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Phosphated polyurethane–acrylic dispersions: synthesis, rheological properties and wetting behaviour

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Abstract

Phosphated polyurethane–acrylic dispersions were prepared by a new method that is free from organic solvents and requires a very low dispersion force. After the carboxylic acid groups of the phosphated polyurethane were neutralised by suitable bases, water was added to form the phosphated polyurethane seed dispersion. Polyurethane–acrylic dispersions were obtained from the phosphated polyurethane seed by emulsion copolymerisation. The polyurethane seed polymer was found to be stable over the initiator concentration used and the rheological properties of the polyurethane acrylics were found to follow Newtonian behaviour under the prescribed experimental conditions. This is a good indication that the dispersions may be used as pigment wetting media. The dynamic contact angle study showed the poor wettability of the phosphated polyurethane–acrylic dispersion films, indicating good hydrophobicity. © 2002 Elsevier Science Ltd All rights reserved.

Keywords: Phosphated polyurethane–acrylic dispersions; Rheological properties; Particle size

1. Introduction

Polyurethane dispersions are a growing field of interest for both academic and commercial reasons. Most commercial polyurethane dispersions are prepared either by the solvent or pre-polymer process [1]. In the case where a high molecular weight polymer is prepared in an organic solvent (acetone or butanone), so as to reduce the viscosity of the reaction mix, distillation of the organic solvent after dispersion in water is required. The amount of solvent used is generally high (40–60%), due to the low temperatures of the urethane-forming reactions resulting in high viscosity. If the organic solvent distilled after the dispersion process is to be reused for a subsequent batch, it has to be recycled to remove all traces of water. Overall, the solvent process yields a low reactor-volume product. Polyurethane dispersions prepared by the pre-polymer process, on the other hand, though free from organic solvents, have higher viscosities and dispersing requires the use of powerful mixers [2]. The chain extenders used in the aqueous phase of the pre-polymer method are also limited to highly nucleophilic amines due to their fast reaction velocity with the isocyanate in the presence of water.

These two processes are currently used to prepare polyurethane, polyurethane–urea and polyurethane–acrylic dispersions. Polyurethane–acrylic dispersions are becoming an increasingly important class of dispersions since it combines the high abrasion resistance and excellent mechanical properties of the polyurethanes and good weathering properties of the acrylics. Many researchers have reported the benefits of aqueous polyurethane–acrylic dispersions, prepared either by the organic solvent or pre-polymer method [3–7]. To our knowledge, the preparation of such dispersions by any other method has not been reported. In the present study, the rheological and wetting properties of phosphated polyurethane dispersions prepared by a new method that are free from organic solvent and that do not require the use of powerful mixers were investigated.

2. Experimental

2.1. Chemicals used

A phosphated polyester macroglycol was synthesised from a phosphate monomer, a dicarboxylic acid and a diol as described in our previous publication [8]. Dicyclohexane–methane–diisocyanate was obtained from Bayer, Germany.

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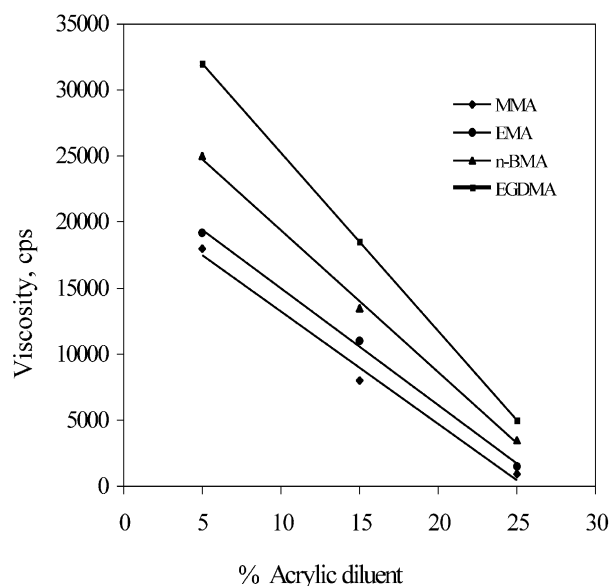


Fig. 1. The effect of the acrylic diluent on the viscosity of phosphated polyurethanes, 70/30 soft to hard segment content.

2,2-Hydroxymethyl propionic acid (DMPA) was purchased from Perstorp Polyols, Sweden. 2-Hydroxyethyl methacrylate (2-HEMA), methylmethacrylate (MMA), ethylmethacrylate (EMA) and *n*-butylmethacrylate (*n*-BMA) were obtained from Mitsubishi Rayon, Japan, while ethylene glycol dimethacrylate (EGDMA) was obtained from Inspec. LiOH, NaOH, KOH, triethylamine, tripropylamine, tributylamine and morpholine were used as neutralising bases. The macroglycol was degassed at 90 °C overnight under reduced pressure to remove any moisture. The other chemicals were used as received.

2.2. Synthesis of the phosphated polyurethane–acrylic resin

A 1 litre-glass reactor equipped with a mechanical stirrer, a charging and sampling port, a nitrogen inlet and outlet was charged with the phosphated polyester macroglycol and excess dicyclohexane–methane–diisocyanate. The reaction took place at 95 °C over 1.5 h. This temperature was maintained to avoid any competitive secondary reactions, such as the formation of allophanates [9]. The temperature was then reduced to 60 °C and DMPA was added and allowed to react with the isocyanate (–NCO) for 1 h. During this stage the acrylic monomer of choice was added to reduce the viscosity. Finally, 2-HEMA was added as a chain extender and allowed to react with the –NCO groups for 2 h, to complete the reaction. The reaction temperature was kept to 60 °C to prevent thermal polymerisation of C=C. Control polyurethane–acrylic polymer was synthesised in a similar way, except that the acrylic diluent was substituted with acetone (which was later distilled off) for particle size analysis.

2.3. Neutralisation of the acid groups, dispersion and copolymerisation

The acid groups of the 2-HEMA-terminated phosphated polyurethanes were neutralised using one of the bases described in Section 2.1 and water was added to form the dispersion. Internally cross-linked phosphated-polyurethane–acrylate particles were obtained by adding an aqueous solution of 0.5% potassium persulphate (based on the total solids content) into the aqueous dispersion over 1 h at 65 °C. The emulsion copolymerisation reaction was carried out for 5 h.

2.4. Characterisation

The rheological properties of the acrylic-modified phosphate-based polyurethane solutions and dispersions were measured with a Brookfield viscometer, model LVTDV-II, over the prescribed temperature range. The viscometer was equipped with a small sample adapter that allows temperature control by means of a circulating water bath. Calibration was done with a viscosity standard, supplied by Brookfield. The temperature of the solution was varied from 15 to 60 °C and the shear rate varied from 0 to 200 s⁻¹, in increments of 40 s⁻¹. Particle-size measurements of the dispersions were done using a Malvern Zetasizer Model 3000HS at 25 °C. Dynamic contact angle measurements were done using a CAHN DCA-322 analyser operating at 25 °C, and a velocity of 100 μm/s.

3. Results and discussion

3.1. Rheological properties

Fig. 1 shows the viscosities of HEMA-terminated and fully reacted phosphated polyurethanes, before dispersion, prepared with different quantities of reactive diluents. The viscosity of the 2-hydroxyethylmethacrylate-terminated phosphated polyurethane was reduced by an order of magnitude during processing. This means that the process of synthesising polyurethane dispersions free of organic solvents was made possible by the use of these reactive diluents. The reduction in viscosities brought about by the methacrylates was in the order: MMA, EMA, *n*-BMA and EGDMA.

The reduction in viscosity upon addition of these monomethacrylates is directly proportional to the viscosity of the pure methacrylate type, as shown in Table 1. The viscosity of *n*-alkyl methacrylates increases with chain length, and as a result, *n*-BMA gave slightly higher resin viscosity than EMA and MMA at the same concentrations. The resin viscosity with the EGDMA was generally higher than the monomethacrylates studied due to the higher viscosity of the dimethacrylate.

The rheological profiles of the phosphated-urethane

Table 1
Solubility and viscosity of the methacrylate monomers and the reduced viscosity of the phosphated polyurethane resin

Monomers	Solubility in water at 25 °C	Viscosity of the acrylate monomer (cps)	Viscosity of the phosphated polyurethane polymer (80/20 soft to hard segment and 20% reactive diluent) (cps, at 20 °C)
MMA	1.72	0.56	950
EMA	0.46	0.62	1500
<i>n</i> -BMA	0.04	0.92	3500
EGDMA	–	–	5000

acrylics before and after dispersion in water are shown in Figs. 2 and 3, respectively. Because of the wide range of the viscosities of the dispersions, different shear rates were necessary to keep within the range of the viscometer. A least-squares fit to the power law [10] was used when necessary to extrapolate the viscosity to 1 s^{-1} .

According to the power law,

$$\eta = m\gamma^{n-1} \quad (1)$$

where η is the measured viscosity, γ the shear rate, m and n are empirically determined parameters for a given system. For Newtonian fluids, n equals 1 and then m becomes the viscosity.

For all the systems depicted in Figs. 2 and 3, n was calculated to be between 0.96 and 1, indicating Newtonian behaviour.

The viscosity of a polymer solution (including water-dispersible systems) depends on temperature [11], the polymer fraction [12] and polymer molecular weight [13]. For coating application, the polymer fraction and temperature are major factors in ensuring proper film thickness and ease of application. Figs. 4 and 5 show the shear stress versus shear rate of the phosphated polyurethane–acrylic dispersions at different polymer concentrations and temperatures, respectively. All the graphs are linear, indicating that the shear stress stays Newtonian with respect to both shear rate and temperature. A number of papers [14,15] have described the more beneficial properties of hydrophobic emulsion polymers containing chemically bound

hydrophilic stabilisers than the adsorbed surfactants used in current emulsion polymerisation. They showed that particle charge derived from copolymerised monomer is more effective against mechanical shear coagulation than adsorbed charge, because of differences in the ability of charges to move about the surface of the particle. Among the prominent advantages of the use of chemically bound stabilisers are higher mechanical stability, better water resistance in paper, textile and other coatings applications, increased ageing resistance and no surfactant migration.

Thus, the phosphated polyurethane–acrylic dispersion formulations of the present study with Newtonian fluid behaviour could be useful as a pigment-dispersing medium. Huang et al. [16] tried polyester-based, anionic polyurethane dispersions as pigment grinding media under standard grinding conditions using a ball-mill. Their findings suggested the possible use of these ionomers for pigment grinding, provided that they are shear stable. In another study, Wang et al. [17] found the shear thinning and pseudoplastic behaviour of polyurethane dispersions synthesised from polyethylene oxide glycol and dimethylol propionic acid which was unstable for use as pigment grinding medium. Non-Newtonian behaviour is associated with pseudoplastic or thixotropic flow. The former is caused by the agglomeration of particles due to destabilisation and the latter when a pre-existing structure, such as that caused by hydrogen bonding, is disturbed. In an earlier study [18], we have described the use of phosphated polyester-based urethane ionomers as dispersion medium for pigments to be

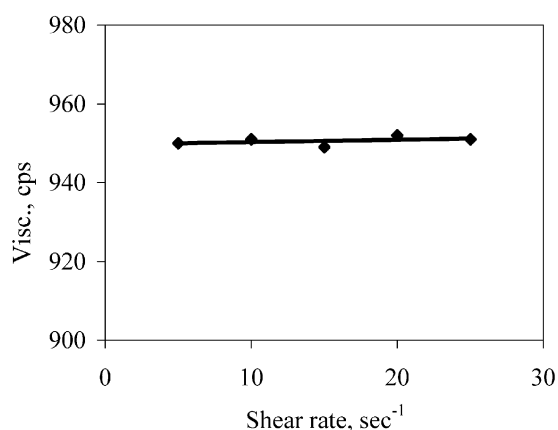


Fig. 2. The effect of shear rate on the viscosity of a phosphated polyurethane before dispersion, 20% MMA.

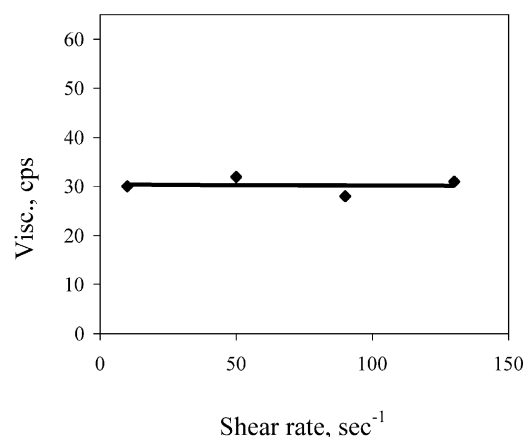


Fig. 3. The effect of shear rate on the viscosity of a phosphated polyurethane–acrylic dispersion; 20% MMA, 35% solids in water.

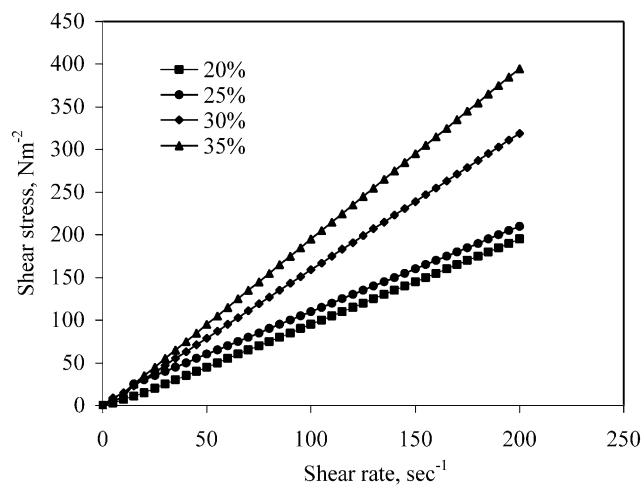


Fig. 4. Shear stress versus shear rate for phosphated polyurethane–acrylic dispersions of different concentration at 25 °C.

used in emulsion system. In the present study the rheological equation of state for the phosphated polyurethane acrylate ionomers also complies with Newtonian behaviour.

3.2. Particle size measurements

The copolymerisation of acrylic and/or methacrylic ester monomers with phosphated polyurethane seed dispersions is a classical seeded emulsion polymerisation system. In a typical emulsion polymerisation system with added surfactant, the seed polymer is first synthesised and may be subjected to a cleaning procedure, for example, ultrafiltration to remove extra surfactants and initiator decomposition products [19]. Additional monomer and initiator are added into the seed and then further polymerisation yields the final

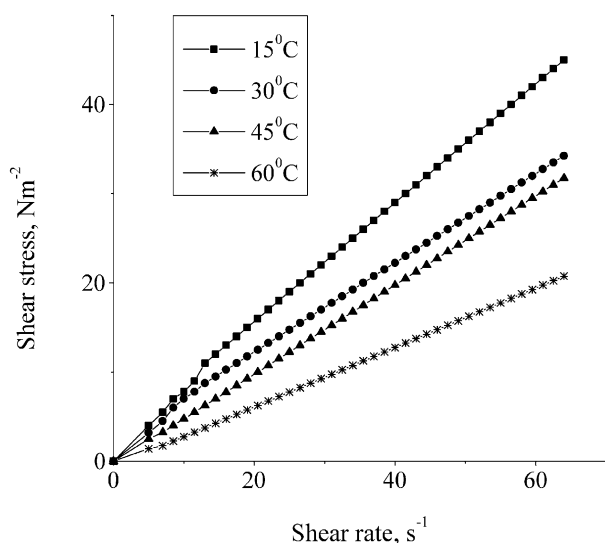


Fig. 5. The dependence of shear stress on shear rate of a 35% phosphated polyurethane–acrylic dispersion at various temperatures.

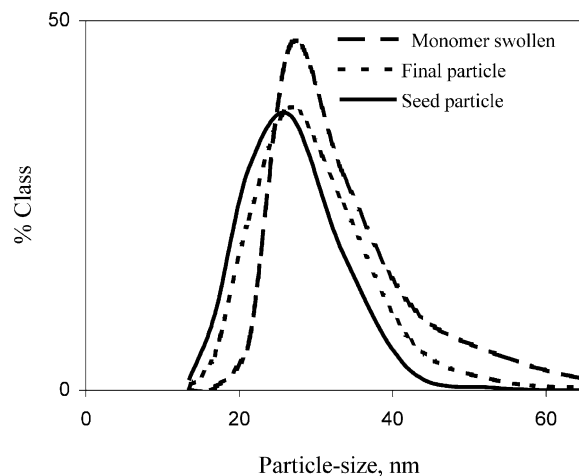


Fig. 6. Particle-size distribution of phosphated polyurethane during polymerisation of acrylic monomer.

polymer. In the present study, cleaning of the polyurethane seed particles was not required. The reason for this is that the seed urethane dispersion is surfactant-free and the stabilising effect stems from the built-in neutralised carboxylic groups. Furthermore, the seed polymer is also free from any residual initiator fragments due to the polyaddition nature of the seed preparation. Particle size measurements of the 2-HEMA-terminated phosphated polyurethane seed were carried out before the acrylic monomers were added. When the acrylic monomer was added into the system, the monomers swelled the seed particles and, as a result, the particle sizes increased, as shown in Fig. 6.

There was a difference between the swollen radius of the monomer-saturated particles and the unswollen radius. After radical polymerisation in the dispersed phase, the particle-size decreased below the particle-size of the swollen particles but was above that of the seed particles. One reason for this was the shrinkage of the particle upon polymerisation. A second reason was that the newly grown particles are more hydrophobic than the swollen particles before polymerisation of the acrylic monomers and expelled water from the particles, as shown in Fig. 6. In general, the copolymerisation of monofunctional and multifunctional acrylic monomers into phosphated polyester-based polyurethane dispersions resulted in a decrease in viscosity and an increase in particle size, as shown in Fig. 7. The particle size increase from 35 to 70 nm that corresponds to a volume increase by a factor of eight may suggest particle aggregation during radical copolymerisation. However, as shown in Figs. 4 and 5 the particles were stable when concentration and temperature effects were investigated at varying shear rates. For polyurethane seed systems using tetraphenylethane as iniferter, Tharanikkarsu and Kim reported a particle size increase from 50 to 300 nm (volume change by 200 times) at 30% MMA content [20]. The reason for such a big change in particle volume is not clear

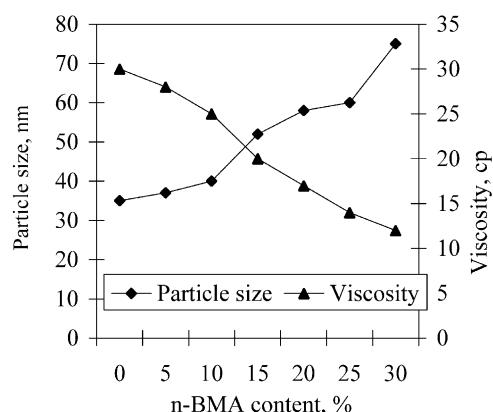


Fig. 7. Particle size and viscosity variation during *n*-BMA copolymerisation.

but may be attributed to the condensation/radical polymerisation nature of the hybrid emulsion and needs more investigation.

During the addition of the acrylic monomer into the polyurethane seed particles in the presence of potassium persulphate, the monomer diffused into the seed particles. If sufficient monomer was added, monomer droplets would also be formed, so that equilibrium concentration of monomers in the particle is attained [19]. The polyurethane seed was stable to secondary nucleation and to flocculation over the initiator concentration range used. The initiator radical is insoluble in the organic phase due to its hydrophilicity and might not enter the particles. The primary radicals can react with the monomers in the aqueous phase until they form a less hydrophilic surface-active radical that can irreversibly enter into the polyurethane seed particle. Particle growth occurred in the absence of secondary particle formation. In most of the experiments, a maximum of 30% acrylic monomers was polymerised into the seed before the particle became too large to be stabilised by the charged carboxylate ions and coagulation began to take place.

The stabilising effect of the seed polyurethane-neutralising

Table 2
Effects of neutralising cation on coagulation (grit) formation using a polyurethane seed latex

Neutralising base	Grits during methyl methacrylate copolymerisation (%)
LiOH	2
NaOH	4.5
KOH	5
Triethylamine (TEA)	6.1
Morpholine	7.3
Tripropylamine (TPA)	Instant coagulation
Tributylamine (TBA)	Instant coagulation

base during acrylic copolymerisation in the dispersed phase has been studied. The amount of the acrylic monomer used was 30% based on the seed. Table 2 lists the neutralising bases used and the percentage coagulation during MMA copolymerisation. It is clearly seen that small, highly solvated cations were required for stabilising the emulsion during copolymerisation in comparison with large and less solvated cations. For the amine series, as the size of the alkyl group increased, the resulting cation became too hydrophobic to stabilise in the aqueous phase and grit formation was much higher.

At high pH, the copolymerised acid (DMPA) of the present study was very effective in promoting colloidal stability. Placing the acid groups on the surface of a latex particle without it becoming buried was important for colloidal stability [21], and a two-step polymerisation as described by Sakota and Okaya [14,15] has been used. First, a carboxyl functional, 2-HEMA-terminated phosphated polyurethane was synthesised. The acid groups were then neutralised and the pH raised to 8–9. In the presence of water the charged carboxylate ions remained on the surface of the particle near the aqueous environment, which in turn provided conventional loci for further emulsion polymerisation.

3.3. Surface tension and wetting properties of phosphated polyurethane acrylic dispersions

The effect of varying the DMPA concentration on the surface tensions of the polyurethane ionomer dispersions is presented in Table 3. The surface tensions of the dispersions decreased and its activity increased as the amounts of carboxyl groups increased in the polyurethane, as is known for other surface-active agents.

3.4. Contact angle studies

Advancing and receding contact angle measurements of the films cast from phosphated polyurethane acrylics could provide more information on the hydrophilicity of dried emulsion-cast films and hence the wettability. A better understanding of the hydrophobicity of the cast films could be obtained from dynamic contact angle studies rather than from swelling studies. Fig. 8 shows the results of the dynamic advancing contact angle

Table 3
Surface tensions of phosphated polyurethane–acrylic dispersions

Mass percent of carboxylic acid in the aqueous polyurethane	Surface tension (N/m)
3	50
4	44
5	39
6	34

Table 4
Advancing contact angles of phosphated polyurethane ionomer films before and after heat treatment

Monomers	Modification							
	0%		10%		20%		30%	
	θ_{adv} before	θ_{adv} after	θ_{adv} before	θ_{adv} after	θ_{adv} before	θ_{adv} after	θ_{adv} before	θ_{adv} after
MMA	45	46.90	60.9	64.2	70.2	74.5	80	83.2
EMA	45	46.90	65.3	68.7	74.1	77	83.8	87.1
EGDMA	45	46.90	66.1	69.8	79.9	82.5	84.7	88.9

study. The water contact angles increased as the amount of acrylic monomers copolymerised were increased. The increased contact angles using water means that the films showed poorer wetting with increasing acrylic content. The increase in the advancing contact angle increased from MMA to EMA and EGDMA.

3.5. The effect of temperature treatment on contact angles

Ionic polyurethane dispersions were made by neutralising the pendent carboxylic acids with tertiary amines which have relatively high boiling points. When films are cast from these emulsions and dried at room temperature for 24 h, all the amines may not be dissociated and evaporated. To study the effect of the retained amines (in this case either triethylamine or tributylamine) in the film, the same samples used for Fig. 8 were heat treated at 100 °C, for 5 min. The films were then cooled to room temperature and the contact angles were measured. Results of water advancing contact angles of the cast films before and after the heat treatment are given in Table 4. It clearly shows that heat treatment at 100 °C for a period of 5 min increased the contact angle (reduced wetting by water). The dissociation of the salt group to give free amines followed by evaporation of these amines changed the surface properties and hence the wetting of the films.

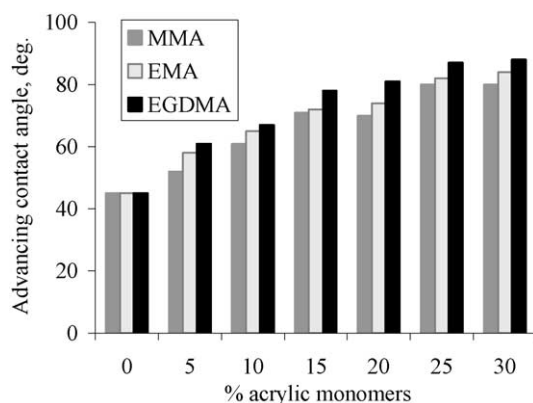


Fig. 8. The effect of the type of the acrylic monomers copolymerised on contact angles of the polyurethane emulsion films.

4. Conclusions

A new method for the synthesis of phosphated polyurethane–acrylic dispersions was developed. It involved the use of acrylic monomers as a diluent in the urethane synthesis reactions. Thermal polymerisation of the diluent during the preparation of the polyurethane was prevented by processing at lower temperature (ca. 60 °C). This method could be a useful substitute for the acetone or pre-polymer process, as each of which has its own limitation. The acrylic monomers used as diluents were copolymerised into the emulsified polyurethane seed. Results of a dynamic contact angle study have shown the improved hydrophobicity of the polyurethane acrylic dispersion films. The phosphated polyurethane acrylics are ideally suitable as a pigment-grinding medium due to their shear stability.

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