruhe, Germany) D-8 Advance X-ray diffractometer with $\text{Cu K}\alpha$ radiation with a wavelength of 1.54×10^{-10} m and a continuous scanning speed of $0.007^\circ/\text{min}$. The static mechanical properties of the samples of the cast films were measured with the help of an Autograph 10kNG universal testing machine (Shimadzu, Kyoto, Japan) with a load cell of 10 kN at a crosshead speed of 10 mm/min. The gauge length of the specimens was fixed at 50 mm. T-peel tests were carried out on adhesive joints produced between two leather strips. An adhesive solution was applied to each strip to be

joined; the strips were placed in contact and left to dry for 24 h, during which the evaporation of the solvent allowed the formation of an adhesive layer. The adhesive joints were kept at $23 \pm 2^\circ\text{C}$ and 50% relative humidity for 72 h before the T-peel test was carried out. The peel rate used was 10 mm/min, and the obtained values were the averages of at least three replicates. For the determination of the lap shear strength, two specimens (leather–leather, leather–canvas, and canvas–canvas) were bonded together (the typical overlap was about $1'' \times 1''$) with an adhesive and cured as specified for the peel test. Contact-angle measurements were performed to determine the hydrophilicity of the films with a contact-angle measuring instrument (Kruss GmbH, Hamburg, Germany) by the sessile drop method, which involves placing a drop of water with a microsyringe on a dry film and then measuring the contact angle at the solid–liquid interface.

RESULTS AND DISCUSSION

Structural confirmation by $^1\text{H-NMR}$ and IR spectroscopy

The dispersion-cast film was dissolved in chloroform, and the solution was coated onto KBr discs to form a thin coating. The pellets were dried in a vacuum desiccator, and the IR spectrum was recorded after complete evaporation of the solvent. To confirm the incorporation of the dihydrazide during the chain-extension step, the prepolymer (obtained by the reaction of the polyol, DMPA, and IPDI) was subjected to IR analysis. The spectra of the dispersion-cast film (ADH2) and the corresponding prepolymer are shown in Figure 1(a,b). Although the prepolymer spectrum exhibited absorption at 2266 cm^{-1} corresponding to the NCO stretching vibration, this absorption band was absent in the IR spectrum of the polymer, and this proved that the dihydrazide added during the chain-extension step reacted with the NCO group completely. Moreover, the bands at 3330 and 1540 cm^{-1} in Figure 1(b), corresponding to the NH stretching and bending vibrations, are further proof of the incorporation of the dihydrazide moiety. The bands around 2900 cm^{-1} are due to the CH stretching vibration of aliphatic CH_2 groups, whereas those around 1710 cm^{-1} reflect the $\text{C}=\text{O}$ stretching vibration of the urethane and semicarbazide groups. The absorptions around 3065 cm^{-1} and those around $1460\text{--}1540\text{ cm}^{-1}$ are due to the NH stretching and bending vibrations of the amine salt ($-\text{NH}_3^+$). The strong band around 1108 cm^{-1} corresponds to the $-\text{C}-\text{O}-$ stretching (asymmetric), and that around 1022 cm^{-1} is due to the symmetrical $-\text{C}-\text{O}-\text{C}-$ stretching vibration.

A PU ionomer based on sebacoyl dihydrazide was dissolved in deuterated chloroform, and the $^1\text{H-}$

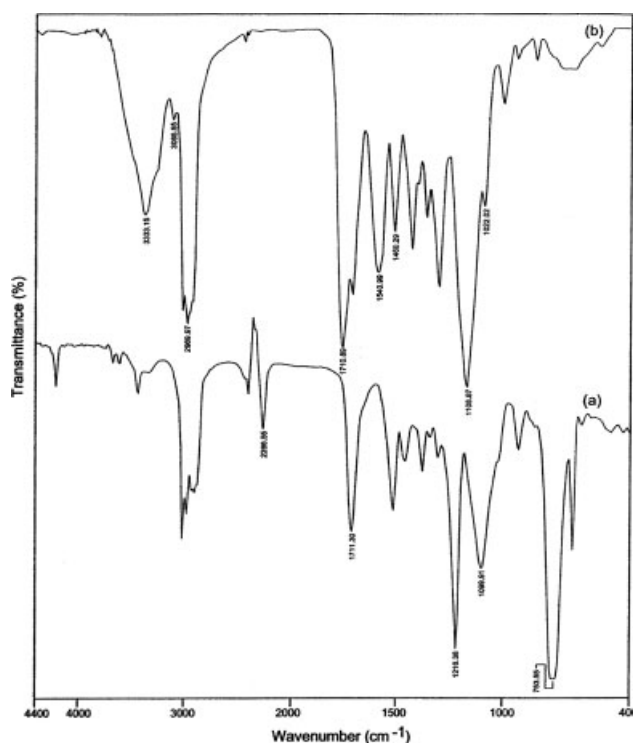


Figure 1 IR spectra of (a) PUS-ADH2 film (b) NCO terminated prepolymer coated on KBr pellets.

NMR spectrum was recorded. The $^1\text{H-NMR}$ spectrum is shown in Figure 2 along with assignments of the various protons in the polymer chain. The signals in the $0.6\text{--}1.3\text{ ppm}$ range are due to the CH_3 groups of the chain extender and PPG moieties, whereas the signals around 3.5 ppm represent the $-\text{OCH}_2-$ groups of urethane and semicarbazide (DMPA and dihydrazide) moieties. The broad peaks (humps) around 4.1 and 4.8 ppm correspond to the $-\text{NH}$ groups of the urethane and semicarbazide linkages. The multiplet in the $2.7\text{--}3.0\text{ ppm}$ range corresponds to the CH_2 groups of the counterions, and signals of the CH_3 groups of counterions merge with those of the CH_3 groups of PPG.

Dispersion properties

The pH of the dispersions was found to be in the range of $7.5\text{--}8.4$, which is slightly basic because of the excess TEA used during the neutralization of COOH groups. The storage stability of the dispersions was good because there was no precipitation of the polymer or yellowing of the dispersions when they were stored over a long period of time. Dispersions were obtained in a very finely divided form, and they had a solution-like appearance. The stability of the dispersions was further substantiated by the particle size distribution, which remained unchanged even after prolonged storage. The solid content was determined as follows: weighed quantities of the dispersion were placed in Petri dishes,

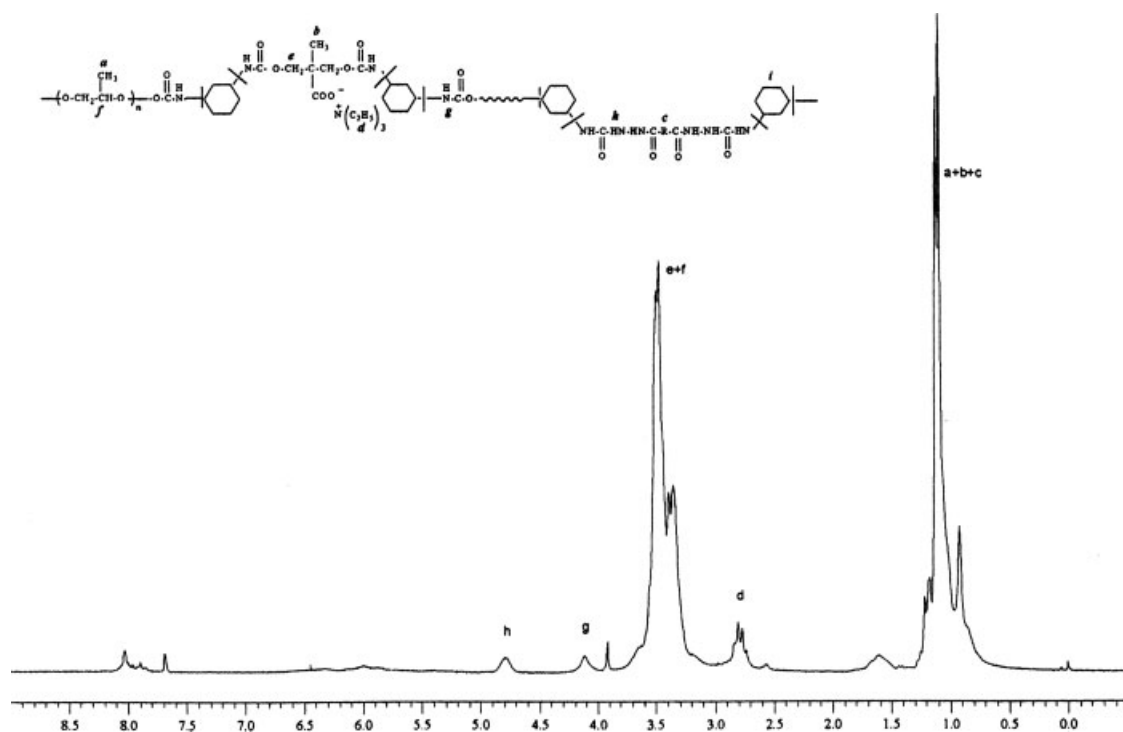


Figure 2 $^1\text{H-NMR}$ spectrum of PUS-SBDH recorded in CDCl_3 .

they were dried in the oven at 50°C for about 3–4 days, and then the dry weight was taken. The solid content was around 20%.

Particle size and viscosity

The particle size and viscosity of PU dispersions depend on many factors, such as the type of isocyanate, polyol, ionic content, degree of neutralization, and crosslink density (in the case of crosslinked systems). In this study, 100% neutralization was achieved with an equimolar amount of TEA (based on the DMPA content). Hence, the amount of the ionizer, that is, DMPA, directly corresponded to the ionic content of the dispersions. Variations were conducted with respect to the ionic content (for a fixed NCO/OH ratio) in the case of compositions containing various amounts of the same chain extender, namely, adipoyl dihydrazide. In all other cases, the nature of the chain extender was changed, with the ionic content and NCO/OH ratio fixed at 5.6 and 2.5, respectively. Because the shear rate during the dispersion, the nature and molecular weight of the macroglycol, the isocyanate, and the neutralization percentage were kept constant, the variations in the particle size and viscosity were influenced by the ionic content in the first case and by the nature of the chain extender in the second case. The particle

size, polydispersity, and viscosity of the dispersions are listed in Table II.

Table II shows that for the dispersions prepared with adipoyl dihydrazide as the chain extender, when the ionic content increased, the particle size decreased, whereas the viscosity increased. The increase in the viscosity was mainly due to the fact that with a reduction in the particle size, the number of particles increased, and this led to an increase in the viscosity. The width of the particle size distribution (i.e., the polydispersity) was in the range of 0.13–0.60, and this indicated that the particles were moderately polydisperse. A particle size distribution graph of PUS-ADH3 is given in Figure 3. Again, when the nature of the chain extender was varied, the particle size was affected. Chain extenders of higher chain lengths led to dispersions with lower particle sizes and higher viscosities. Chain flexibility affects particle size reduction because flexible particles are more deformable in a shear field, so during phase inversion, the dispersed phase can more easily be broken into smaller particles.²¹ Generally, smaller particles are preferred when deep penetration of a dispersion into a substrate is an essential step, such as the case of adhesive applications to substrates including paper, wood, leather, and textiles. In this investigation, the PU dispersions were used to bond leather, a permeable substrate. The smaller particle size aided in the penetration process, whereas the

TABLE II
Properties of Dispersions and Dispersion-Cast Films and Bond Strengths of Joints

Sample code	Particle size (nm)	Viscosity (cPs)	Contact angle	Dispersion-cast films		Lap shear strength (N/mm ²)		Leather-leather peel strength (N/linear inch)
				Tensile strength (N/mm ²)	Elongation (%)	Leather-leather	Leather-canvas	
PUS-HH	87.9	21.8	34.0	0.60	>1000	0.453	0.423	10.9
PUS-MDH	26.1	11.9	35.0	0.70	>1000	0.918	0.530	20.5
PUS-ADH1	218	9.5	24.0	2.79	512	0.707	0.170	20.2
PUS-ADH2	217	14.8	36.5	1.03	300	0.505	0.479	9.7
PUS-ADH3	26.0	17.0	38.5	3.03	216	0.652	— ^a	20.7
PUS-ADH4	27.8	32.0	37.0	1.39	202	0.688	— ^a	1.4
PUS-SBDH	30.6	13.8	35.0	1.71	>1000	0.445	0.458	11.0
PUS-TDH	42.4	90.8	31.0	0.64	>1000	0.272	0.283	4.1

ADH, adipoyl dihydrazide; HH, hydrazine hydrate; MDH, malonic dihydrazide; PUS, poly(urethane semicarbazide); SBDH, sebacyl dihydrazide; TDH, terephthaloyl dihydrazide.

^a Cohesive failure.

lower viscosity helped with easy application and spreadability.

Properties of the dispersion-cast films

X-ray studies

PUs, which are highly elastic in nature, consist of essentially linear primary polymer chains, the structure of which consists of long, flexible chain segments that have been joined end to end by rigid chain segments through covalent chemical bonds.

The hard segments are single urethane bridges, which result when a diisocyanate couples two hydroxyl molecules or longer chain segments formed by the reaction of diisocyanates with small diol or diamine chains. These segments are rigid and provide pseudocrosslinking sites.

The polar nature of the recurring rigid urethane chain segments results in their strong mutual attraction, aggregation, and ordering into crystalline and paracrystalline domains in the mobile polymer matrix. The abundance of urethane hydrogen atoms, as well as carbonyls and ether oxygens in the urethane

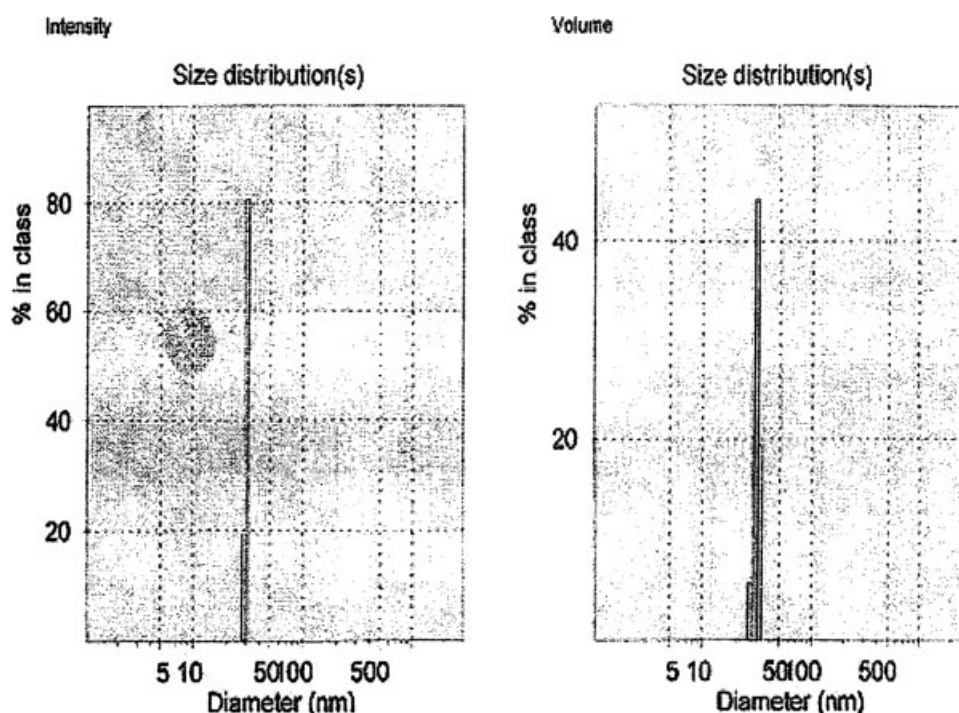


Figure 3 Representative particle size distribution graph of a dispersion (PUS-ADH3) showing a narrow particle size distribution.

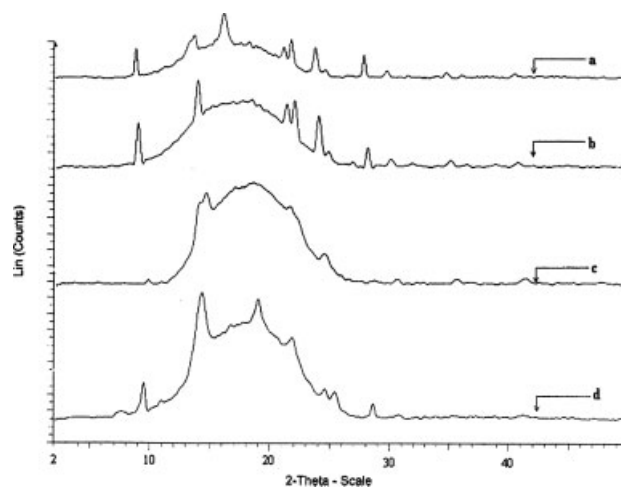


Figure 4 X-ray diffractograms of dispersion-cast films of various ionic contents: (a) 4.1, (b) 4.5, (c) 4.9, and (d) 5.6%.

linkages, permits extensive hydrogen bonding among the polymer chains, and this restricts the mobility of the urethane chain segments in the domains and thus their ability to form into crystalline lattices. As a result, semioordered regions are described as a paracrystalline result. The ultimate effect of these physical forces is to provide pseudo or mechanical crosslinking, which is similar to the chemical crosslinking that occurs in reactive thermosetting PUs.

The diffractograms of the ionic systems (Fig. 4) showed some crystallinity for all the compositions (which is expected to be absent in the case of non-ionic systems). The main changes observed in the spectra with increasing ionic content are associated with the intensity of the four diffraction peaks. Because the crystallinity of the hard segment is substantially related to the formation of diverse hydrogen bonds between urethanes, X-ray diffraction results showed that a good hard-segment order arrangement existed in the ionomeric PUs with increased ionic content. This crystallinity was responsible for the adhesive nature of the ionic dispersions in water. The amorphous state of the PUs provided good wetting of the substrate surface, and when the adhesive recrystallized, the crystalline portion provided its high cohesive strength.

Contact-angle measurements

Contact-angle measurements were performed to evaluate the hydrophilicity of the films. The contact angles that formed between the water drops mounted onto the surface of the samples (films) was measured. The contact angles of the uniform-thickness films, which were coated onto glass plates through the dipping of the glass plates into the dispersions and dried in an air oven at 50°C for 24 h, are given in Table II. The compositions with the

same chain extender (adipoyl dihydrazide) and increasing ionic content did not show any specific trend in the contact angles. All other compositions exhibited the same values, and this indicated that the nature of the chain extender or the ionic content did not influence the contact angle. It was reported earlier that the surface properties of PUs depend on the degree of this orientation, which in turn depends strongly on the ionic content and viscosity of the PU emulsion upon coating.²² To self-assemble, the polymer chains need sufficient time and space to orient their polar and nonpolar segments on the substrate during the coating process. To achieve optimum self-assembly, the mobility of the polar and nonpolar segments of the PU emulsion particles must be controlled. In this study, the improper self-assembly of the PU chains led to erratic results, so the influence of the chain-extender length and the nature of the backbone on the surface properties could not be studied.

Static mechanical properties (tensile strength and elongation)

The tensile strength and elongation values of the compositions are shown in Table II. Because the hard segment is a constant, any variation in the static mechanical property is attributable to the ionic content and the nature of the chain extender. In the PU ionomers, the mechanical strength was governed mainly by the hard segments and the flexibility of the soft segments. There was no regular trend in the tensile strength values for compositions containing various ionic contents, but the elongation percentage decreased with the ionic content. The decreased elongation at break can be explained by the increased chain rigidity and intermolecular interactions, such as (1) electrostatic forces between ionic centers, (2) hydrogen bonding between urethane groups, and (3) association of hydrophobic segments. For all other compositions having the same ionic content and different chain extenders, the elongation percentage was greater than 1000.

Adhesion properties

PUs make good adhesives for several reasons: (1) they effectively wet the surfaces of most substrates, (2) they readily form hydrogen bonds with the substrates, (3) their small molecular size allows them to penetrate porous substrates, and (4) they form covalent bonds with substrates that have active hydrogen atoms. Generally, PU adhesives are used to attach soles to footwear and in general footwear construction. Hence, the prepared dispersions were applied to leather and canvas, and their bond strength was tested.

Lap shear strength and peel strength

The lap shear strength of the adhesives was tested through the bonding of leather to leather, leather to canvas, and canvas to canvas. In the case of specimens in which the dispersions were used to bond leather to leather, the shear strengths were almost the same for the adhesives with the same ionic content, whereas the one with terephthalic dihydrazide as the chain extender showed the lowest value. The small particle size of the dispersions allowed for easy penetration into the porous leather substrate, and bonds were formed with the protein chains of leather. In the case of the specimens in which leather was bonded to canvas, cohesive failure occurred in some cases, as shown in Table II. Generally, cohesive failure occurs when the bond to the substrate exceeds the internal strength of the adhesives. Substrate failure was observed in the case of canvas–canvas bonding.

The T-peel strength of joints formed by the bonding of the leather specimens with dispersions of various compositions was determined, and the results are compiled in Table II. The behavior was very similar to that of the shear strength measurements: there was no particular trend observed in the case of ionic content variations. In fact, the composition with the maximum ionic content (PUS–ADH4) exhibited the lowest peel strength. It has been reported that the coulombic forces of attraction between counterions is the deciding factor for the adhesive strength,²³ but in this study, no specific explanation can be given for the results obtained.

Effect of moisture on joints

Because PU dispersions are ionic in nature, it was expected that moisture would weaken the adhesive material and displace adhesive bonds at joints by the preferential attraction of water. To study the effect of moisture on the adhesive layer between the leather substrates, the bonded leather specimens were soaked in water for 24, 48, and 72 h. Even at the end of 3 days, the adhesive bond at the joints did not weaken; this proved that once the bond is formed, it is resistant to moisture.

CONCLUSIONS

Water-borne poly(urethane semicarbazide) dispersions of various ionic contents and compositions, exhibiting excellent adhesion to leather and good storage stability, were prepared. Although the contact-angle measurements revealed a highly hydrophilic nature of the films cast from dispersions, the adhesive layers at the interface of leather substrates after bonding were moisture-

resistant. The effect of the ionic content on dispersion properties such as the particle size and viscosity revealed that the particle size decreased and the viscosity increased with increasing ionic content. X-ray studies revealed that the increase in the ionic content led to increasing intensities of the diffraction peaks due to increased secondary forces of bonding between the chains. The tensile strength measurements on the films showed a marked difference in the elongation for compositions of various ionic contents. Lap shear strength analysis was performed to study the bond strength of adhesives on substrates such as leather and canvas, and it proved that the dispersions worked well for bonding leather, whereas peel strength tests were performed on leather specimens only. With a view toward eliminating the use of volatile organic compounds, the development of a water-based adhesive for footwear applications to bond shoe soles to uppers has been achieved.

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