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LEADING CONTRIBUTION

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Aqueous polyurethane dispersions

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Abstract This review describes basic chemistry, preparation process, and physical properties of aqueous polyurethane dispersions and the derived films, along with the methods of post treatment to modify the properties. Basic way to render a polyurethane water dispersible without external emulsifier has been described. Regarding the methods of preparation, four major processes are described and compared. Methods to improve the relatively poor water and solvent resistance of aqueous polyurethane dispersions which is introduced by the hydrophilicity and linear structure of polyurethane have been discussed with an emphasis on acrylate incorporations.

Introduction

An aqueous polyurethane (PU) dispersion is a binary colloid system in which PU particles are dispersed in a continuous aqueous medium. PU dispersions have been on the market since the late 1960s and have been commercially important since the early 1970s. One technical advantage of aqueous dispersion is that the viscosity of dispersion is normally independent of the molecular weight of the polymer. Thus, PU dispersion can be prepared at a high solid content with a molecular weight high enough to form films with excellent performance solely by physical drying. This means that film formation can occur by simple evaporation of water even at ambient temperature.

Aqueous PU dispersions can be formulated into coatings and adhesives containing little or no cosolvent, and hence they are nontoxic, nonflammable, and do not pollute the air. Such environmental advantages coupled with increasing solvent price and the quality of those materials have steadily expanded their usages in textile coatings, fiber sizings, and adhesives for a number of polymeric materials and glass surfaces. Over 1000 patents have been issued in the last ca. 50 years of their existence. These are well reviewed and documented in Dieterich [1] and Rosthauser and Nachtkamp [2]. A major portion of the newer patents centers on the modification and tailormaking of aqueous PU for specific end uses. A variety of aqueous PU dispersions has in fact been commercialized in many countries. They are predominantly linear polymers [3]. Modification is mainly directed to improve the water and solvent resistance properties of the derived films, which on the other hand, is introduced by the very nature of dispersion, i.e., hydrophilicity and linearity of the waterborne PUs. Improvements in these properties have more or less been achieved by grafting of other polymers [4, 5], external and internal crosslinkings [6, 7], and blending or interpenetrating polymer network formations [8, 9].

This review describes the methods of preparation of aqueous PU dispersions, physical properties of dispersions and dispersion derived films, and important methods to modify the film properties together with the applications.

Chemistry and dispersions

Basic polyurethane chemistry

Polyaddition reactions between molar excess of diisocyanates and polyols lead to the formation of NCO-terminated polyurethane prepolymers, which are chain extended with diamines to form polyurea groups. Therefore, typical segmented polyurethanes are polyurethane-polyurea. Linear products are obtained if the reactants are bifunctional but higher functionality leads to the formation of branched or crosslinked materials. Unlike polycondensation, the urethane forming reactions normally evolve no by-products that require removal as the macromolecules are built up.

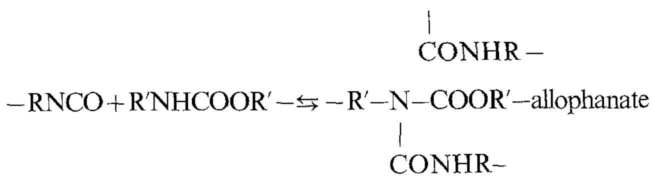
Since PU dispersions are formed in water, the reaction of diisocyanate with water should be minimized. Water hydrolyzes the isocyanate groups with the evolution of carbon dioxide resulting in severe foaming, which is detrimental in bubble-free castings and continuous surface coatings [10, 11].

$$\sim NCO + H_2O \rightarrow \sim NH\text{–}COOH \rightarrow \sim NH_2 + CO_2$$

The amino groups can react with the remaining NCO groups yielding urea linkages, which can contribute to the chain extension and physical properties of high performance PU. However, aqueous PU dispersions which have been extended predominantly with water have inferior properties to those extended with polyamines. This is simply because two NCO groups yield only one urea group in water extension, whereas each NCO group produces one urea group upon amine extension.

$$\sim NH_2 + \sim NCO \rightarrow \sim NH\text{–}CO\text{–}NH\sim$$

Additional reaction of isocyanate with urea, urethane and amide groups is also possible. Then chain branching or crosslinking occurs due to the formation of acyl urea, biuret and allophanate links onto the main chain. In order to make a linear product, water must be strictly excluded from the reaction.



$$\sim RNCO + \sim R'NHCOR' \rightarrow \begin{array}{c} R'NCOR' \\ | \\ CONHR- \end{array} - \text{acylurea}$$

$$-RNCO + R'NHCONHR'- \leftrightarrows \begin{array}{c} -R'\text{–}N\text{–}CONHR'- \\ | \\ CONHR- \end{array} \text{biuret}$$

$$-RNCO + R'NHCOOR'- \leftrightarrows \begin{array}{c} -R'\text{–}N\text{–}COOR'- \\ | \\ CONHR- \end{array} \text{allophanate}$$

Regarding the raw materials suitable for the preparation of aqueous PU dispersion, nearly any known type of polyisocyanates, polyols, and polyamines have been described. However, on isocyanate side, aliphatic isocyanates such as 4,4′-dicyclohexylmethane diisocyanate ($H_{12}MDI$), isophorone diisocyanate (IPDI), and 1,6-hexamethylene-diisocyanate (HDI) are preferred because of the lower reactivity of their NCO with water. Among cycloaliphatic isocyanates, aqueous PUs from $H_{12}MDI$ generally give finer dispersion and higher mechanical properties than those from IPDI [12]. Closer solubility parameter of $H_{12}MDI$ ($17.75(\text{cal cm}^{-3})^{1/2}$) to water (24.41) over the IPDI (13.27) and the enhanced ordering of hard segment domains due to the more symmetric structure of $H_{12}MDI$ should respectively account for the finer dispersion and better mechanical properties of $H_{12}MDI$ based PU. The use of mixed isocyanates is likely to disturb the hard segments and contribute to the soft segment–hard segment phase mixings [13]. Aromatic polyisocyanates can also be used if suitable preparation processes are followed.

Regarding the type of polyols, wide range of linear polyether, polyester and polycarbonate polyols can be used [2]. Typically polytetramethylene ether glycol (PTMG), poly(tetramethylene adipate) glycol (PTAd), and polycaprolactone glycol (PCL) are often used. Short chain diols, typically 1,4-butane diols are also used to control the hard segment content. Basic design variables are type and molecular weight. Generally, polyester gives better physical properties due to the stronger hydrogen bondings within the soft segment domains. In addition hydrogen bonding formations between ester groups of soft segment and urethane groups of hard domains contribute to the soft segment–hard segment phase mixings. On the other hand, polyether shows relatively poor physical properties and greater hydrolytic stability. Polycarbonate combines these two properties properly [10]. Soft segments from polyesters and polycarbonates having sufficiently high molecular weight (>1500) can be crystallized when the soft segment fraction is high enough [14].

Regarding the chain extender, the aliphatic or cycloaliphatic di- or triamines react with the isocyanate groups order of magnitude faster than water does. Therefore it is possible to extend the NCO-terminated prepolymer in the form of dispersion. Chain extension with polyamines such as diethylene triamine (DETA) and triethylene tetramine (TETA) leads to the internal crosslinkings [6, 15, 16]. With increasing extender functionality, modulus, strength and thermal stability as well as the water and solvent resistance of the dispersion cast films are generally increased.

Conventional polyurethane, like most polymeric materials are immiscible with water. NCO-terminated hydrophobic PU prepolymers can be dispersed or emulsified with suitable external emulsifier and strong shear forces. However the dispersions obtained in this way are coarse and storage unstable. Therefore certain type of hydrophilic modification is necessary before dispersion in aqueous media is possible. This is normally done by incorporating ionic groups [17] or hydrophilic polyether chain segments into the PU structure [18]. Polyurethanes containing ionic group in their backbone is called ionomer. Both zwitter anionic [19, 20] and cationic [21] groups have been utilized in the preparation of PU ionomer. The ionic groups are hydrophilic in nature and function as internal emulsifier. Therefore PU ionomers are self-dispersible under mild conditions.

Internal emulsifier

The main advantages of this self-emulsification are: i) dispersing processes do not require strong shear force, ii) fine particles with improved dispersion stability are obtained, iii) water sensitivity of the films after evaporation of water is reduced, and iv) resistance to nonpolar agents is high.

Ionomer

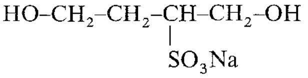
PU ionomers are structurally much more suitable for the preparation of dispersions. Though PU ionomer can be prepared in three types, i.e., anionomer, cationomer, and zwitterionomer, anionomer and cationomer are often encountered in the preparation of aqueous PU. Table 1 gives typical potential anionic and cationic compounds. Polyurethane cationomers used in aqueous dispersion are generally prepared by incorporating tertiary amine functionality into the backbone [21–23]. Some cationic PUs show unusually good adhesion to various ionic–mostly anionic–substrates such as glass and leather. They also have been proven useful in special applications, i.e., additives in the coagulation process used to make poromerics [10]. PU cationomer blends with polyacrylonitriles containing substantial amount of anionic species showed significantly improved morphology and physical properties as compared with PU anionomer and nonionomer blends [24]. Nevertheless, cationic dispersions are not used widely at present [3].

Anionic dispersions are commercially predominant. Sulfonates and carboxylates groups are most often incorporated in PU anionomers. The acid group is subsquently neutralized with a base, typically triethylamine, resulting in the formation of polyurethane anionomer. Polycarboxylates provide good hydrophobic character while polysulfonates give dispersions with excellent stability even under unfavorable conditions [1, 2]. Among dihydroxyl carboxylic acids, α, α-dimethylol propionic acid (DMPA) is most often encountered in the literature as a potential ionic center. The advantage of DMPA lies in the steric hinderance of the COOH group which prevents it from reacting with the isocyanate groups. This side reaction is not desirable because it would consume the potential ionic groups and cause high viscosities due to branching of the PU. Recently, the effect of countercations have also been reported, where ammonia, trimethylamine, triethylamine, LiOH, NaOH, and KOH were used to neutralize the COOH group [20].

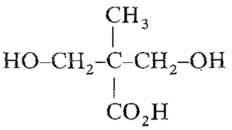
Table 1 Ionic internal emulsifiers

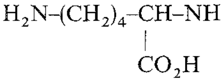
Sulfonate types

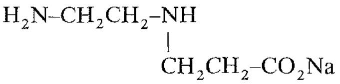
$H_2N\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}(CH_2)_x\text{-}SO_3Na$
$x = 2$ or 3


$HO\text{-}CH_2\text{-}CH_2\text{-}\underset{SO_3Na}{\underset{|}{CH}}\text{-}CH_2\text{-}OH$

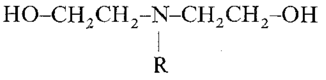
Carboxylate types

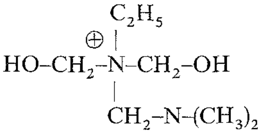

$HO\text{-}CH_2\text{-}\overset{CH_3}{\overset{|}{\underset{CO_2H}{\underset{|}{C}}}}\text{-}CH_2\text{-}OH$ + Base


$H_2N\text{-}(CH_2)_4\text{-}\underset{CO_2H}{\underset{|}{CH}}\text{-}NH_2$ + Base


$H_2N\text{-}CH_2CH_2\text{-}\underset{CH_2CH_2\text{-}CO_2Na}{\underset{|}{NH}}$

Cationic Types


$HO\text{-}CH_2CH_2\text{-}\underset{R}{\underset{|}{N}}\text{-}CH_2CH_2\text{-}OH$ + Acid/Alkylating Agent


$HO\text{-}CH_2\text{-}\overset{C_2H_5}{\overset{\oplus\,|}{\underset{CH_2\text{-}N\text{-}(CH_3)_2}{\underset{|}{N}}}}\text{-}CH_2\text{-}OH$ + Acid/Alkylating Agent

Nonionomer

Another approach to obtain internally emulsifiable PU employs polyether, predominantly from ethylene oxide, chain segment [18]. Though it appears convenient to replace some of the hydrophobic polyols by polyethylene oxide (PEO), this technique is not very effective. It is necessary to build a high number of hydrophilic polyether segments into the PU to obtain stable dispersions. This makes the film very water sensitive. The dried coatings are often water swellable or even water soluble. For most coatings applications, water sensitivity should be minimized. A balance between dispersibility and water resistance of the dried products can be achieved by incorporating PEO segments into lateral or terminal positions of the PU chains [25–27]. This is possibly done by using either modified diols or diisocyanates as building blocks or by employing monofunctional PEO as such. However the dispersions obtained by this way have generally poor storage stability [28]. Another distinctive feature of nonionic dispersion is that thermocoagulation is possible due to the negative temperature gradient of solubility of hydrophilic polyether segments in water [1]. This often poses problems during the process of emulsification [28].

Combination of ionic groups and hydrophilic segments

Since the incorporation of ionic centers and hydrophilic PEO segments leads to a different stabilization mechanism, a considerable difference in marcroscopic properties is expected. Advantages of one type of dispersion may be offset by disadvantages.

Nonionic dispersions have technical advantages over the ionic ones in terms of stability against electrolytes, freezing, and strong shear forces. Among these, stability against the electrolytes and additives are especially important since many of the practical formulations include pigments, fillers, thickner, and other additives. On the other hand, nonionomer dispersion is unstable to heating due to the decrease of polyether solubility in water with increasing temperature.

Fortunately, combination of ionic and nonionic hydrophilic segments in the same PU has been attempted and desirable synergistic effects in terms of dispersion stability and fine particle size at an overall reduced hydrophilic group content have been reported [25–27]. For example, in PTAd-IPDI-DMPA system, when 20% of the PTAd was replaced by PEO, particle size decreased from 0.3 to 0.1 μm [29].

Dispersion mechanism

PU ionomer solution in polar solvent such as acetone and methyl ethyl ketone spontaneously form dispersion when water is stirred in. The transformation of an organic solution into an aqueous dispersion takes place in several steps. Following Dieterich [1], the initial addition of water results in a sharp drop of viscosity owing to the reduction of ionic associations. The ionic associations, formed upon the neutralization of potential ionic centers, are a reversible process, and any water present reduces the interchain ionic associations. As more water is added, the solvation sheath of the hydrophobic chain segments decreases owing to the decrease in acetone concentration, and the viscosity increases via the hydrophobic interactions induced by the alignment of hydrophobic chain segments. Further addition of water produces a turbidity, indicating the beginning of a dispersed phase formation, and subsequently turbidity increases and the viscosity drops owing to the rearrangements of the agglomerates to microspheres where the ionic groups are situated on the particle surfaces.

Recent studies on dispersion suggested, based on the viscosity and conductivity measurements, that water is first adsorbed on the surface of the hard segments microionic lattices, and then enters successively into the disordered and ordered hard domains [21]. Dispersion can disrupt the order of hard domains, and hence the phase separations between the soft and hard segments.

Particle stabilization

The stabilizing mechanisms of ionomer dispersion and nonionomer dispersion are different [1, 2]. The ionomer dispersion is stabilized by the formation of electrical double layers between the ionic constituents which are chemically bound to the PU, and their counterions which migrate into the water phase around the particle. The interference of the electrical double layers of different particles results in particle repulsion, leading to the stabilization mechanism of dispersion. Addition of inert electrolytes to the ionomer dispersion provides additional ions in the water phase which reduces the range of double layer repulsion, and induces coagulation.

In nonionomer dispersion, the hydrophilic PEO segments are anchored on the surface of the particle, stretching into the water phase. The stabilization mechanism for this type of particle structure can be explained in terms of entropic repulsion. When the particles approach closely, the freedom of motion of PEO chains in water phase is restricted, leading to a reduction of entropy. Therefore repulsion between particles is driven spontaneously.

Preparation process

The earliest process to prepare the aqueous PU dispersion was the acetone process which still remains technically important [10]. During the last couple of decades several new processes have been developed. A common feature to these processes is however that the first step is to prepare the NCO-terminated PU prepolymers of medium molecular weight. The critically different step among the various processes lies in the chain extension step which is normally performed using amines [2]. In chain extension step, control of extremely fast NCO–NH reaction accompanied by the viscosity rise is the most important parameter to control.

Acetone process

NCO-terminated PU prepolymers are chain extended with diamine in an organic solvent such as acetone, methyl ethyl ketone, or tetrahydrofuran, followed by mixing with water to form dispersion, and removal of the solvent by distillation. This well established process uses an organic solvent to control the viscosity during the chain extension step. Acetone is especially suitable because it is inert with the PU forming reactions, miscible with water, and has a low boiling point. In addition, it reduces the high NCO–NH reactivity through reversible ketimine formation. The advantages of acetone process includes wide scope of variation in structure and emulsion, high quality of end products, and reliable reproducibility. These advantages are mainly due to the fact that the polymer formation is accomplished in a homogeneous solution. However, PU obtained in acetone process is predominantly linear and soluble in acetone since the chain extension is carried out in acetone. Distillation of large amount of acetone makes the process economically unfavorable. This process also suffers from a low reactor volume yield due to the large quantities of solvent used.

Prepolymer mixing process

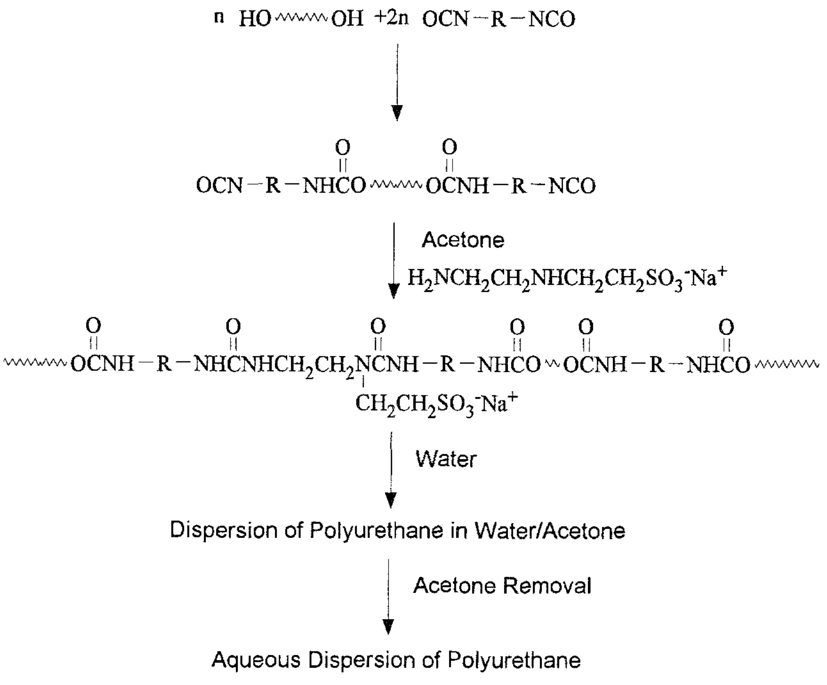
The prepolymer mixing process avoids the use of large amounts of solvent. Hydrophilically modified NCO-terminated PU prepolymers are mixed with water to form emulsion. The viscosity of prepolymer is critical and must be limited or the dispersion step will be difficult. Therefore this process is suitable for low viscosity prepolymer. A small amount of solvent can be added to the prepolymer to reduce the viscosity. Chain extension is accomplished by the addition of di- or polyamines to the aqueous dispersion. Dispersion step has to be carried at low enough temperature so that the NCO–water reaction is insignificant. For this reason, cycloaliphatic diisocyanates are most often used due to their low reactivity with water.

Since the chain extensions are performed in a heterogeneous phase, they do not proceed in a quantitative way. As a result, the properties of PU dispersion prepared in this process are generally inferior to those from acetone process.

Melt dispersion process

Problems related to the amine chain extension are avoided in this process. The NCO-terminated PU prepolymers are reacted with an excess of ammonia or urea, resulting in a prepolymer with terminal urea or biuret groups. This capped oligomer can be readily dispersed in water without

Fig. 1 Acetone process



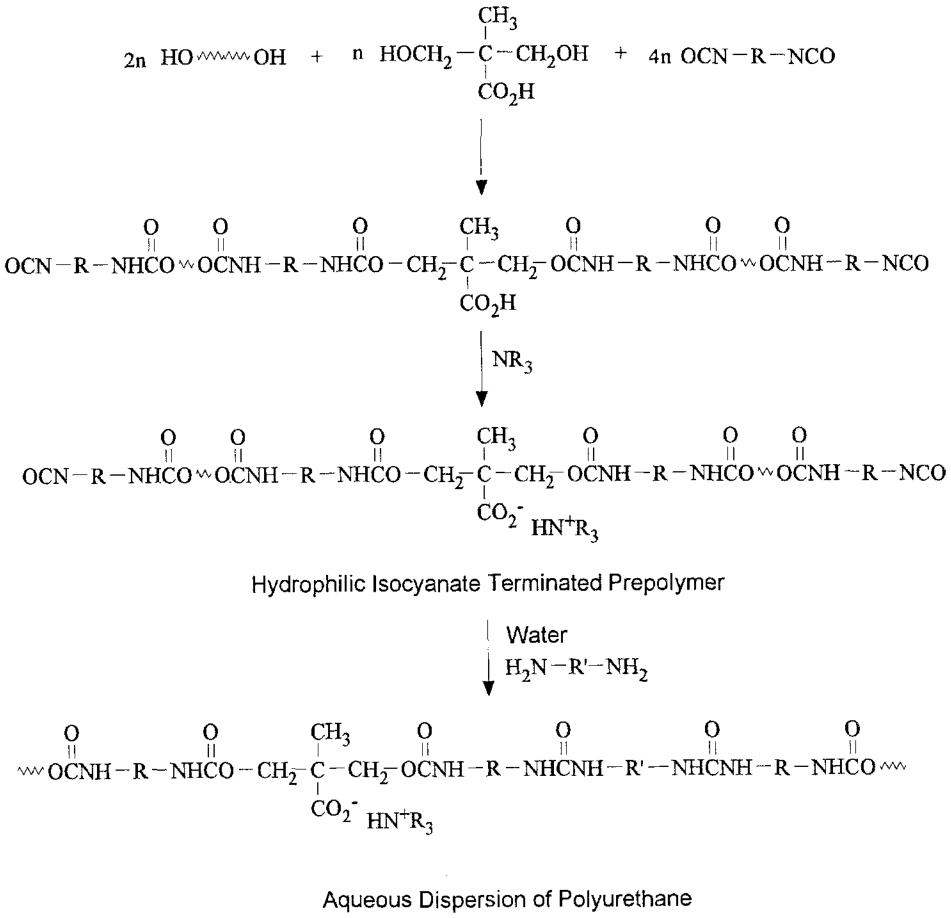


Fig. 2 Prepolymer mixing process

any organic cosolvent. The reaction with urea is carried out at high temperature ($>130\,^{\circ}C$), and the resulting oligomers are usually dispersed at sufficiently high temperature ($>100\,^{\circ}C$) to reduce the viscosity. Chain extension is accomplished by methyololation of the biuret groups with formaldehyde.

Ketimine and ketazine processes

The ketimine and ketazine processes are similar to the prepolymer mixing process, with one important difference that a blocked diamine and a blocked hydrazine are respectively used as a latent chain extender. Diamines and hydrazines are reacted with ketones to yield ketimines and ketazines, respectively. Ketimines and ketazines are practically inert toward the isocyanates in normal processing conditions. These are mixed with the NCO-terminated prepolymers containing ionic groups without premature extension. Chain extension occurs simultaneously with dispersion formation. Reaction with water liberates the diamine or hydrazine, which reacts with the prepolymer. Dispersions prepared by this process yield high performance coatings. PU dispersion from aromatic isocyanates are easily accessible in this process.

Physical properties

In this section some typical physical properties of PU dispersion along with those for derived films and film forming properties will be discussed.

Dispersion properties

Unlike the solvent-borne PU, the particles must first rejoin into a continuous organic phase before the individual polymer chains can entangle and develop the ultimate film. Poor coalescence can result in low gloss films, and usually in a reduction of overall physical properties. The particle size of aqueous dispersions can be varied from about 0.01 to 5 μm and has a direct impact on the dispersion stability. Dispersions with relatively large average particle size (1 μm <) are generally unstable with respect to sedimentation. Dispersions with smaller average particle size are

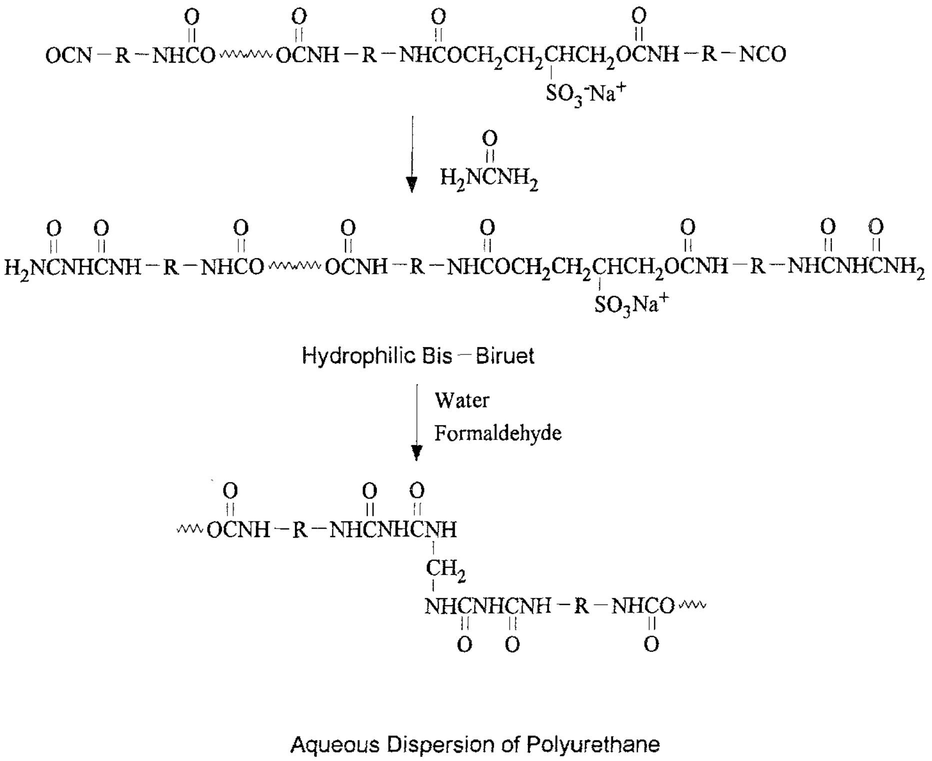


Fig. 3 Melt dispersion process

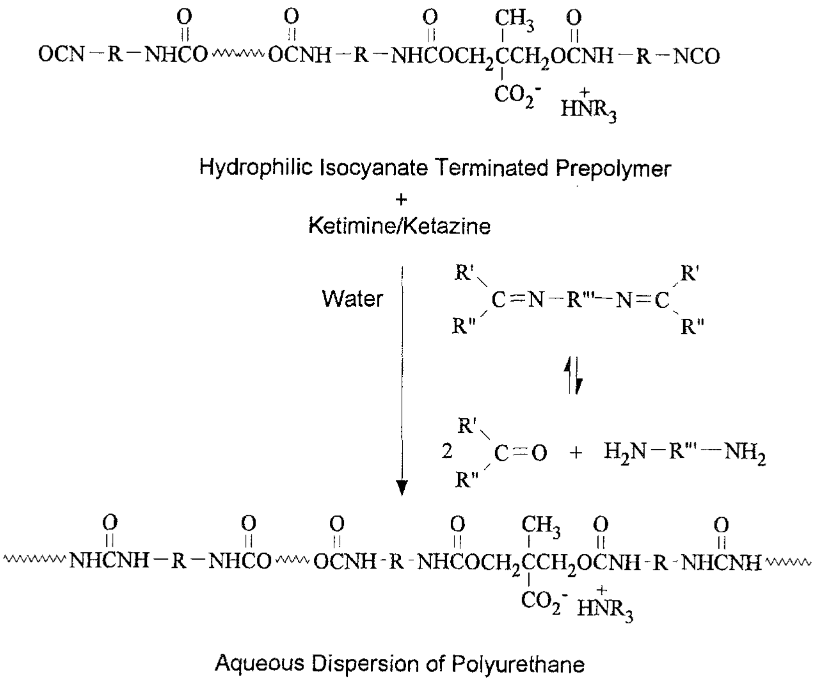


Fig. 4 Ketimine and ketazine process

more useful since such dispersions are storage stable and have high surface energy, which results in a strong driving force for film formation [3]. Therefore ability to control the particle size is practically important. Since the particle diameter lies over several orders of magnitudes the appearance can vary from an opaque translucent sol to a milky white dispersion [30]. In fact, PU dispersion is a good example in that there is no distinct boarderline between solution, colloidal sol, dispersion, suspension and latex [1].

The particle size of PU dispersion is more or less controlled by such mixing conditions as rpm and temperature. However, it is mostly governed by the overall hydrophilicity of the PU, i.e., higher hydrophilicity of PU leads to smaller particle size [31]. Typical examples are shown in Fig. 5 for PU cationomer dispersions [22]. The decrease of average particle size with increasing *N*-methyldiethanolamine (MDEA) content is clearly seen.

The ionomer dispersions show an asymptotic decrease of particle size with ionic content. This behavior is due to the dual effect of ionic centers. That is, particle size is decreased due to the increased hydrophilicity, and increased by the increased water swell, and an overall asymptotic behavior is expected.

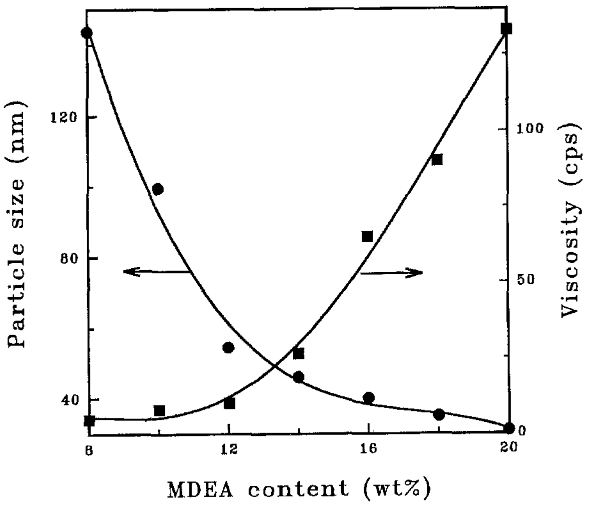
Aqueous PU dispersion has relatively low viscosity. Typical commercial grades have their room temperature viscosity, 10–700 cP, with typical solid content, 30 ~ 40%. Typical dispersion viscosities are also shown in Fig. 5 where a dramatic variation of viscosity with ionic content is noted.

Dispersion viscosity (η) is directly proportional to the effective volume fraction of dispersed phase (ψ) at low dispersed phase concentration ($\psi < 0.02$), and concentration dependence becomes more pronounced at high ψ, generally expressed as follows [32]:

$$\frac{\eta}{\eta_s} = 1 + k_1\psi + k_2\psi^2 + \cdots ,$$

where η_s is the viscosity of medium, and k's are constant. Since net solid content of typical PU dispersion is over 30 wt%, higher order terms should contribute significantly as shown in the figure. Swellability, which generally increases with increasing hydrophilicity of raw materials also contributes to the effective volume fraction of the dispersed phase in the above equation. Electroviscous effect of ionomer dispersion also increases the viscosity.

Fig. 5 Average particle size and dispersion viscosity as a function of cationic content



Film properties

PU dispersions exhibit excellent film-forming properties even at low temperature. They can be improved by the addition of high boiling coalescent solvents such as *N*-methylpyrrolidinone or ketone, or by addition of plasticizers. Coalescent agents are often necessary with crosslinked PU dispersions, since the film forming ability decreases with increasing crosslink density. Film forming properties are also improved with higher drying temperature.

General structure-property relationship of dispersion derived film is essentially the same with solvent-borne PU. The overall film properties are determined by the type and amount of soft and hard segments, soft segment–hard segment phase separation, crosslinking density, etc. [33]. However, there are certain properties of dispersions that are generally inferior to the solvent-borne two-component PUs. These include water swell resistance, hydrolytic stability, and solvent resistance [1]. Since these properties are related to the very nature of dispersion, the improvement is also limited [2]. Water swell resistance and hydrolytic stability increases with decreasing amounts of ionic centers, in which case formation of stable and fine dispersions becomes difficult. Solvent resistance could be improved with increasing crosslinking density, which on the other hand, makes the film formation difficult due to increased glass transition temperature and hence the film-forming temperature. It is however possible to minimize these disadvantages by using formulations which have a careful balance in terms of the amount of hydrophilic groups and the degree of crosslinking.

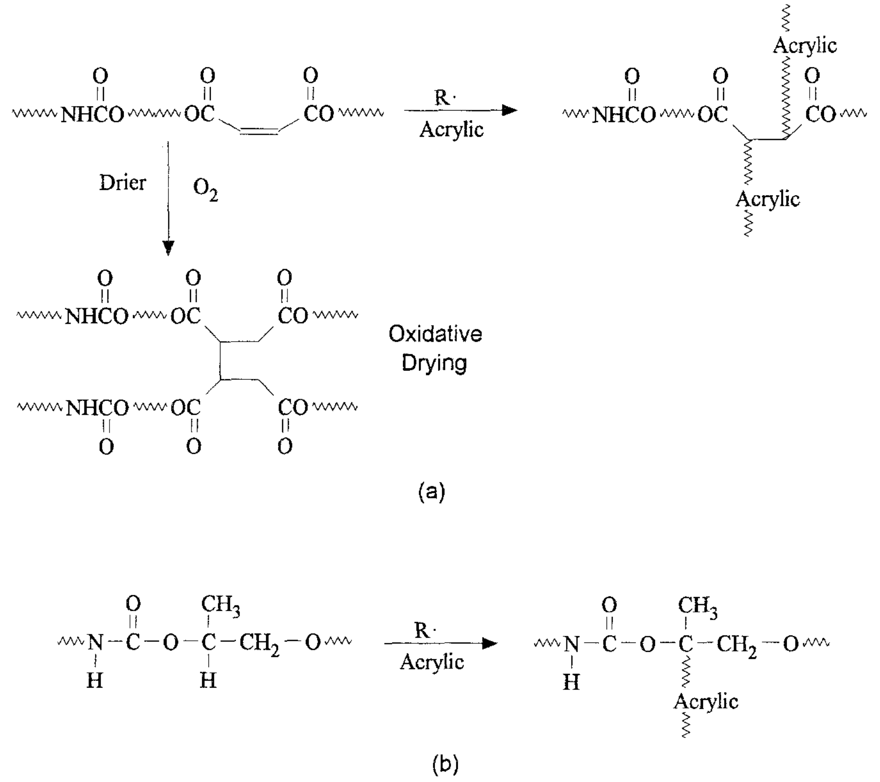
Modifications

The objective of modification is to improve certain properties such as water, solvent, and general chemical resistance, and the mechanical properties of the films. Among others, graftings, and crosslinkings are most often encountered [2, 30]. Blending and interpenetrating polymer network are also subjects of recent attempts to modify these properties [8, 9].

Grafting and block copolymerization

Grafting is usually accomplished in the aqueous phase using the conventional emulsion polymerization techniques.

Fig. 6 Grafting of acrylic monomer onto unsaturated polyester polyvol (a) and propylene glycol (b) segment of polyurethane ionomers



Monomer and free radical initiator are added to the aqueous phase [5]. Both anionic and cationic PUs containing unsaturated polyester polyols (Fig. 6a) and polypropylene glycol (Fig. 6b) in their backbone have often been used to graft acrylate monomers onto the main chain [2]. Anionic PUs containing carboxylate salt can be further crosslinked with epoxy resins.

Though grafting is a useful technique to modify the PU ionomer, it is generally limited to PU containing unsaturated polyester and polypropylene glycol segments. PU ionomers can be modified in a similar way to the ultra violet (UV) curing. NCO-terminated PU prepolymers containing potential ionic groups are first capped with a reactive diluent such as 2-hydroxy ethyl acrylate (HEA) via polyaddition. Then the potential ionic groups are neutralized and acrylate monomers polymerized at the HEA termini via a radical polymerization mechanism. The solution is dispersed with water stirred in. As a result, block copolymers of PU ionomers and polyacrylates are obtained. Various types of acrylates such as methyl methacrylate (MMA), ethyl methacrylate (EMA), *t*-butyl methacrylate (*t*-BMA), cyclohexyl methacrylate (CHMA), tripropylene glycol diacrylate (TPGDA), and trimethyl propane triacrylate (TMPTA) have been incorporated in PU ionomers from H_{12}MDI–PCL–DMPA [4]. With MMA incorporation, swell in water is significantly decreased, together with the increase in contact angle with water (Fig. 7). With acrylate incorporation, hardness, modulus, and elongation at break are significantly increased.

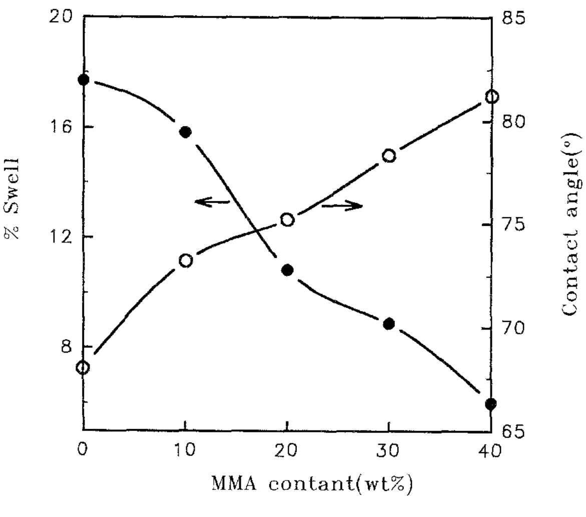


Fig. 7 Effect of MMA content on water swell and contact angle of PU acrylate films (% based on solid)

Regarding the microstructure, acrylates contribute to the hard segment domains since they are more likely miscible with the hard segment of PU. As a result, soft segment characteristics disappear. Then with increased

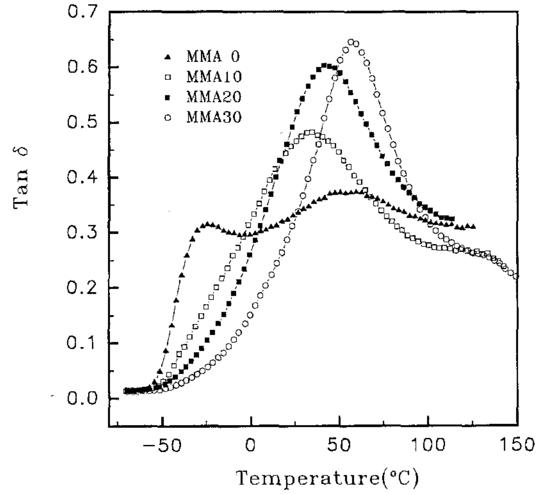


Fig. 8 The tan δ curve of PU acrylate films as a functions of MMA content

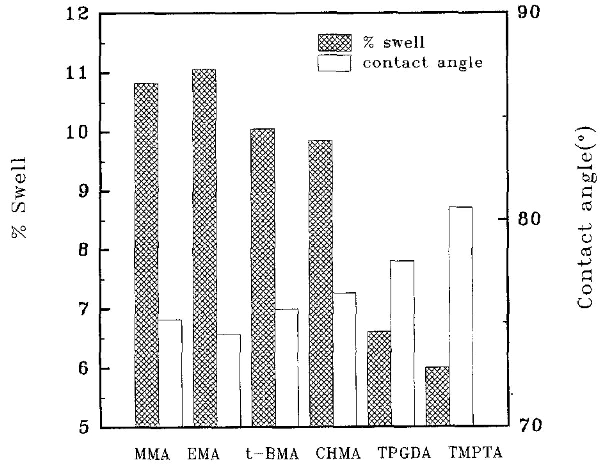


Fig. 9 Effect of acrylate type on water swell and contact angle of PU acrylate films

hard domain fraction, the soft segment glass transition disappears and hard segment glass transition moves toward the higher temperature (Fig. 8).

Regarding the effect of acrylate type contact angle with water increases with increasing acrylate functionality, due probably to the increased crosslinking density of the PU acrylates, especially in their hard domains (Fig. 9). Among monoacrylates such as MMA and EMA monomer with a large substituent group generally shows relatively little swell and large contact angle, due presumably to the hydrophobicity of large alkyl substituents. It seems that mechanical properties as well as water resistance of PU ionomers can be properly improved by proper selection of acrylate monomer to incorporate in PU.

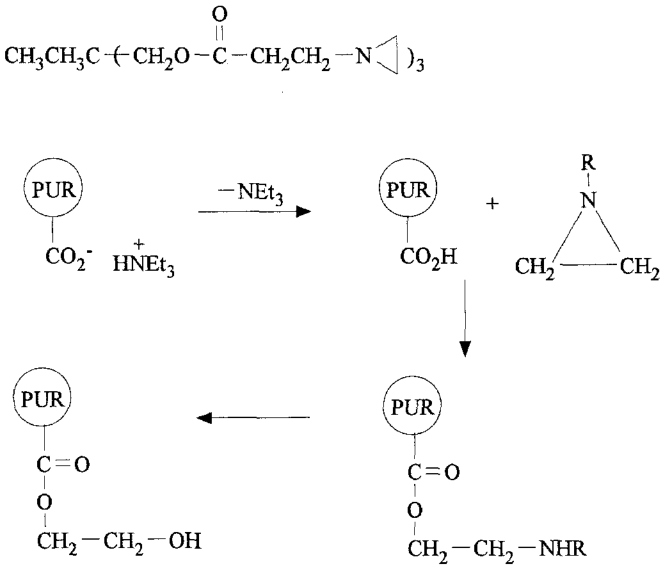


Fig. 10 Crosslinking with polyfunctional aziridine

External crosslinking

Aqueous PU dispersion can be crosslinked in much the same way as the other water-borne polymers. Most reactions center on the carboxylic acid groups [34].

Aziridines

Polyaziridines, especially trifunctional aziridines have been extensively used for crosslinking anionic type PU dispersions. The aziridine must be added just prior to the application since it can lose activity after 2 days' storage in water at room temperature [2]. A desirable feature of polyaziridines is that the cross-linking reaction proceeds at low temperature. A negative feature is that there is some doubt about the toxicity of this class of products.

Blocked isocyanates

A blocked isocyanate is an isocyanate which has been reacted with a material which will prevent its reaction at room temperature with compounds that conventionally react with isocyanates but will permit that reaction to occur at higher temperature [35]. Blocked isocyanates have been widely used both in conventional and water-based polyurethanes [36]. Examples of blocking agents which have been commercially used are caprolactam and methyl ethyl ketoxine. Water-based blocked PU prepolymers can be made by blocking the NCO-terminated prepolymers with a suitable blocking agent, followed by

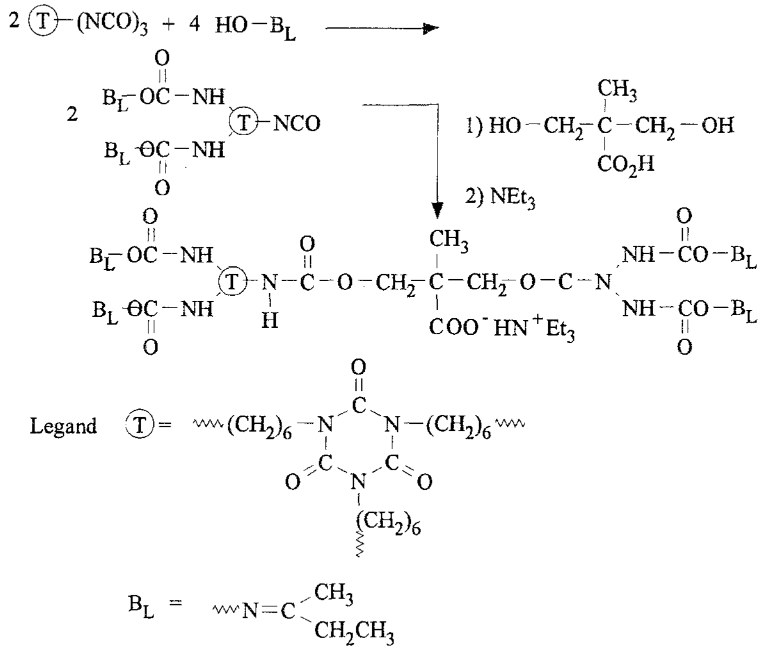


Fig. 11 Crosslinking with blocked isocyanate

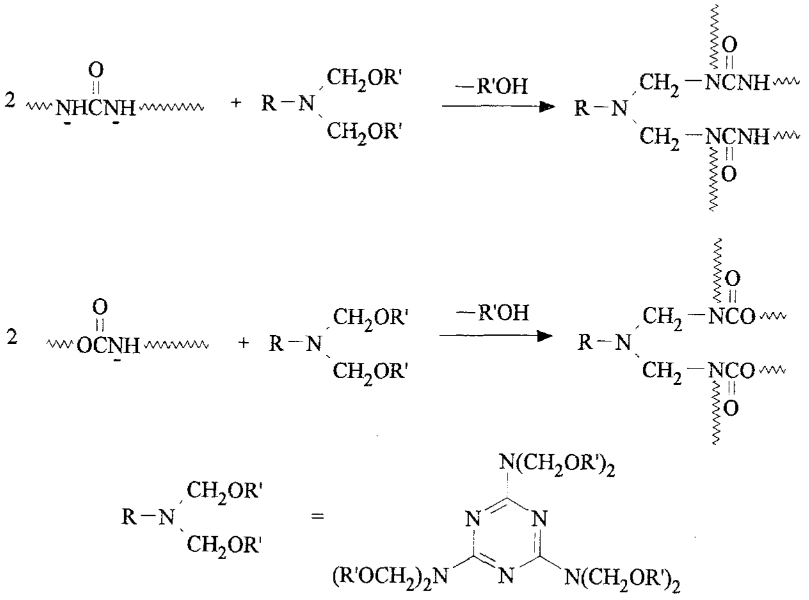


Fig. 12 Crosslinking with melamine/formaldehyde resin

neutralization and emulsification in the normal fashion. Dispersions of this type may either be used as the sole component of a coating formulation or alternatively used as crosslinkers for the linear types.

Melamine/formaldehyde resin

The use of melamine/formaldehyde as crosslinkers is well established, especially in connection with acrylic polymers. In the case of polyurethane dispersion, the crosslinking generally occurs at elevated temperatures, and proceeds via either the urethane or urea linkages [2].

Radiation induced crosslinking

The UV or electron beam curing saves energy, and reduces or eliminates solvent emission. Therefore, this technique has become commercially important ranging from protective coatings to photoresists for fabrication of microelectronic devices [36–38]. Most of the commercial systems use acrylic-based monomers and resin which cure by a free radical mechanism. Recently, there has been a growing trend in this area for the use of water-based radiation curing [39]. The main reason for this is that the amount of acrylic monomer used as reactive diluent can either be greatly reduced or even eliminated. This implies that usually better physical properties of the derived cured system are achieved. The low dispersion viscosity is another advantage compared with the conventional solid type which requires a very high proportion of reactive diluent to reduce workable viscosities, with corresponding decrease in physical properties [2].

To prepare the water dispersible PU acrylates, the NCO-terminated PU ionomer prior to emulsification is reacted with a hydroxy acrylate [38, 39]. Then the mixture of PU acrylates, reactive diluent, and photoinitiator are cast on a glass plate, and irradiated. Considerable work has recently been devoted to develop water soluble photoinitiators for this system.

Applications

Aqueous PU dispersions are predominantly linear polymers and have found applications in area previously dominated by conventional solvent-borne polyurethane coatings. In addition, aqueous dispersions find their applications as adhesives on a variety of substrates. Some of these applications are listed below [3]:

Coatings for flexible substrates

- textile
- paper
- rubber
- leather
- vinyl
- film and foil

Coatings for finishing

- machine housing
- metal primer
- plastic parts

Coating for wood

- furniture
- paneling
- flooring
- sealers

The earliest application of aqueous PU dispersions was for textile coating which is still one of the largest market area [40, 41]. Coagulation of films of aqueous PU dispersion and subsequent lamination onto textile results in promerics. Promerics are microporous plastics which are permeable to air and water vapors, but impermeable to water. Promerics are used as coating on split leather, and especially in the preparation of leather substitutes.

Aqueous PUs are used as sizing agent for textile fibers to provide increased tensile strength and resistance to dry cleaning solvents and aqueous detergent solutions [41, 42]. Paper fibers are also sized with aqueous PUs to increase the strength of paper as well as to reduce the tendency to ink to run on the surface [42]. Isocyanate or blocked isocyanate containing PUs show excellent adhesion to cellulous materials. Wood coating, especially for flooring, are made using aqueous PU as such or with waterborne acrylics. PU coatings provide high gloss, high abrasion resistance, and high fouling resistance to most household cleansers. Organic solvent aggressively attack many plastic surfaces. Aqueous PU dispersions having good adhesion properties are useful for plastic coatings.

For adhesive applications, aqueous PU dispersions have been used for a number of polymer substrates, usually in combination with other polymer to lower cost. Polyurethane ionomers have good adhesion to natural and synthetic rubber surfaces, and can be used in the manufacture of footware [42, 43].

PU ionomer dispersions have been used as media in which monomers have been polymerized. This technique is known as latex interpenetrating polymer network, and is useful to control the phase separation. Aqueous PU dispersions are also used for metal coatings such as metal primers, coil coating resins, and as wire coatings. Cationic electrodeposition coatings are widely used for automotive metal primers which provide excellent corrosion resistance to car bodies. More details regarding the patent applications are found in ref. [2].

Conclusions

The development of aqueous polyurethane dispersions has been motivated primarily by environmental considerations. A variety of aqueous polyurethane dispersions have been developed and successfully applied for textile coatings, fiber sizings, and adhesives for a number of substrates. They are basically one component fully reacted and predominantly linear polymers. There are certain types of properties such as resistance to water and solvent which are inferior to the conventional solvent-borne polyurethanes. These properties are related to the very nature of dispersion, viz. hydrophilicity and linearity, which apparently make the improvement limited. However, these problems have properly been reduced or even resolved by introducing crosslinkings, graftings and other methods.

Since the performance of aqueous polyurethane dispersion is comparable in many ways to that obtained from solvent-borne polyurethane and air pollution regulation becomes stringent in many countries, the market for aqueous polyurethane dispersion seems to grow continuously.

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