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Nano-structure phosphorus-containing polyurethane dispersions: synthesis and crosslinking with melamine formaldehyde resin

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Abstract

Nano-particle-size phosphated polyurethane dispersions were synthesised from phosphorus-containing macroglycol, bis (hydroxymethyl) propionic acid and methylene-bis-(4-isocyanatocyclohexane) (H_{12}MDI). After the carboxylic acid groups of the phosphated polyurethane were neutralised by suitable bases, water was added to form the phosphated polyurethane dispersion. Chain flexibility affected particle-size reduction because flexible particles are more deformable in a shear field. During phase inversion the dispersed phase can more easily be broken into smaller particles. Depending on the number of hydrophilic groups present, the dispersion can be obtained in a very finely divided form, so that it practically has the appearance of a solution.

Crosslinking of the dispersions with melamine showed that hexamethoxymethyl melamine does not self-condense during the curing and co-condensation was predominant. It was further shown that the cure response of the polyurethane dispersions was affected by the nature of the neutralising amine. Triethanolamine neutralised dispersions gave very poor cure response compared with triethylamine due to the low-volatility and the tendency to enter side reaction with the melamine.

Keywords: Phosphorus-containing polyurethane dispersions; Particle size; Particle-size distribution; Crosslinking

1. Introduction

The study of polyurethane ionomer dispersions involves both organic macromolecular chemistry and the inorganic chemistry of salts. Such a seemingly incompatible combination in one molecule prompts expectations of novel and interesting properties. As in the case of conventional segmented polyurethanes, polyurethane ionomers contain low-polarity flexible segments and urethane groups which are polar and capable of interchain interaction via hydrogen bonds. Ionic groups in a polyurethane tend to interact with each other and aggregate but are attached to the 'alien' hydrophobic neighbourhood [1].

To understand the complexities of these new aqueous polymer systems, to improve and tailor-make them for various innovative end-uses and to solve technical problems related to volatile organic compounds (VOCs) is a scientific and technological challenge, as well as a common responsibility towards the safekeeping of the environment. Aqueous dispersions of polyurethanes are environmentally compatible and safe, since water is the only solvent. Viscosity and flow behaviour are independent of the molecular masses, which can be adjusted to very high values. Aqueous dispersions of polyurethanes are used for many applications, including: coatings for plastics, fabrics, metals, wood and also for applications in which water, for technological reasons, is required as a solvent, such as for glass-fibre sizing and gelatine plasticisers for photographic layers [2].

The outstanding properties of polyurethane dispersions and ease with which the chemical compositions of the polyurethane dispersions can be varied have lead to an increase in the application areas of these fascinating polymers. However, polyurethane dispersions generally have large particle sizes and broad distribution that could limit their application performance [3]. Since particle size and particle-size distribution play major roles in stability, film formation and surface penetration for such an application as surface coatings, it is imperative that such parameters be controlled [4]. Smaller particle sizes may be obtained by increasing the hydrophilicity of the

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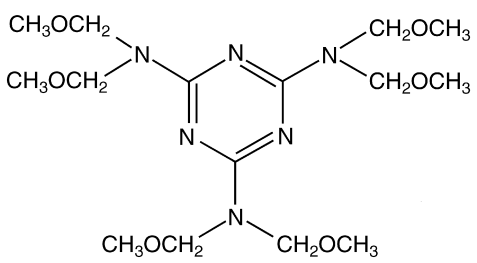
polyurethane but the dried films are generally water sensitive due to the presence of hydrophilic groups [5].

In order to improve their properties such as solvent and chemical resistance, polyurethane dispersions must be crosslinked. Polyurethane ionomer dispersions can be crosslinked at room temperature, elevated temperature and photochemically. Both low-temperature and high-temperature crosslinking agents are available for crosslinking. For low-temperature crosslinking through the carboxylic acid groups, polyaziridines [6,7], carbodiimides [8] and inorganic salts, particularly ammonium zirconium carbonate [9], can be used. Aqueous dispersions of epoxy resins and anionic polyurethane dispersions can be crosslinked to tough films at temperatures above 150 °C [10]. Curing proceeds via the carboxylic acid groups of the polyurethane and the epoxide groups of the epoxy dispersions. However, melamine formaldehyde (MF) polymers are the most versatile crosslinking agents for many polymer systems that may include polyurethane dispersions [11]. Crosslinking can be accomplished through the reaction of the MF resin with the hydroxyl and/or carboxyl functional groups of the polymer. Melamine crosslinking agents are, however, not without problems; they tend to self-condense [12,13]. The melamine ring has three pendant nitrogen atoms. Each nitrogen atom can be substituted twice; therefore, each melamine ring will have six functional sites. Melamine-formaldehyde resins are mixtures of monomeric and oligomeric molecules. In self-condensation, functional groups on the MF resin molecules react with each other, causing undesirable properties. The different groups that are found in the MF resin are imino (–H), methylol ($-CH_2OH$), alkoxymethyl ($-CH_2OR$), acetal ($-CH_2OCH_2OR$), methylene bridge ($-CH_2-$), and methylene ether bridge ($-CH_2-O-CH_2-$) moieties.

To overcome the undesirable self-condensation of melamine resins, a model crosslinking compound, hexamethoxymethyl melamine (HMMM) is often used [14]. As shown in Scheme 1, all six sites are substituted by methoxymethyl groups, which can react with the hydroxyl and/or carboxyl functional polymer. This substitution pattern should not lead to self-condensation, thereby enhancing the level of co-condensation with the polymer.

In this paper, nano-particle-size phosphorus-containing polyurethanes with particle-size distribution approaching unity are synthesised. The dispersions are then crosslinked with HMMM resin and the dynamic mechanical properties are investigated.



Scheme 1. Structure of hexamethoxymethyl melamine (HMMM) resin.

2. Experimental

A polyester macroglycol that contains phosphorus in the main chain was synthesised from 1,4-cyclohexane dicarboxylic acid (Eastman Chemicals, USA), neopentyl glycol (Perstorp Polyols, Sweden) and 1,2,4-phosphonobutane tricarboxylic acid (Bayer, Germany) in a standard polycondensation reaction to a low acid value (less than 4 mg KOH/gm) as reported in our previous publications [15–17]. The macroglycol was then dried at 90 °C under reduced pressure to remove any traces of moisture before use. A control polyester macroglycol without 1,2,4-phosphonobutane tricarboxylic acid was also prepared in a similar way.

Polyurethanes were synthesised in a 1L-glass reactor equipped with a mechanical stirrer, a charging and sampling port, a nitrogen inlet and outlet. The reactor was first charged with dimethylol propionic acid (DMPA) (Perstorp Polyols, Sweden) and excess methylene-bis-(4-isocyanatocyclohexane) (H_{12}MDI). The reaction took place at 75 °C over 1.5 h. This temperature was maintained to avoid any competitive secondary reactions, such as the formation of allophanates [18]. Methyl ethyl ketone was then added to reduce the viscosity of the reaction mix and the phosphorus-containing polyester macroglycol (50% in methyl ethyl ketone) was added and allowed to react with the isocyanate (–NCO) for 1 h. Completion of the reaction was evidenced by measuring the disappearance of the isocyanate peak by means of FTIR at 2265 cm^{-1}. The carboxylic acid groups of the dimethylol propionic acid in the above polyurethanes were then neutralised either by triethylamine or triethanolamine and water was added at a moderate shear force. Finally the methyl ethyl ketone was removed under vacuum to obtain the polyurethane anionomer dispersion in water.

2.1. Characterisation

The average particle size and particle-size distribution of the dispersions were determined by light scattering. Approximately 0.2 ml of the dispersion was diluted with deionised water to an approximate concentration of 0.1% and was measured at 25 °C. Particle structure was investigated by atomic force microscopy (AFM) and transmission electron microscopy (TEM). Crosslinking of the polyurethane dispersions using HMMM as crosslinker was investigated by dynamic mechanical analysis (DMA). The samples for the DMA test were prepared by mixing the dispersion and the melamine resin, followed by impregnating on a carbon-fibre mat.

3. Results and discussion

3.1. Dispersity, particle size and particle-size distribution of anionic polyurethane dispersions

In contrast to an emulsion polymer obtained by radical polymerisation whose stabilisation arises from the presence of charged polymerisation initiators, adsorbed surfactants, or co-polymerisable surfactants; colloidal stability of self-emulsifying polyurethane dispersions arises entirely from the presence of ionised carboxylic acid groups, and as a result they are unstable below the pK_a of the acid[3]. It is also well known that all ion-containing polymers are not water dispersible and a minimum amount of ionic content is required for the formation of stable dispersions [19].

In this experiment, a series of phosphorus-containing polyurethane dispersions with different contents of dimethylol propionic acid (DMPA) were prepared in order to study the effect of ionic content. It was found that in self-emulsified polyurethanes, particle size decreased with increasing hydrophilicity, as shown in Fig. 1. Particle size decreased sharply at lower ionic contents while at higher concentration it exhibits an asymptotic behaviour. It seems that a certain number of ionic groups are required to achieve smaller particles, beyond which no significant changes are noticeable.

Polyurethane dispersions are generally believed to have broader particle-size distributions than those dispersions prepared by free-radical polymerisation [3]. The statistical nature of both the condensation polymerisation and the subsequent chain extension process have been suggested to be reasons for the broad size distribution. The particle size and particle-size distribution of the polyurethanes derived from the control polyester macroglycol are shown in Fig. 2(a)–(c).

3.2. Effects of 1,2,4-phosphonobutane tricarboxylic acid (PBTCA) on particle size and particle-size distribution

When the phosphorus-containing macroglycol was used as a soft segment for the polyurethane, smaller particle sizes and narrower particle-size distributions were obtained. The particle-size distributions obtained for the phosphorus-containing macroglycol were less than the values given in the literature for most polyurethane dispersions [20]. Studies performed by Chen and Chen [20] showed a minimum particle-size distribution of 1.3–1.4 when metal hydroxides were the neutralising agents. According to their

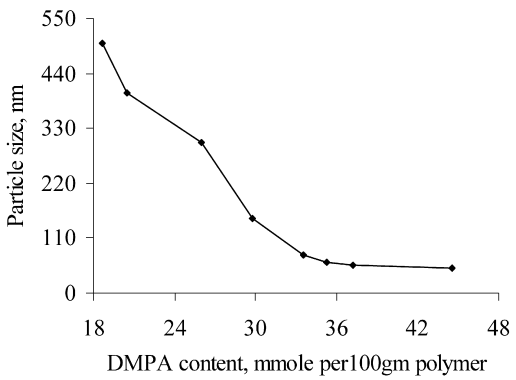


Fig. 1. Particle size reduction of polyurethane dispersions as a function of DMPA content.

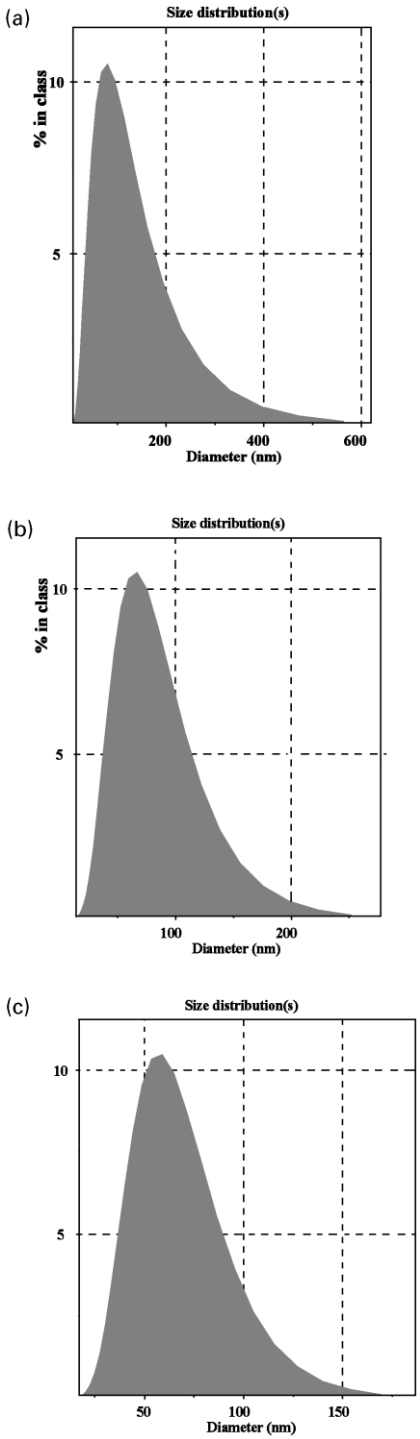


Fig. 2. Particle-size distributions of polyurethane dispersions prepared from the control polyester macroglycol; (a) 4% DMPA, (b) 4.5% DMPA and (c) 5% DMPA.

findings the alkali metal cation was more easily hydrated than the ammonium salt in the aqueous phase. The particle-size distributions of the phosphorus-containing polyurethanes obtained in the present study were between 1.05 and 1.1.

The effect of PBTCA on particle size and particle-size distribution is presented in Fig. 3. The same amounts of ionic contents as used for Fig. 2 were used. However the smaller particles are evident in Fig. 3. This result is attributed to the additional chain flexibility caused by the PBTCA monomer. Chain flexibility affects particle-size reduction because flexible particles are more deformable in a shear field such that, during phase inversion, the dispersed phase can more easily be broken into smaller particles [21]. Therefore, the assumption advanced by early researchers [3] that the broader particle-size distributions of polyurethane dispersions was due to the statistical and polycondensation nature of the synthesis, may not hold true. Depending on the number of hydrophilic groups, the dispersion can be obtained in a very finely divided form, so that it practically has the appearance of a solution. Very coarse particulate dispersions, which are also satisfactorily stable, may also be formed.

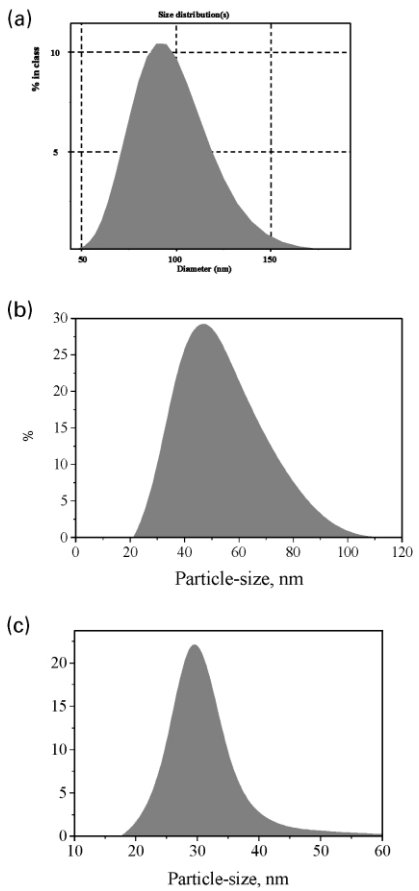


Fig. 3. Particle-size distributions of polyurethane dispersions prepared from the phosphorus-containing macroglycol; (a) 4% DMPA, (b) 4.5% DMPA and (c) 5 % DMPA.

3.3. Effects of ion concentration on particle number

As mentioned in Section 3.1, all ion-containing polymers are not water-dispersible and a minimum ionic content with choice of favourable counter ions has to be met for water dispersibility and stability [19]. While ionic groups associated in polymers in the solid state act as physical crosslinkers and improve mechanical properties [22], their role in a dispersion is different; they need to stabilise the dispersed phase in the presence of water. Dispersibility is governed by the hydration of the neutralising cation, and the hydrophilicity of the chains. Under favourable conditions, an increasing amount of ionic groups in a dispersion leads to smaller particles and hence, more particles. The relationship between ion concentration and number of latex particles formed, N_p, was calculated from the mean particle diameter, D_T (obtained from r_u), obtained from light scattering measurements and using the relationship:

$$N_P = \frac{m_p}{4/3\pi r_u^3 d_p} \quad (1)$$

where: m_p is the mass of the polymer, r_u is the radius of the particle and d_p is the density of the polymer.

A plot of N_p versus concentration of bound stabilisers is shown in Fig. 4. The line of the linear relationship does not pass through the origin. The slope of the graph gives information on the efficiency of the bound ionic groups for dispersion formation and the intercept is the minimum number of ionic groups required for the formation of stable dispersions, below which no stable dispersion could ever be formed.

3.4. Atomic force microscopy

The use of AFM offers the possibility of providing very high-resolution images of non-conducting film surfaces. Very little sample preparation is required and analyses can be done under ambient conditions. This method is of considerable value in examining the properties of latex

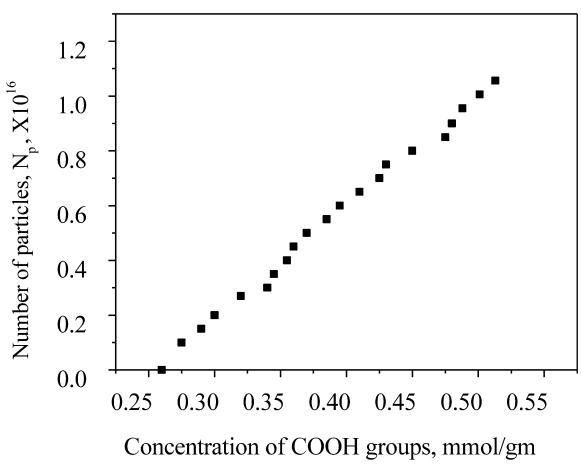


Fig. 4. Number of latex particles, N_p, versus carboxylate ion concentration.

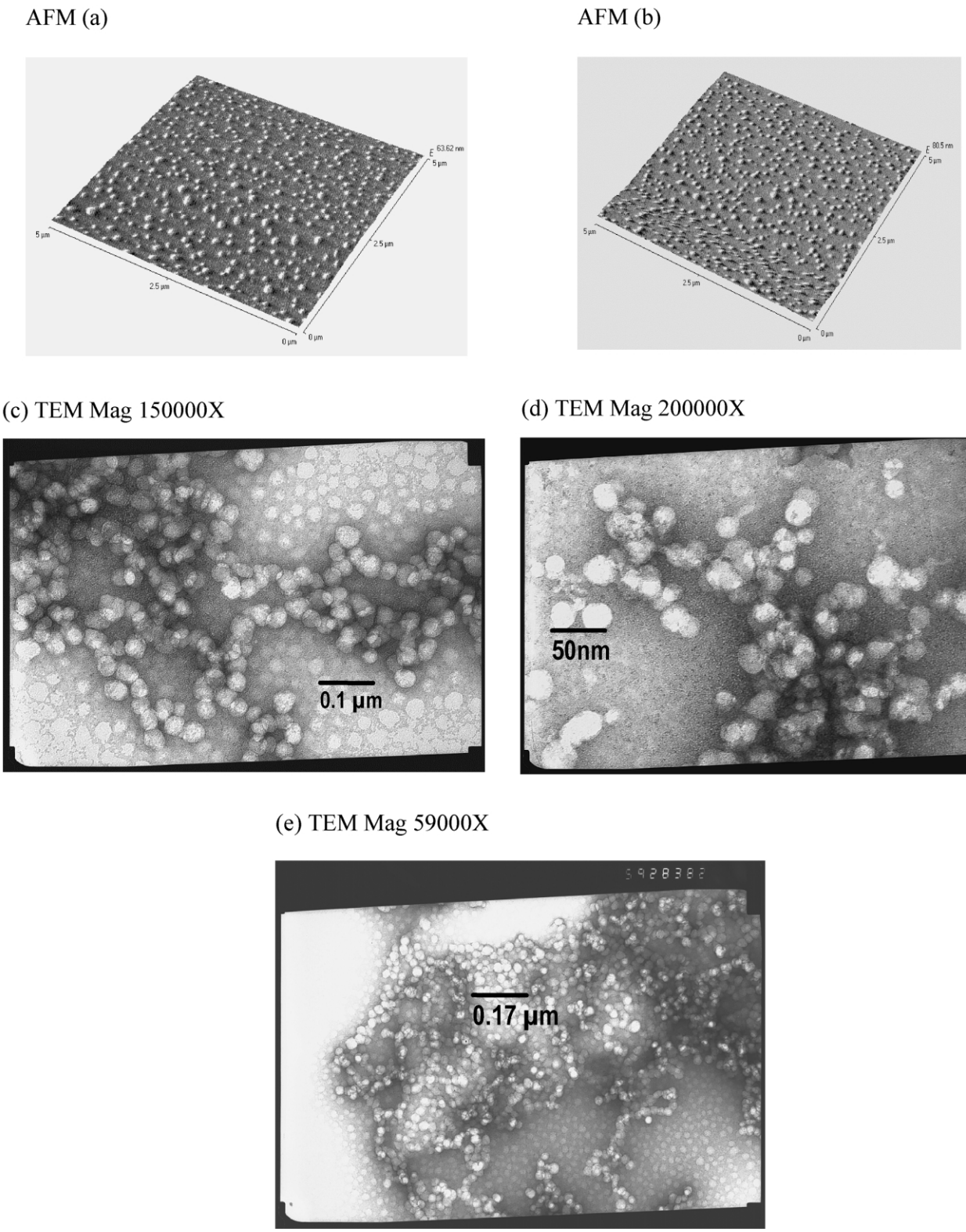


Fig. 5. AFM images: (a): dispersions from the control macroglycol and (b): dispersions from the phosphorus-containing macroglycol and (c)–(e): TEM images of polyurethane dispersions from the phosphorus-containing macroglycol.

particles and in carrying out the non-destructive examination of surfaces after accelerated weathering, or in any other tests, down to the nanometer size scale.

The system basically comprises a very fine-point tip, mounted on a spring cantilever, which is brought into close proximity with the surface to be scanned. The tip is then moved across the surface to scan the desired area. As this is done, a laser beam is reflected from the tip and vertical movements, due to variations in distance, are tracked by a photodetector. In this way a three-dimensional map of a surface can be compiled in a computer and analysed.

The AFM images presented in Fig. 5(a) and (b) support the results from the light scattering in terms of particle sizes. In Fig. 5(a), the polyurethane particles obtained from the 'control' macroglycol have non-uniform sizes while the polyurethane particles obtained from the phosphated-macroglycol are much smaller and uniform (Fig. 5(b)). The smaller sizes and uniformity of the particles for the phosphated polyurethane dispersions compared to the 'control' were further investigated by TEM and the results are presented in Fig. 5(c)–(e). The particle diameter was in the region of 20–35nm.

3.5. Curing studies by dynamic mechanical analysis (DMA)

DMA is the most sensitive method for measuring the viscoelastic properties of a polymer as crosslinking proceeds. The ratio of polyurethane to HMMM resin used was 60:40, 70:30, 80:20, 90:10 and 100:0. The cure behaviour of the polyurethane anionomer dispersions with HMMM at different crosslinker ratios is shown in Figs. 6 and 7.

The crosslink densities of the films as they cure were expected to vary with the amount of crosslinker present in the formulation from which the films were prepared. Changing the amount of HMMM from 10 to 40% changed the viscoelastic property of the films. The increase in storage modulus at temperatures above 150 °C, due to chain entanglements caused by crosslinking, was observed, except for the sample with 0% crosslinker content which was used

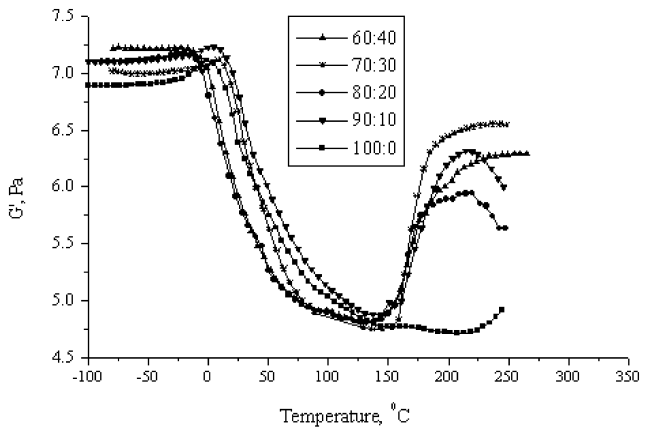


Fig. 6. Storage modulus (G') of polyurethane films as curing progress.

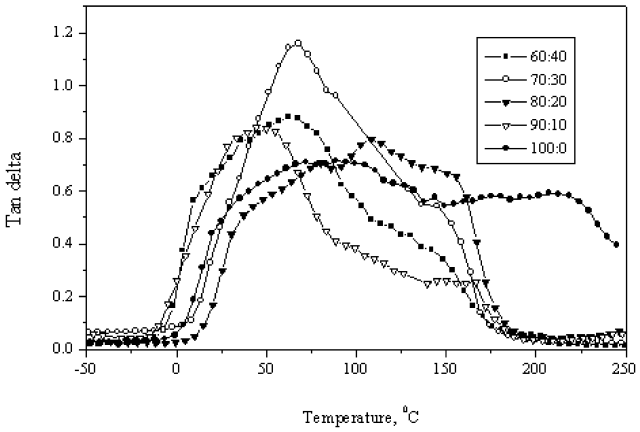


Fig. 7. Tan delta of polyurethane films as curing progress.

as a control. At around 230 °C, the storage modulus for 30% HMMM content was increased whereas it dropped for the samples with 10, 20 and 40% HMMM contents. Fig. 6 indicates that films cured with 40% melamine have a storage modulus, lower than those cured with 30% melamine as the curing proceeded. This can be interpreted in terms of co-condensation and self-condensation. If self-condensation took place in addition to co-condensation, then the 40% HMMM sample should have storage modulus higher than that of the 30% HMMM sample. On the other hand, if network formation is only between the –OH and/or –COOH groups of the dispersion and the methoxymethyl groups of the melamine, storage modulus values should increase by up to a stoichiometric amount and then decrease when the stoichiometric amount is exceeded. This is what is observed from the 40 and 30% HMMM contents above 150 °C.

Failure to detect the modulus increase with excess HMMM is attributed to the absence of self-condensation of the excess HMMM [23]. In our current experiment, calculation of the stoichiometric amount of the HMMM resin required to fully crosslink the dispersion from the equivalent weight of the reactants was found to be 28%, which was very close to that of 30% used for the DMA.

It was found that highly etherified melamine resins such as HMMM did not self-condense if heated alone or with weak acid such as phathalic anhydride [24], whereas moderately etherified melamine resins containing a substantial amount of both hydroxy methyl and secondary amino groups could easily self-condense. Calbo [25] studied the reaction of HMMM with hydroxylated acrylic polymers and found that self-condensation was much slower than co-condensation. Self-condensation increased as the concentrations of –NH and $-NCH_2OH$ increased and became dominant, even in the presence of primary hydroxyl-containing polymers. Self-condensation proceeded either between the two hydroxy methyl (methylol) groups or between the secondary amino (NH) and methylol groups, to form methylene bridges as shown in Fig. 8.

Co-condensation between HMMM and a hydroxyl

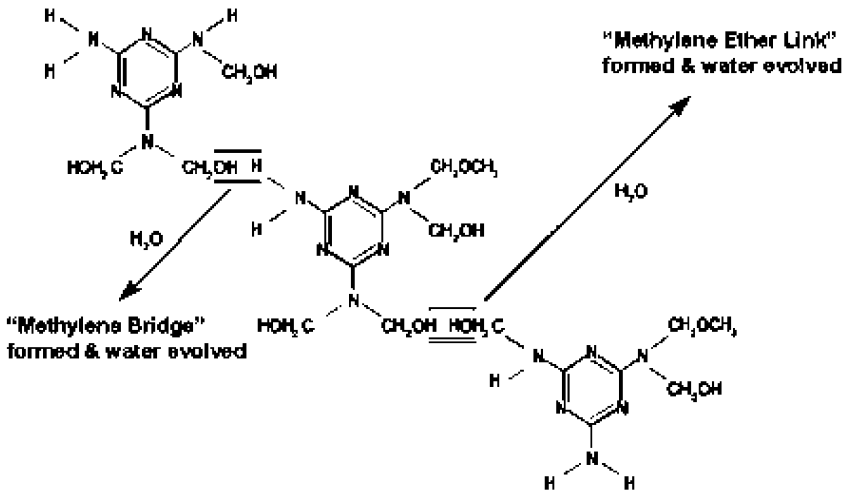


Fig. 8. Self-condensation of the partially etherified melamine resin [14].

and/or carboxyl functional polyurethanes is shown schematically in Figs. 9 and 10.

From the DMA data, it was possible to obtain the temperature at which irreversible gel formation takes place for the phosphated polyurethanes as presented in Fig. 11. At a temperature below the onset of crosslinking the polyurethane had a loss modulus (G'') which was much higher than the storage modulus (G') since the liquid polymer exhibited low elasticity and high damping during the test. Both (G') and (G'') values were almost equal at about 150 °C, and then (G') exceeded (G'') as curing continued. The crossover of (G') and (G'') is referred as the gel point, from which it is possible to predict the curing behaviour of thermoset resins [26]. In this test, irreversible gel was formed for only a 30% HMMM content. Above and below the 30% there was no irreversible gelation. This proved the absence of HMMM self-condensation when it is used in excess and inadequate crosslinking when the content is lower than 30%. Although irreversible network formation was not evident for the other samples, some crosslinking is inevitable and this will cause an increase in molecular mass and hence an increase in the value of (G').

3.6. The effect of the neutralising amine on curing

The choice of tertiary amines to neutralise the pendent carboxylic acid during the synthesis process plays a role in the cure response. The choice of the amines depends upon its base strength, water miscibility, toxicity, equivalent weight, boiling point and tendency to enter side reactions during the curing process, which may cause discoloration of

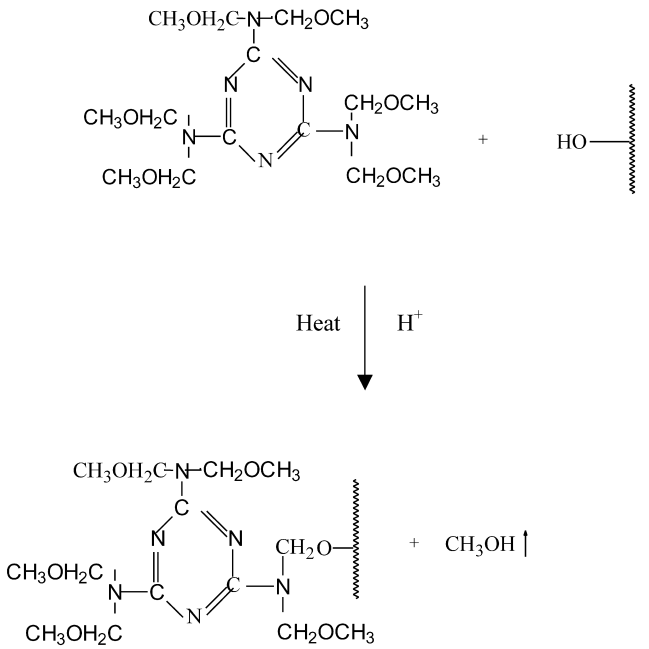


Fig. 9. Co-condensation between HMMM and hydroxyl functional polymers.

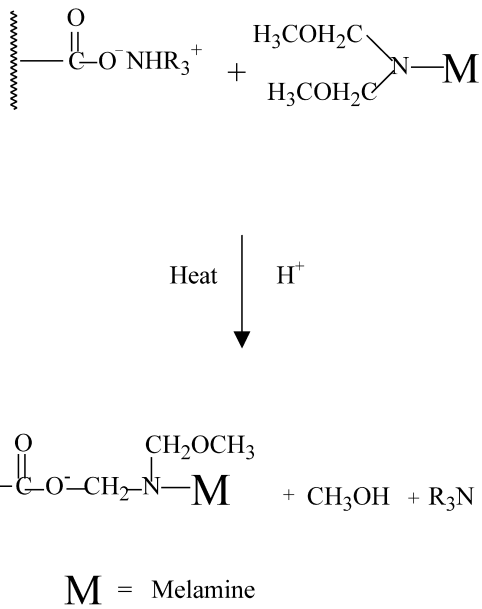


Fig. 10. Co-condensation between HMMM and carboxyl functional polyurethane.

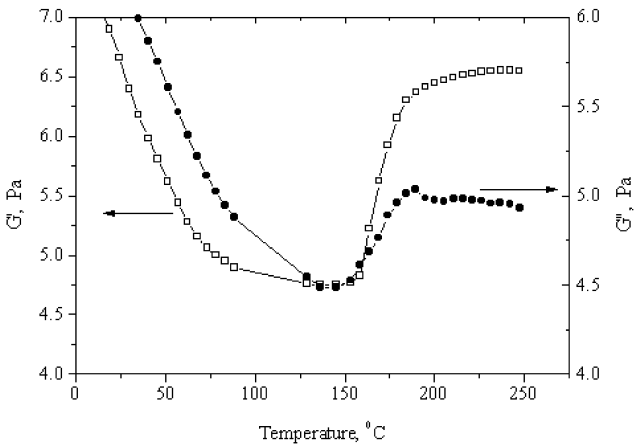


Fig. 11. Irreversible gel formation temperature for polyurethane crosslinked by HMMM.

the cured film [27]. Triethylamine is a good choice but it is highly toxic. Triethanolamine is less toxic to handle than triethylamine but the volatility is very low and its hydroxyl groups may enter side reactions.

The cure response of the dispersions under investigation differed, depending on the neutralising base used. Dispersions neutralised by triethanolamine showed poor cure properties compared with triethylamine-neutralised dispersions. For two identically formulated dispersions that differed only in the neutralising amine, it was found that triethanolamine gave poor mechanical properties compared with triethylamine, as shown in Fig. 12.

The storage modulus of the triethanolamine-neutralised dispersion was lower than that of the triethylamine one. A sharp drop in storage modulus was observed in the sub-zero temperature region, since the low-molecular-mass polymer/melamine mixture exhibited low elasticity and high damping as it flowed. At a temperature well above 150 °C the polymer acquired elasticity due to crosslinking. There was a sharp increase in storage modulus in the case of the triethylamine-neutralised dispersions. The storage modulus of a triethanolamine-neutralised dispersions increased slowly, but not sharply, to about 230 °C, above which it decreased. This showed the possible side reactions of the retained triethanolamine via its hydroxyl groups to form amine-esters that reduces the mechanical properties. Therefore it was not surprising that the non-functional amine (triethylamine) gave better mechanical properties as compared with triethanolamine.

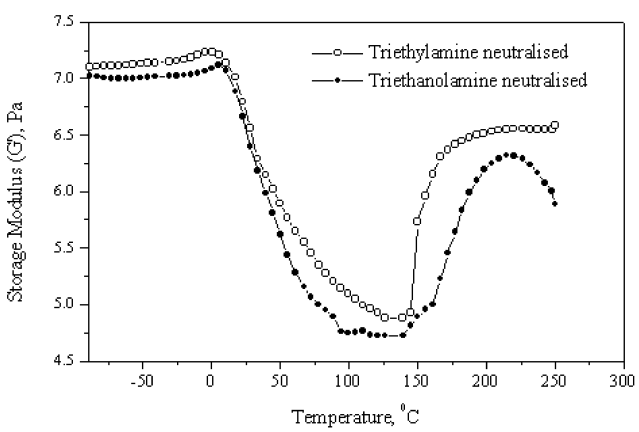


Fig. 12. The effect of the neutralising amine on the cure response opf polyurethane dispersions crosslinked with HMMM resin.

Both co-condensation and self-condensation reactions are acid catalysed. Although external acid catalysts were not added during the crosslinking, it was likely that the dissociated carboxyl groups (on complete removal of the amine) of anionic polyurethane dispersions be sufficient to catalyse the reaction [28]. The high-boiling point of triethanolamine means less dissociation. From the Fig. 12, it is seen that the curing reaction started at 150 °C, which is lower than the boiling point of triethanolamine but above the boiling point of triethylamine. This suggests that there was less loss of triethanolamine by volatilisation before transesterification could take place, and therefore secondary reactions led to less apparent cure due to the formation of ester-amines. This finding is consistent with our previous observation [29] on the poor adhesion properties of thermally cured phosphated polyurethane dispersions neutralised by triethanolamine compared with those dispersions neutralised by triethylamine due to the high boiling point and retention in the film.

4. Conclusions

Polyurethane dispersions with smaller particle sizes and narrower particle-size distributions than those polyurethanes previously published can be obtained from phosphate-containing polyester macroglycol. This was due to the chain flexibility imparted by the phosphate monomer used to synthesise the macroglycol. Chain flexibility affects particle-size reduction since during the phase inversion the dispersed phase can easily be broken into smaller particles.

In order to improve their dynamic mechanical properties and solvent and chemical resistance, polyurethane dispersions can be crosslinked with melamine crosslinking agent. HMMM resin is the ideal crosslinker due to its low self-condensation reaction. It was further demonstrated that the neutralising amine has a profound effect on the cure response of the dispersions.

References

[1] Dieterich D. Prog Org Coat 1981;9:281.
[2] Dieterich D. US Patent, 3,374,095; 1963.
[3] Satguru R, McMahon J, Padget J, Coogan R. Surf Coat Int 1994;10:424–31.
[4] Kim B, Kim T. J Appl Polym Sci 1991;43:393–8.
[5] Monock H. J Oil Colour Chem Ass 1993;9:348–52.
[6] Munir A, Goethals E. J Polym Sci: Polym Chem 1985;1985.
[7] Wolfrey A, US Patent, 4,301,053; 1981.

[8] Parodi F. Comprehensive Polymer Science. New York: Pergamon Press; 1989. pp. 387–411.
[9] Davies W. Proc Royal Soc Chem Symp Additives Water Borne Coat, Liverpool 1988;9:181–209.
[10] Waterborne and Solvent-borne epoxies and their end uses, SITA Technology, London, 1996.
[11] Santer U. J Prog Org Coat 1994;12:309.
[12] Bauer D. J Appl Polym Sci 1982;27:3651.
[13] Bauer D, Dickie R. J Poly Sci, Polym Phys 1980;18:2015.
[14] Vaughn G, Downie J, Ball P, Bowers G, Ferrell P, Lee S, Jacquin J, Hill L. Paper presented at the 26th International Waterborne, High-Solids, and Powder Coatings Symposium February 10–12, 1999; New Orleans, LA, USA.
[15] Mequanint K, Sanderson R, Pasch H. Polymer 2002;43:5341–6.
[16] Mequanint K, Sanderson R, Pasch H. Polym Deg Stab 2002;77: 121–8.
[17] Mequanint K, Sanderson R. Macromol Symp 2002;178:117–30.
[18] Saunders J, Frisch K. Polyurethane Chemistry and Technology, Part I. New York: Wiley/Interscience; 1962.
[19] Bungardt E, Mutschler E, Ullmann's Encyclopaedia of Industrial Chemistry, vol. 24. Weinheim: VCH Verlagsgesellschaft mbH, D-6940.
[20] Chen Y, Chen Y. J Appl Polym Sci 1992;46:435–43.
[21] Lee Y, Lee J, Kim B. Polymer 1994;35:1095–9.
[22] Dietrich D, Keberle W, Witt H. Angew Chem Int Edn 1970;9:40.
[23] Hill L, Kozlowski K. J Coat Technol 1987;59:63–71.
[24] Saxon R, Lestienne F. J Appl Polym, Sci 1964;8:475–88.
[25] Calbo L. J Coat Technol 1980;52:75–83.
[26] Mequanint K. MSc Thesis, University of Stellenbosch, South Africa, 1997.
[27] Curtis L. J Coat Technol 1980;52:49–53.
[28] Mequanint K, Sanderson R. US Patent 6,221,955; 2001.
[29] Mequanint K, Sanderson R, Pasch H. J Appl Polym Sci 2003;88(4): 900–7.