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ORIGINAL CONTRIBUTION

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Aqueous dispersions of polyurethane cationomers: a new approach for hydrophobic modification and crosslinking

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Abstract Polyurethanes (PUs) containing tertiary nitrogen atoms were synthesised from poly (tetramethylene oxide) glycol, toluene diisocyanate and *N*-methyl diethanolamine. These polymers were converted into cationomers by quarternising with alkyl bromides of different chain lengths and then dispersed in water. Finally the cationic PU dispersions were further crosslinked with dibromo compounds of different spacer lengths. The effect of percent ionisation, percent crosslinking, chain length of the ioniser and crosslinker on particle size, viscosity and interfacial tension of the dispersions and on the thermal, mechanical and surface tension properties of the dispersion cast films were studied. The hydrophilicity of the polymer is more in the dispersed state than when cast as a film, which exhibited low critical surface tension values. With increase in chain length of the ioniser and the crosslinker, the hydrophobicity of the dispersion cast film increases without appreciable change in the hydrophilicity of the polymer in the dispersed phase, as can be seen from the interfacial tension and critical surface tension values.

Keywords Polyurethanes · Cationomers · Crosslinking · Hydrophobic modification · Quaternisation

Introduction

Polyurethanes (PUs) are noted for their high performance due to their excellent chemical, solvent and abrasion resistance, as well as outstanding hardness and toughness combined with low temperature flexibility. These desirable properties make PUs suitable for many coating applications. In the raw material stage the di- or poly-isocyanate used in the synthesis is highly moisture sensitive, which, without any option, forces the use of volatile organic solvents in the preparation and dissolution. The effects of volatile organic solvents on the environment are detrimental and hence there is a growing concern about solvent emissions. In addition to the environmental issues, the escalating price of petroleum-based solvents has led to an increased emphasis towards the development of water-borne coatings.

Basically, PUs are hydrophobic. However, it is possible to emulsify, disperse or even dissolve the polyurethanes in water if necessary structural modifications are done. PUs can be dispersed in water with the aid of a protective colloid, external emulsifier or by structural modification [1]. The first two methods suffer a few disadvantages as they require strong shear force to disperse the polymer, which results in coarse particles and poor dispersion stability. A unique method of dispersing PU in aqueous media is by structural modification, i.e. modifying the hydrophobic PU backbone with built-in ionic groups [2]. PUs with in-built hydrophilic groups are termed internal emulsifiers or self-emulsifiers. The advantages of the latter method are:

- The hydrophilic modification of PU enables dispersion under mild conditions
- Dispersions with finer particle size are obtained and hence the stability of the dispersion is subsequently increased
- The films formed from these dispersion have improved solvent and water resistance

Depending on the type of ionic group incorporated, dispersions can be classified as anionic [3, 4], cationic [5, 6] and zwitterionic [7]. Anionic dispersions are commercially predominant while little literature is available on cationic dispersions. Cationic PUs show unusually good adhesion to various ionic substrates, especially anionic substrates like leather and glass. They also have proven useful in special applications, such as additives in the coagulation process used to make poromerics [8]. Cationomers are predominantly made by quaternising the tertiary nitrogen already introduced into the system. Since any group that can quaternise the tertiary nitrogen can be used, it gives the opportunity to introduce special functional groups such as photochromic azo groups into the polymer backbone [9, 10, 11].

Recently, research work has been oriented towards improving mechanical properties along with resistance to solvent, water, scratch and abrasion. Aqueous polyurethane dispersions are generally made of linear polyurethane chains having ionic groups. Due to the uncrosslinked structure, solvent-resistance properties are poor and hydrophilic modifications lead to poor water resistance. These drawbacks can be overcome by hydrophobic modification [12] and crosslinking of the PU chains [13, 14, 15]. The unique properties of polyurethanes arise from the high degree of intermolecular hydrogen bonding. In order to further enhance the properties of the polyurethane, crosslinking can be achieved by the introduction of reactive groups. Suitable crosslinking mechanisms are stoving systems (heat-activated crosslinking), UV-crosslinkable systems or two-component systems. These crosslinking mechanisms have their own disadvantages. Heat-activated systems and UV-crosslinkable systems need either an oven or UV source, which limits their use in industrial applications. A two-component system has a limited pot life after mixing and involves handling of carcinogenic crosslinkers like aziridine. These factors have limited the scope of these systems.

Another way of crosslinking, which is widely used, is crosslinking through -NCO-terminated polymer because of the simplicity with which the -NCO-terminated polymer, in the form of dispersion, can be crosslinked with poly-functional alcohols or poly-functional amines. Since crosslinking is performed in aqueous medium, the reaction of -NCO with water should be minimised otherwise it may lead to undesirable side reactions. Aliphatic isocyanates, commonly employed in the preparation of dispersions, are less reactive with water than aromatic isocyanates. Due to the low reactivity of aliphatic isocyanates, the molecular weight of the prepolymer is low and they require a longer time for completion of the reaction. Aromatic isocyanates, on the other hand, are highly reactive with water, and hence they are seldom preferred even though they impart better mechanical properties to the films than their aliphatic analogues. Hence, it is of interest to find an alternative method of crosslinking that does not require the presence of -NCO at the ends and also allows the use of aromatic isocyanates in the preparation of aqueous PU dispersions. This paper gives a novel method for the hydrophobic modification and crosslinking of polyurethane dispersion at ambient temperatures.

Experimental

Materials

Poly(tetramethyleneoxide)glycol (PTMG, Aldrich, USA) of molecular weight 1000 (PTMG 1000) was dried under reduced pressure at 100 °C before use. Tolylene diisocyanate (TDI, mixture of 80% 2,4- and 20% 2,6-isomers) and dibutyl tindilaurate (DBTDL) (Aldrich, USA) were used as received. *N*-Methyl diethanolamine (NMDEA, Sisco, India) was distilled under reduced pressure and the middle portion was stored in nitrogen atmosphere. *N*,*N*-Dimethylformamide (Merck, India) was distilled under reduced pressure and stored over molecular sieves (type 4 Å) prior to use. Bromo alkanes and dibromo alkanes (Sisco, India) were used as received.

Cationomer synthesis

A 250 mL three-neck flask fitted with a mechanical stirrer, nitrogen inlet and a pipette outlet was used as the reaction vessel. The amounts of various reactants for different compositions are listed in Table 1. A calculated amount of TDI was placed in the reaction vessel and the required amount of PTMG was added to it drop-wise. The reaction temperature was maintained at 75 °C until the NCO content reached half of its initial value, as determined by dibutylamine titration. Then the reaction was cooled to room temperature and the required amount of NMDEA, dissolved in calculated amount of DMF, was added drop-wise. The reaction was carried out at 60 °C until completion, as confirmed by the disappearance of the NCO peak in FT-IR spectrum. The reaction mixture was then cooled to room temperature and the calculated amount of alkyl halide was added (cf. Table 1). The quaternisation reaction was carried out at room temperature for 24 h. The various steps involved in the preparation of cationomeric dispersion are given in Scheme 1.

Dispersion and crosslinking

Water was added drop wise at a constant rate to the solution of the cationomer in DMF, and the mixture stirred using a mechanical stirrer at a constant speed. A sharp drop in viscosity indicated the completion of the dispersion process. Dispersion mechanisms have been proved by changes in viscosity and conductivity during dispersion process by Deitrich et al and Chan

Table 1 Polymer composition and codes

Polymer code	Polymer composition (g)					Hard segment content[c] (%)
	Polyol	Isocyanate	NMDEA	Alkyl halide	Cross-linker	
IV 16	9.0	9.5	5.4	5.5	0.6	53.8
IV 18	7.2	10.0	6.0	6.2	0.6	61.4
IV 20	5.3	10.6	6.6	6.9	0.6	69.9
IV 22	3.5	11.1	7.2	7.6	0.6	79.2
CL 0	8.9	9.5	5.4	6.2	-	54.1
CL 2	7.2	10.0	6.0	6.2	0.6	61.4
CL 4	5.4	10.6	6.6	6.2	1.2	69.6
CL 6	3.6	11.2	7.2	6.2	1.8	78.5
BrC2[a]	8.9	9.5	5.4	4.9	-	52.5
BrC3[a]	8.9	9.5	5.4	5.6	-	53.3
BrC4[a]	8.9	9.5	5.4	6.2	-	54.1
BrC5[a]	8.9	9.5	5.4	6.8	-	54.8
DBB[b]	7.2	10.0	6.0	6.2	0.5	61.9
DBH[b]	7.2	10.0	6.0	6.2	0.6	61.4
DBD[b]	7.2	10.0	6.0	6.2	0.8	62.4

[a] BrC2, BrC3, BrC4, BrC5 represent bromo ethane, bromo propane, bromo butane and bromo pentane, respectively

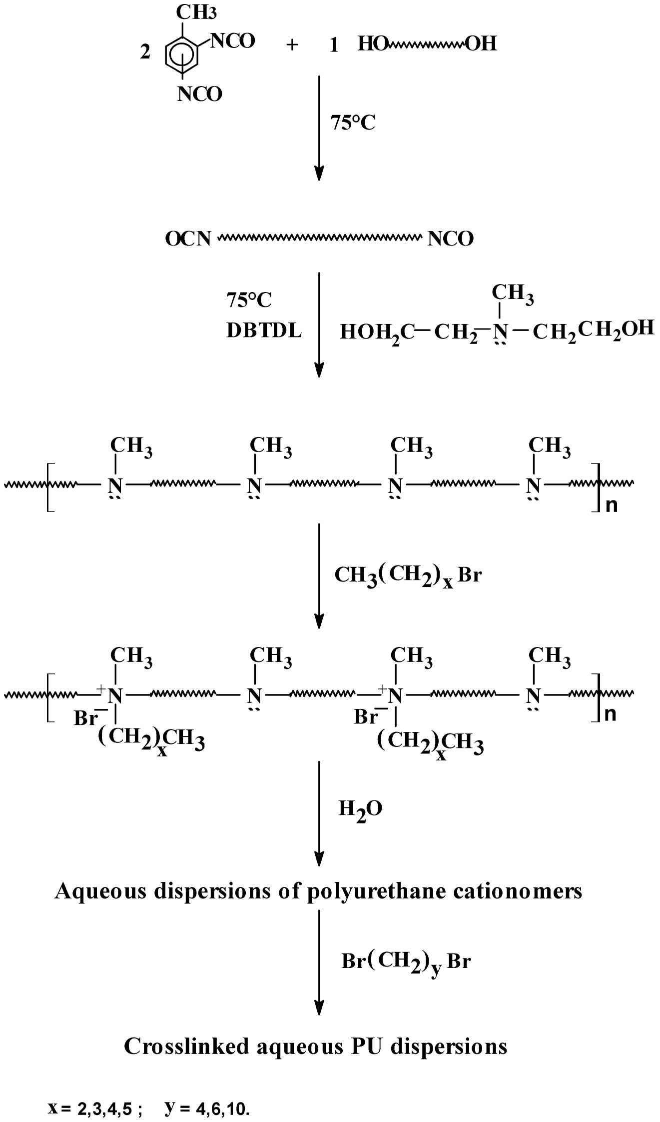
[b] DBB, DBH, DBD denote dibromobutane, dibromo hexane and dibromo decane, respectively

[c] HSC = Weight of (isocyanate + NMDEA + alkyl halide + crosslinker)/Total weight

et al [2, 4, 16]. A calculated amount of dibromo alkane was added to the dispersion and the mixture stirred at room temperature for 12 h to effect cross linking. The amount of DMF and water added were calculated by fixing the solid content of the dispersions at 35%. A portion of the dispersion was poured into a silicon mould, dried in an air-circulating oven at 120 °C for 2 h and then in a vacuum desiccator for 24 h to prepare films for characterisation.

Characterisation techniques

The viscosity of the dispersions was measured with an advanced rheometer (AR 500, TA Instruments, USA). Particle size was measured using master sizer 2000, (Malvern Instruments, UK). Interfacial tension of the dispersions was determined by Wilhelmy plate technique. Critical surface tension (γ) of the polymer surfaces was measured from static contact angle. Contact angle (θ) was measured by a custom-built instrument and was directly read off a projected image of the liquid volume, 20 μL, placed on the film. Alkanes (HPLC grade dodecane, tetradecane, hexadecane, heptadecane and octadecane from Lancaster Chemicals, UK) were used to measure the contact angle. Rectangular strips (20×10×0.5 mm^3) of each film were characterised with a dynamic mechanical analyser (DMA 2980, TA Instruments, USA) using the tension film mode in the temperature range of −100 °C to +100 °C at a heating rate of 5 °C min^{-1}, strain amplitude of 20 μm and frequency of 1 Hz. Thermogravimetric analysis was done with TGA 951 thermogravimetric analyser (Dupont Instruments), at a heating rate of 20 °C min^{-1} in nitrogen atmosphere (flow rate 50 mL min^{-1}.). The microtensile dumbell specimen (three each) for stress-strain analysis was cut to a size of 40×10 mm^2 and kept for conditioning at a temperature of 20 ± 2 °C and relative humidity of 65 ± 2% for 24 h before testing. The specimen conformed to ASTM D 6385. The tensile testing was done using an Instron universal testing machine model 4501 at a crosshead speed of 100 mm min^{-1}.



Scheme 1 Synthesis of crosslinked aqueous polyurethane dispersions

Results and discussion

FT-IR

Representative FT-IR spectra of polyurethane and its cationomer (IV 22) are shown in Fig. 1. Spectra showed characteristic bands of urethane >NH at 3300 cm^{-1} and >C=O stretching of urethane linkage at 1750 cm^{-1}. The broad nature of the >C=O band shows that this group is involved in hydrogen bonding. The symmetric and asymmetric stretching of CH_2 of PTMG were observed between 3000 and 2750 cm^{-1}. The aromatic >C=C< band of TDI was observed around 1600 cm^{-1}. The band at 1540 cm^{-1} is due to the C-N stretching and NH

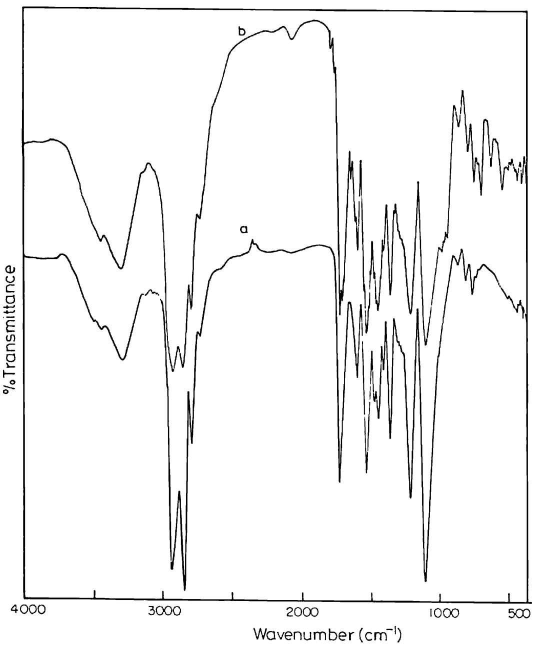


Fig. 1 FT-IR spectra of *a* polyurethane *b* polyurethane cationomer (IV 22)

deformation. The >C-O-C< stretching of the polyurethane is seen as a broad band at 1100 cm^{-1} showing that the ether groups are also involved in hydrogen bonding. When the block copolymers were converted to their cationomers, the tertiary nitrogen atoms were converted to quaternary ammonium groups, which gave rise to peaks around 980–930 cm^{-1}, characteristic of aliphatic quaternary ammonium salts.

Particle size and viscosity

The two inter-related factors—particle size and viscosity are crucial in any coating application. Particle size plays a major role in deciding the properties of dispersion and has direct impact on the stability of dispersion. Dispersions with relatively large average particle size are generally unstable with respect to sedimentation. Dispersions with smaller particle size are more useful since such dispersions have high surface energy which enhances film formation. Hence, the ability to control the particle size becomes important. In PU dispersions the particle size depends on several factors such as stirring speed, prepolymer viscosity and the rate of water addition, but the major factor is the ionic content [2, 4].

Effect of NMDEA content

An increase in NMDEA content led to an increase in both hard segment content and ionic content. Particle size, generally, decreases with increase in ionic content.

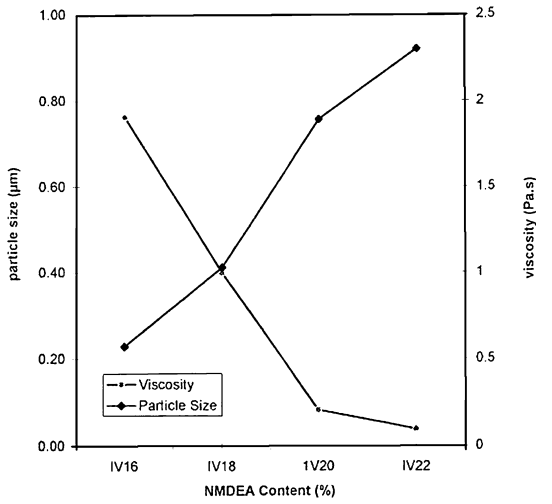


Fig. 2 Effect of NMDEA content on particle size and the viscosity of the polyurethane dispersions

Hard segment content also affects the particle size. With increase in the hard segment content, the chain flexibility reduces, affecting the particle size in two ways: (i) The rigid particles are less deformable in the shear field [17, 18]. Under constant shear, this leads to coarse particles during phase inversion. (ii) Since the chain is rigid, the solution viscosity is high, leading to coarse particles [19]. In the present case when NMDEA content increased, particle size increased. Hence, the effect of hard segment content predominated over the effect of ionic content.

Generally, viscosity increases with increase in ionic content due to an increased electroviscous effect and decreases with increase in particle size [20]. However, in the present case, increase in NMDEA content increased ionic content as well as hard segment content. Due to increased chain rigidity, localisation of ionic groups on the surface of the micelles is hindered and hence the expected electroviscous effect was absent [4, 19, 21], leading to decreased viscosity. In addition to this, increase in particle size also reduces the viscosity due to reduced total effective volume of the particle [20]. The effect of NMDEA content on particle size and viscosity is given in Fig. 2.

Effect of percent crosslinking

Figure 3 shows the dependence of particle size and viscosity on the percent crosslinking. Both the viscosity and particle size of the dispersion increased with increase in crosslinking. Since the crosslinking is between the tertiary nitrogen atoms, in order to increase the percent crosslinking, the amount of NMDEA used in the reaction was increased. This in turn resulted in increased chain rigidity. As explained earlier, when this polymer was subsequently dispersed, the increase in rigidity led to

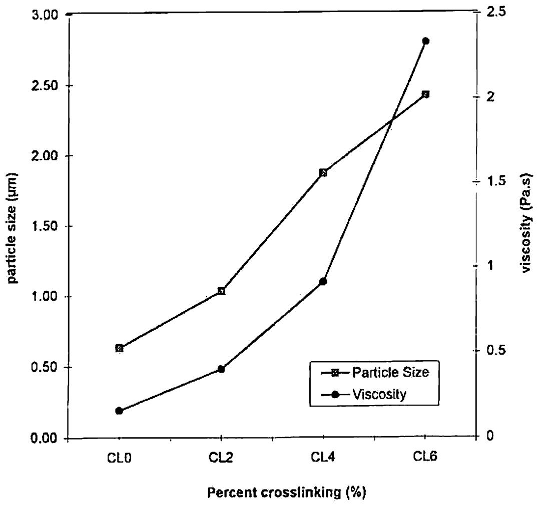


Fig. 3 Effect of percent crosslinking on particle size and viscosity of the polyurethane dispersions

an increase in particle size [22]. When crosslinking increased, more polymer chains are held together by strong covalent bonds. Hence, there is an increase in the total effective volume of the particles and the viscosity of the dispersion increased with increase in crosslinking.

Effect of chain length of ionising agent

The effect of chain length of the alkyl halide on the viscosity and particle size is depicted in Fig. 4. With increase in the chain length of the alkyl halide there was no change in the hard or soft segment content but there was a marked increase in the amount of hydrophobic component. Due to the increased hydrophobic to hydrophilic ratio, the particle size increased. Dispersions prepared from the alkylating agents having more than 5 carbon atoms were unstable due to repulsion between water and the hydrophobic alkyl chains. This was also accompanied by an increase in viscosity due to the increased hydrophobic repulsion in water. Particle size and viscosity increased with increase in hydrophobic content.

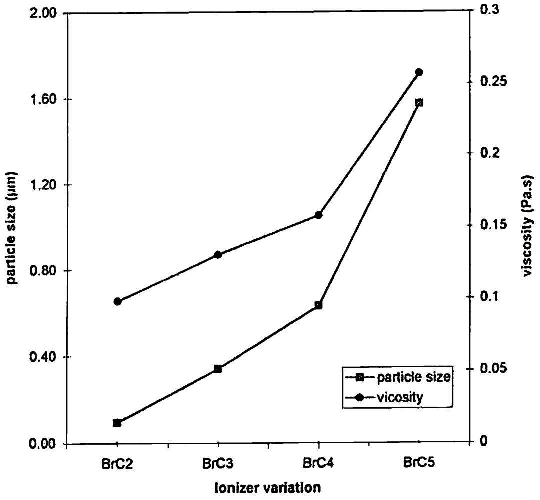


Fig. 4 Effect of chain length of the ioniser on particle size and viscosity of the polyurethane dispersions

Effect of chain length of crosslinking agent

When dibromo butane (DBB), dibromo hexane (DBM) and dibromo decane (DBD) were used as crosslinkers, no significant change in the particle size and viscosity was observed.

Interfacial tension and surface studies

The ratio of the hydrophilic to hydrophobic groups in a polymer is crucial in determining the dispersion and the film properties. Increase in hydrophilicity enhances storage stability whereas increase in hydrophobicity is desired to avoid swelling of the coated films in a moisture-prone atmosphere. Thus, for an ideal dispersion there should be a perfect balance between hydrophilicity and hydrophobicity. The properties of the polymer in the dispersed state, and as a cast film, can be determined from the Interfacial tension (IFT) and contact angle measurements.

Polymer molecules at the surface have a greater freedom due to the mobility and flexibility of their constitutional units to rearrange themselves in order to accommodate the change of chemical potential in the surrounding environment [23]. Owen et al [24] have proposed the following ways for the hydrophobic recovery of a polymer surface.

1. Reorientation of surface hydrophilic groups away from the surface
2. External contamination of the polymer
3. Changes in surface roughness

Thus, a polymer can restructure or reorient its non-polar components if it is exposed to an environment of air, creating a hydrophobic surface to minimise the free energy. If the polymer is exposed to a highly polar environment, the polar components orient towards the interface [25, 26]. In this work, a hydrophilic polymer was cast as a film and the observed change in the surface energy profiles showing a fairly low surface energy can be explained as follows: In the first step, possibly, movement of the macromolecular chains occurs followed by the movement of the alkyl side chains leading to orientation at the surface. These motions take place at room temperature.

In order to understand the forces between the hydrophobic and hydrophilic segments of the polymers and their distributions at the water/polymer interface, and solid/liquid interface, studies on IFT using the Wilhelmy plate technique [27] and static contact angle measurements have been carried out using alkanes of varying polarity (dodecane, tetradecane, hexadecane, heptadecane and octadecane) by the sessile drop method. The liquid drops were placed on the films and the the projected image was directly read off a custom-built instrument to find θ. The critical surface tension values were obtained from plotting the cosθ vs. surface tension γ of the various alkanes (Zismann plot). The CST values are given in Table 2. The values of IFT (γ) clearly indicated that the dispersions show a hydrophilic character with more polar groups at the interface, thus giving rise to high energy values. This is desirable because this will enhance the pot-life of the dispersion. However, the CST values of the films obtained from the dispersions are low ($\approx$25 mN m^{-1}), almost half of the IFT values, indicating that the hydrophobic domains are present predominantly on the surface possibly due to reorganisation and ordering at the solid/liquid interface. Thus, alkyl chains orient themselves on the surface, giving rise to this interesting property.

Also, the polar and dispersive energy component of the groups present in the surface of the films can be calculated from Fowkes equation [28] (Eq. 1), which relates the contact angle of the liquids of varying polarities to the polar and dispersed components of the solid surface. Thus one can evaluate the proportion of hydrophilic/hydrophobic groups of the polymer on the surface.

$$\gamma_{\mathrm{Li}}(1+\cos\theta) = 2[(\gamma_s^d \times \gamma_{\mathrm{Li}}^d)^{1/2} + (\gamma_s^p \times \gamma_{\mathrm{Li}}^p)^{1/2}] \qquad (1)$$

Here γ_{Li}^p represents the polar component and γ_{Li}^d, the dispersive component of the liquid used to measure the contact angle. γ_{Li} is the surface tension of the liquid.

γ_s^d and γ_s^p give the dispersive and polar component present on the surface of the film. The Fowkes equation can be solved by using two different liquids of varying polarity in which one is highly nonpolar so that the polar component (γ_{Li}^p) present in the system is 0. The pair of simultaneous equations give the values of γ_s^d and γ_s^p, respectively and are tabulated in Table 2.

The interfacial tension of the dispersions and the solid surface energy (SSE) of the polymer films (γ_s^p) are given in Table 2. Since NMDEA is completely used for ionisation and crosslinking, increase in NMDEA content contributes towards the increase of total ionic content. Hence, both the solid surface energy and IFT increased with the increase in NMDEA content indicating an increase in hydrophilicity. Since crosslinking is effected by diquaternisation, when percent crosslinking increased there was increase in the ionic content and hence both solid surface energy and IFT increased.

With the increase in the alkyl chain length of the ioniser, SSE values decreased. In the case of IFT, although there was increase in hydrophobic content there was only a slight decrease in the IFT values. This is possibly because in the dispersion, only the ionic groups are present on the surface of the micelle and there is no change in the percent ionisation. The same results were observed when the chain length of the crosslinker was increased. With increase in chain length there was no change in ionic content but there was increase in the hydrophobic content. This is borne out by a decrease in SSE and IFT values. The variation in the CST and solid surface energy values with variation in the NMDEA content and percent crosslinking, are given in Fig. 5 and

Table 2 Interfacial tension, critical surface tension and solid surface energy values of PU cationomeric dispersions

S. no.	Polymer code	Interfacial tension (mN m^{-1})	Critical surface tension[a] (mN m^{-1})	Solid surface energy[a] γ_s^p (mN m^{-1})
1	IV 16	52.9	21.60	8.18
2	IV 18	55.3	23.45	10.63
3	IV 20	62.0	25.15	14.52
4	IV 22	64.0	26.00	24.40
5	CL 0	53.8	22.00	8.68
6	CL 2	55.3	23.45	10.63
7	CL 4	56.5	25.15	13.88
8	CL 6	59.3	26.50	16.19
9	BrC2	54.2	26.25	15.17
10	BrC3	54.0	24.85	12.97
11	BrC4	53.8	23.45	8.68
12	BrC5	53.4	20.56	6.36
13	DBB	55.6	25.52	11.67
14	DBH	55.3	23.45	10.63
15	DBD	55.0	22.00	6.86

[a]Results for the films obtained from the dispersions

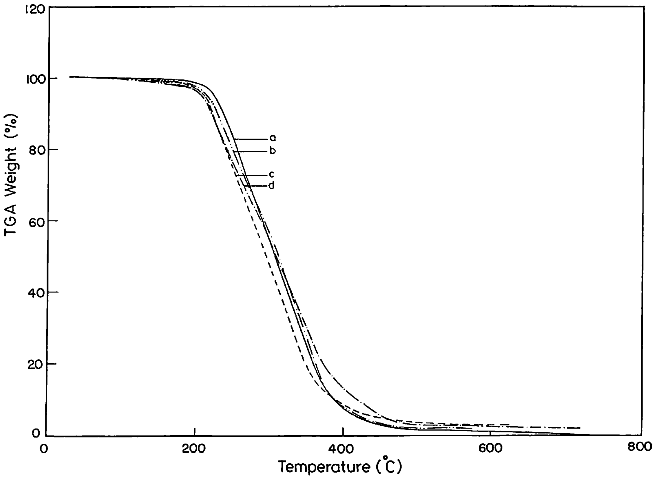


Fig. 5 Effect of NMDEA content on critical surface tension and solid surface energy of dispersion cast films

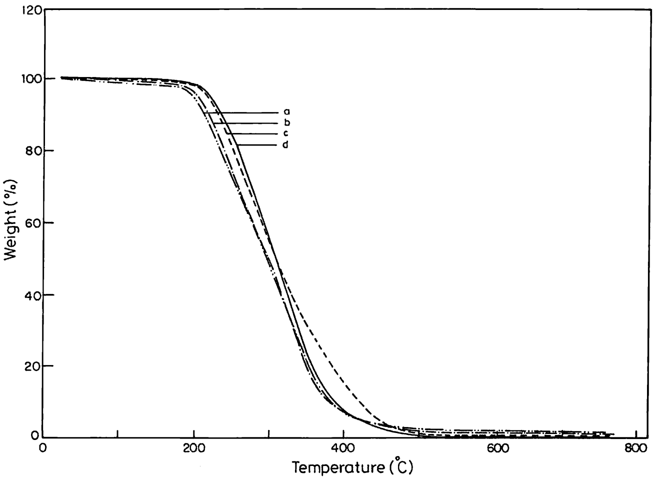


Fig. 6 Effect of percent crosslinking on critical surface tension and solid surface energy of dispersion cast films

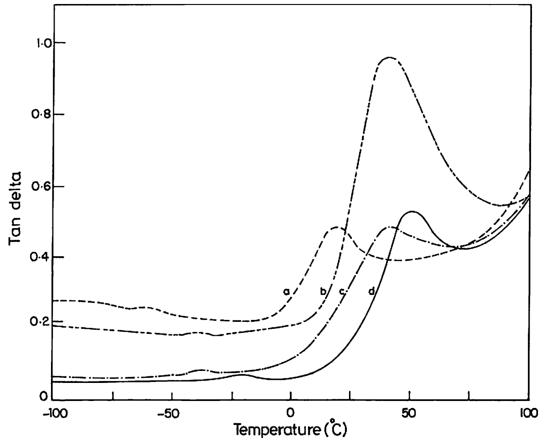


Fig. 8 Effect of chain length of the crosslinker on critical surface tension and solid surface energy of dispersion cast films

Fig. 6. Both CST and SSE increased with increase in the NMDEA content and percent crosslinking. This is due to the increase in ionic content with increase in NMDEA content and percent crosslinking. Figs. 7 and 8 give the change in the CST and solid surface energy value with change in chain length of the ioniser and crosslinker. Both CST and SSE values decreased with increase in the chain length of the ioniser and crosslinker due to the increased hydrophobic interactions of the alkyl chain.

Thermogravimetric analysis

The effects of variation in ionic content, crosslinking percentage, length of the ioniser and crosslinker on the thermal stability of the cationomers were assessed by thermogravimetric analysis. All compositions exhibited a single-step degradation pattern and no weight loss was observed up to 200 °C. With increase in ionic content from 16% to 22%, there was a slight increase in the onset point of degradation, which is due to two reasons—increase in ionic interactions between the polymer chains and increase in hard segment content (Fig. 9). The effect of percent crosslinking on the thermal stability is shown in Fig. 10. When percent crosslinking is increased, chain rigidity increases due to strong covalent crosslinking, which in turn leads to a more compact structure. In addition to this, the hard segment content also increases. Hence, the thermal stability increased with increase in crosslinking. When the crosslinkers were varied, there was no marked difference in the thermal stability of DBH and DBD. DBB showed lower thermal stability compared to the other two systems, which may be attributed to ineffective crosslinking of DBB, due to

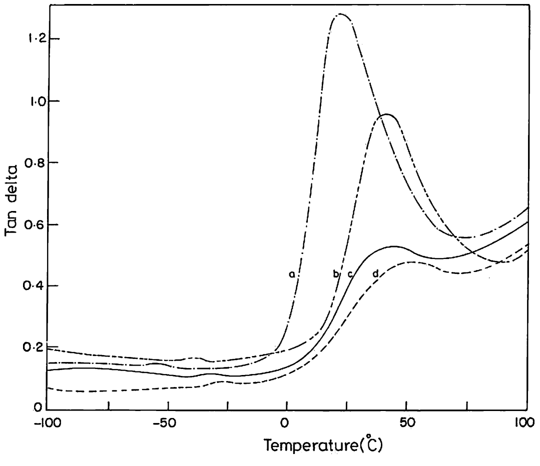


Fig. 7 Effect of chain length of the ioniser on critical surface tension and solid surface energy of dispersion cast films

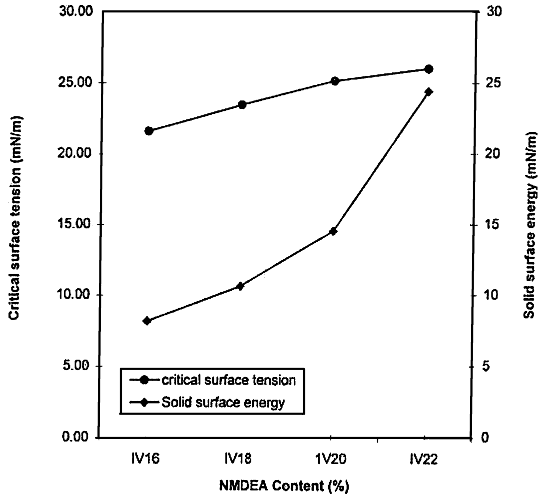


Fig. 9 Effect of NMDEA content on thermal stability of polyurethane cationomers *a* IV 22, *b* IV 20, *c* IV 18, *d* IV 16

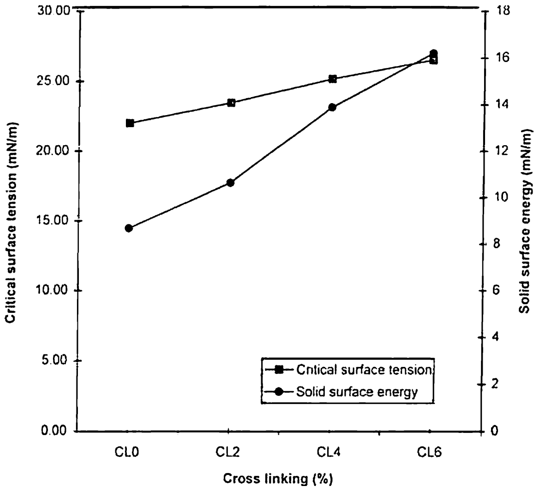


Fig. 10 Effect of percent crosslinking on thermal stability of polyurethane cationomers *a* CL 0, *b* CL 2, *c* CL 4, *d* CL 6

increased steric hindrance between the polymer chains. There was no marked difference in thermal stability of polymers prepared with ionisers of varying chain length.

Mechanical properties

Static mechanical properties

Tensile strength and elongation at break values are given in the Table 3. Increase in NMDEA content resulted in an increase of both hard segment content and ionic content. Increase in percent ionisation favours increase in tensile strength due to columbic interactions [29] and increase in hard segment content also leads to increase in tensile strength [10, 29, 30, 31]. Both the ionic content and hard segment content increased by increasing NMDEA and hence there was an increase in the tensile strength with increase in NMDEA content [7, 30]. While increase in ionic content leads to increase in elongation at break, increase in hard segment content leads to a decrease in elongation [10]. In this case, the effect of hard segment content predominates over that of ionic content, thereby leading to a decrease in elongation with increase in NMDEA content.

Table 3 Mechanical properties of cationomeric dispersion cast films

S. no.	Polymer code	Stress-strain		DMA	
		Tensile strength (N mm^{-2})	Elongation (%)	T_{gs} (°C)	T_{gh} (°C)
1	IV 16	1.8	162	−54.7	21.9
2	IV 18	9.7	59	−40.7	37.7
3	IV 20	11.3	20	−32.9	42.3
4	IV 22	15.9	18	−28.4	51.4
5	CL 0	12.3	23	−59.7	18.5
6	CL 2	9.6	20	−40.7	37.7
7	CL 4	5.0	20	−48.8	36.8
8	CL 6	3.7	18	−21.6	47.2
9	BrC2	12.2	22	−55.0	21.9
10	BrC3	12.2	23	−55.3	18.6
11	BrC4	12.3	23	−59.7	18.5
12	BrC5	12.1	23	−57.7	16.5
13	DBB	1.5	38	−43.8	39.4
14	DBH	9.7	20	−40.7	37.7
15	DBD	16.1	25	−39.9	17.8

With increase in crosslinking, which is accompanied by both an increase in hard segment content (54–78%) and hard segment cohesion, the tensile strength is expected to increase and elongation at break to decrease [20]. On the contrary, increase in crosslinking led to a decrease in both tensile strength and elongation. This is because the crosslinking is through short-chain dibromo compounds, which impart brittleness to the film thereby decreasing both tensile strength and elongation.

When the chain length of the crosslinker was increased, without significant change in the hard segment content, it increased the flexibility of the system and hence both the tensile strength and elongation increased. The tensile strength and elongation shown by the system crosslinked with dibromobutane can be attributed to the ineffective crosslinking due to increased steric hindrance resulting in only mono quaternisation. This resulted in increasing the ionic content without crosslinking, which led to decreased tensile strength and increased elongation. As expected, the dispersion crosslinked with dibromodecane-based films had better mechanical properties compared to dibromohexane crosslinked films.

When the chain length of the ioniser was increased, there was no significant change in the mechanical properties since both the percent ionisation and hard/soft segment content were the same. All the films had tensile strength around 12 N mm^{-2} and elongation at break around 23%.

Dynamic mechanical properties

Table 3 gives the dynamic mechanical data of the crosslinked cationomers. With increase in NMDEA content, both the soft segment T_g and hard segment T_g increased as shown in Fig. 11. The increase in hard segment content resulting from an increase in NMDEA content influences the soft segment T_g, which is shifted to a higher temperature [32]. Since there is increase in both ionic content and hard segment content with increasing NMDEA content, there was an increase in the T_g value of the hard segment.

When percent crosslinking increased from 0% to 6%, the hard segment content increased from 54% to 78%. This is reflected in the shift in the T_g. The T_g of the soft

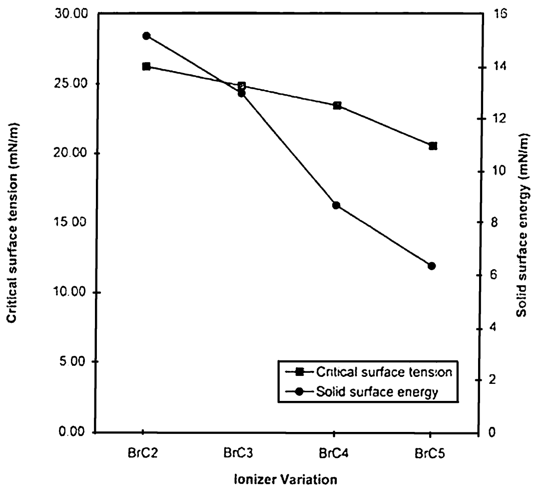


Fig. 11 Tan δ vs. temperature plots of compositions with varying NMDEA content *a* IV 16, *b* IV 18, *c* IV 20, *d* IV 22

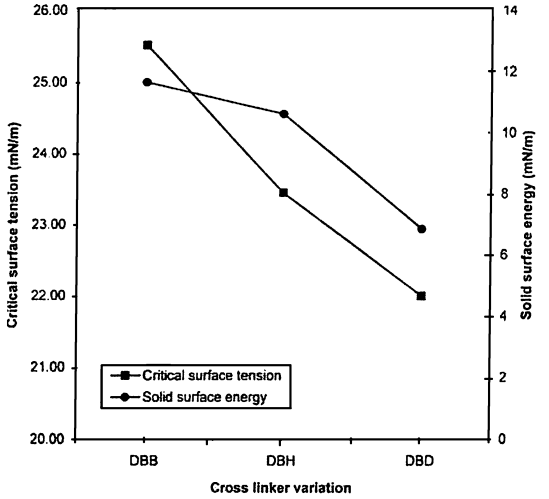


Fig. 12 Effect of percent crosslinking on damping curves of polyurethane cationomers *a* CL 0, *b* CL 2, *c* CL 4, *d* CL 6

segment (T_{gs}) increased due to the influence of the increasing hard segment. With the increase in crosslinking, the hard segments are held together by strong covalent crosslinking and, hence, there is increase in the hard domain cohesion. This led to an increase in the hard segment T_g (T_{gh}). The effect of percent crosslinking on the dynamic mechanical properties is shown in Fig. 12. With increase in percent crosslinking, rigidity of the polymer increased, which resulted in increase in storage modulus.

Compared to dibromohexane (DBH) and dibromodecane (DBD), dibromobutane (DBB) is not an effective crosslinker. Maybe DBB acts only as a quaternising agent due to steric effects, thus only ionic content increases leading to phase separation and thereby shifting the T_g of the soft segment to a lower temperature region [33]. When DBH and DBD were used as crosslinkers, the T_{gh} was found to decrease with increase in crosslinker chain length. This may be because in DBH the hard domains are much more closely packed and this leads to a more compact structure compared to DBD. Hence the T_{gh} for DBH is higher than for DBD.

No significant variation in the transition temperatures of the soft segment was observed by changing the length of the ioniser groups. A slight decrease in the T_g of the hard segment was observed, which might be due to the disruption in the hard domain ordering brought about by the increasing chain length of the ioniser.

Conclusion

Polyurethane cationomeric dispersions were prepared with varying NMDEA content, percent crosslinking and chain length of the ionising agents and crosslinkers. These dispersions were characterised for particle size and viscosity, which varied with NMDEA content, percent crosslinking and ioniser chain length but not with increase in chain length of the crosslinker. CST and IFT measurements revealed that the cationomers are more hydrophilic in the dispersed state but have a hydrophobic surface when cast into films. With increasing chain length of ioniser and crosslinker, the hydrophobicity of the film surface increased. Dynamic mechanical analyses revealed that the glass transition temperatures varied with NMDEA content, crosslinking percent and chain length of the ioniser and crosslinker. Similarly, the static mechanical properties were affected by NMDEA and crosslinking percentage. The increase in the chain length of the crosslinker resulted in improved tensile properties. TGA measurement revealed that the thermal stability increased with increase in ionic and crosslinking percentage.

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