Macromol. Symp. ***178,*** *117–130 (2002)*

Phosphated Polyurethane Dispersions: Synthesis, Emulsification Mechanisms and the Effect of the Neutralising Base

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SUMMARY: Phosphate-containing polyester macroglycols with different phosphate contents were synthesised from a phosphorus-containing monomer, a dicarboxylic acid and a diol. The macroglycols were then used as a soft segment for the preparation of segmented polyurethane dispersions. Aqueous dispersions were made by phase inversion from the organic solvent after the carboxylic acid groups were neutralized. Phase inversion was found to take place in three distinct stages. The stability and particle size of the polyurethane dispersions were dependent of the amount of carboxylic acid groups present, the degree of neutralisation and the neutralising cations. Metal-neutralized polyurethane dispersions gave smaller particle sizes and the corresponding films showed higher swelling in water due to the ease of hydration. The particle size and stability of the tertiary amine-neutralised polyurethanes were found to be related to the water solubility of the amines at a given dispersion temperature. Particle size increases for the higher alkyl chain neutalising amines due to the poor hydration of the corresponding cations.

1. Introduction

Due to their outstanding resistance to solvents and chemicals and good weather stability, polyurethane dispersions have been used extensively for coatings applications. Aqueous polyurethane dispersions continue to become industrially and economically more important as high-quality coating polymers. They are environmentally compatible and safe to work with. The formulation of coatings without wetting agents is now also possible[1] since their pigment wetting properties are excellent.

Polyurethane dispersion ionomers are superior to those products in which conventional surface-active agents are used for emulsifying non-ionic hydrophobic polyurethanes. High and low molecular weight polyurethane ionomers are also good emulsifiers for emulsion polymerisation. Since the introduction of aqueous polyurethanes into the class of ionic polymers in the 1960s, research work has focused on their end uses rather than obtaining an understanding of their property relationships.

In emulsion polymerisation the role of each component, the mechanism of the reaction, including the kinetics, are well understood. However, there is very little information available

CCC 1022-1360/00/$ 17.50+.50/0

on structure-property relationships of polyurethane ionomers for commercial applications. There is a gap between understanding traditional emulsion technology and polyurethane ionomers. Cooper et.al[2-6] have done extensive work on polyurethane ionomers but their characterisation studies were done mainly on solid-state sulphonated ionomers with the sodium salts attached, which is undesirable for coatings applications.

Whilst the end use of polyurethane dispersion ionomers in high-quality coating systems has been driven by their outstanding performance over many of the waterborne dispersions and emulsions, basic property-relationships of these fascinating polymers are not well understood. As a result of this, it was deemed necessary to obtain a clearer understanding of the mechanism of dispersion formation and the effects of the neutralising base on the stability and other properties of the dispersion, such as swelling of these ionomers.

2. Experimental

2.1 Chemicals Used

2,2-Dimethyl propane diol and 2,2-hydroxymethyl propionic acid (Perstorp Polyols), adipic acid and 1,2-ethane diol (BASF), 1,4-cyclohexane dicarboxylic acid (Eastman Chemicals Co.), 1,2,4-phosphonobutane tricarboxylic acid and dicyclohexane-methane-diisocyanate (Bayer), and all the neutralising bases were used as received. Butanone was dried over 4Å molecular sieve prior to use.

2. 2 Synthesis of Phosphated Polyester Macroglycols

The mass percentages of reactants used for the synthesis of phosphate-containing polyester macroglycols and their analytical values are listed in Table 1. The synthesis procedure used for the preparation phosphated macroglycols with different compositions is as follows. A typical reaction procedure involves charging a 3L- glass reactor with all the reactants and heating to the desired esterification temperature (ca 215-225^{0}C). During heating, the water from the 1,2,4-phosphonobutane tricarboxylic acid was first distilled at 105^{0}C and then the temperature was gradually increased by 10^{0}C/30 min until it reached 215-225^{0}C. In the reaction between a polybasic acid and a polyhydric alcohol to form esters, water is liberated as a by-product. It was important to remove this water to drive the reaction equilibrium towards the ester formation.

$$R_1\text{-COOH} + R_2OH \rightleftharpoons R_1COOR_2 + H_2O\uparrow$$

Table 1: Mass % of monomers used and the analytical value of the macroglycols

Chemicals	**Mass % of the reactants**				
	PMG-1	PMG-2	PMG-3	PMG-4	PMG-5
2,2-dimethyl propane diol	48	50	50	50	50
Hexanedioc acid	20	20	20	20	20
1,4-cyclohexane dicarboxylic acid	20	16	14	12	10
1,2,4-Phosphonobutane tricarboxylic acid	12	14	16	18	20
Analytical values					
Acid value, mg KOH/gm	7	8	7.8	8.4	9.1
Final OH-number, mg KOH/g	100	105	110	95	104
Molecular weight, Mn	2500	2500	2550	2600	2500
Polydispersity, Mw/Mn	2.3	2.42	2.45	2.5	2.52

PMG: phosphated macroglycol

It was very difficult to remove the last traces of water from the product and a slight vacuum had to be applied to drive the forward reaction. From calculations based on the number of charged moles, a large decrease in reaction rate was observed below an acid number of 35 mg KOH/gm. When vacuum is applied during the synthesis, all the remaining water, any excess free diols and side-reaction products such as lower molecular weight ethers, ketones and aldehydes were distilled off. Thus phosphated-polyester macroglycols with terminal hydroxyl groups were synthesised.

2.3 Synthesis of Segmented Polyurethanes from Phosphated Polyester Macroglycols

The phosphated polyester macroglycols were heated to 90^0C and degassed under reduced pressure for 1 h prior to use. A 1L-glass reactor equipped with a nitrogen inlet and outlet, condenser, mechanical stirrer, charging and sampling port, was charged with 2,2-hydroxymethyl propionic acid, 1,2-ethane diol and dicyclohexane-methane-diisocyanate. The reaction mixture was heated in an oil bath to 100^0C. The urethane-forming reaction proceeded at this temperature for 1½ h to form isocyanate-terminated hard urethane segments. After 1.5 h, the temperature was reduced to 80^0C and a butanone solution of the phosphated polyester macroglycol was added. The temperature was kept at 75-80^0C for a further 3 h. After the isocyanate peak disappeared from an infrared spectrum at 2265 cm^{-1}, the reaction was cooled to 60^0C and a neutralising base was added. Dispersion into water was done at different temperatures (30-60^0C) and the butanone distilled off. Polyurethane ionomers with bound carboxylate ions on the hard segment were obtained. The hard segment content was 20-50% and the ionic content was 3-8%.

2.4 Characterisation

Changes in viscosity of the polyurethane ionomers, during neutralisation and addition of water, were measured by a Brookfield synchro-lectric viscometer with spindles LUT number 1-4. The conductivity measurements of the polyurethane ionomers, during the dispersion process of the ionomers, were measured in a digital conductivity probe (Model TESTRONIX-15 from Manish Instruments and Chemicals, India). The instrument had a digital display unit, a progressive printout screen, and a 1000 Hz frequency. The probe was dipped into the ionomers before addition of water and conductivity change was recorded accurately.

Particle-size measurements of the dispersions were done using a Malvern Zetasizer (Model 3000HS at 25^0C).

Specimens for swelling tests were prepared by weighing small amounts of the dispersions (4-5g) in an aluminium dish and evaporating the water in an oven at above 100^0C. The resulting films were then removed from the dish, cut into appropriate sizes and accurately weighed to ±0.001 mg. Their thickness was about 2-5mm. The specimens were suspended on a copper wire and completely submerged in distilled water at 20 ± 1^0C. The relative water-absorption masses were determined by weighing the specimens after they had been dried with filter paper, and subtracting these value from values of the initial mass.

$$\text{Swelling}\,(\%) = \frac{\mathrm{W_s} - \mathrm{W_d}}{\mathrm{W_d}} X 100 \qquad (1)$$

where: W_s is the weight of the swollen sample and W_d is the weight of the dried sample.

3. Results and Discussion

3.1 Emulsification Mechanisms

Special methods are necessary for the production of polyurethane dispersions because of the thermodynamically unstable nature of these two-phase systems. use of the well-known emulsion polymerisation techniques[7] for the preparation of isocyanate-based emulsion polymers is not possible because of the reactivity of the isocyanate group with water. Generally, it is the extreme water sensitivity of all polyurethane preparation procedures which often call for complete absence of water, that was a deciding factor for using the different emulsification method described here.

Unlike traditional emulsion polymerisation or even those so-called new generation emulsion polymers obtained from co-polymerisable surfactants and surface-active initiators, polyurethane emulsions are quite different due to the absence of water during their synthesis. They are prepared by a polyaddition reaction with or without organic solvent. The polymerisation locus is not the 'micelle' as the polymer is in discrete solution. However, post-polymerisation modifications allow these polymers made by polyaddition reactions to become water-dispersible emulsions. The emulsification or phase-inversion of the polyurethanes in this study, from organic solution phase to aqueous phase, was found to take place in three stages. These are discussed below.

Stage One: Changes in Viscosity during Neutralisation

During this stage the polymer was fully reacted in an organic solvent (butanone). When calculated stochiometric amounts of the neutralising amine, triethylamine, was added to form the ionomers, the viscosity increased as shown in Figure 1.

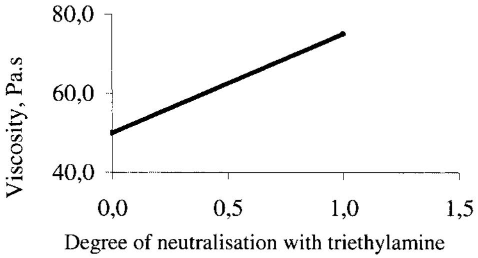

Fig. 1: Increase in viscosity of phosphated polyurethane resin upon neutralisation, 30% in butanone

However, neutralisation of the acid groups to convert the polyurethane into ionomer had no effect on molecular weight increase and the increase in viscosity was attributed to the formation of micro-ionic lattices. Micro-ionic lattices form as a result of inter- and intra-molecular coulombic interactions between the carboxylate groups, formed upon neutralisation of the acid groups of the stabilising monomer, and the positive counterions. Inter- rather than intra-molecular ion clustering is more likely because of the repulsion of the negative charges along a single chain[8]. Thus, as in the solid state where the ion association leads to pseudocrosslinking and elasticity, the same phenomenon was responsible for the anomalously high viscosity. This phenomenon was proved by the addition of small quantities of a high dielectric solvent, for example water, to the ionomers, which resulted in a sharp decrease in viscosity to below that before neutralisation. Ionic association is reversible and any water present solvated the ionic clusters and reduced the viscosity. This situation is shown in Figure 2

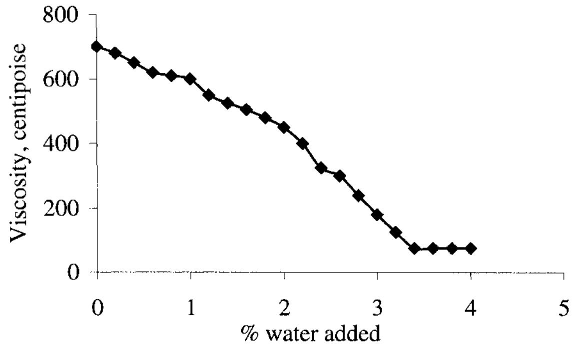

Fig. 2: Decrease in the viscosity of a 10% solution of an anionic polyurethane in butanone on addition of water

Stage Two: Changes in Viscosity as Concentration is Reduced

As the agitation (stirrer) speed was increased and more water added, the viscosity again increased although the solids content decreased. Since the butanone concentration was reduced, the solvation sheath of the hydrophobic segments was also reduced. During this stage the viscosity increased to a maximum, as shown in Figure 3. At this stage, as water was added it was adsorbed by the carboxylate anions situated on the surface of the hard segment micro-ionic lattices, causing a separation of neighbouring chains and aggregates. Each micro-ionic lattice, which is considered to form in the organic medium, is an aggregation of unsolvated salt segments stabilised by coulombic forces[9]. As the amount of water was increased, it started to enter the interior of the more disordered hard segment micro-ionic lattices and, subsequently, the soft segment formed aligned hydrophobic aggregates, which eventually became the dispersed phase.

Stage Three: Particle Formation

In stage one and two discussed above, the solution was clear since the ionomers were molecularly dispersed. As the last portion of water was added turbidity, which was an indication of the formation of a dispersed phase, was observed. During this stage turbidity reached a maximum and the viscosity dropped sharply due to the rearranging of the aggregates to form microspherical particles (Figure 3, stage 3). In this stage a discontinuous phase of polyurethane was dispersed in a continuous aqueous phase. When butanone was removed by distillation, a polyurethane ionomer emulsion in water was obtained. The three stages of emulsifications are schematically shown in Figure 4.

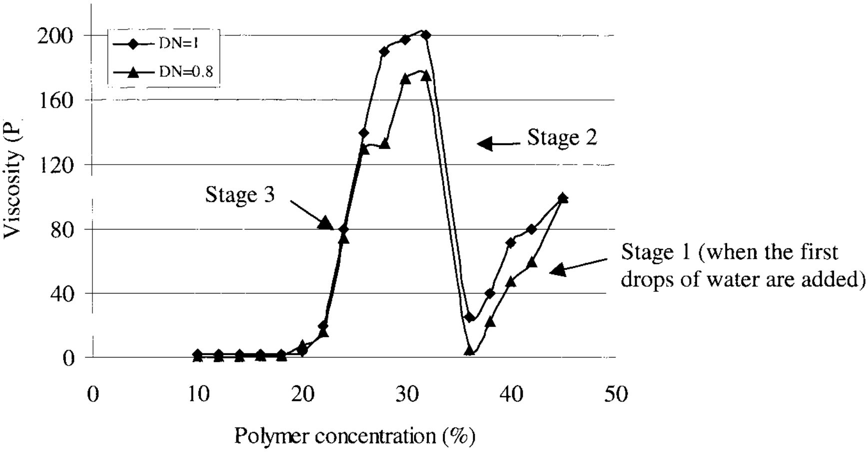

Fig. 3: Change in viscosity of TEA-neutralised phosphated-polyurethanes during the dispersion process at 30^0C

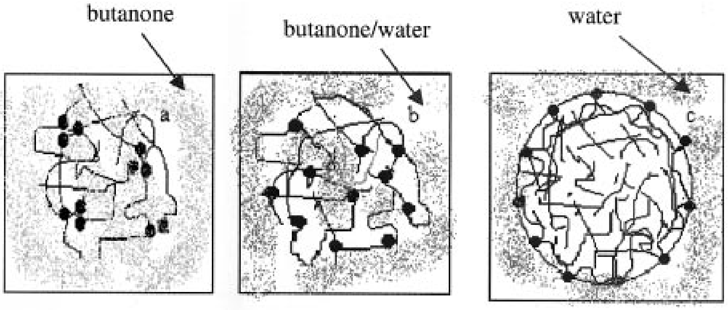

Fig. 4: Schematic representation of the three stages in the emulsification of polyurethane ionomers: (a) ionic association during stage 1 (b) interchain association of hydrophobic egments during stage 2, and (c) rearrangement of the hydrophobic chains into microspheres in stage 3

3.2 Conductivity Measurements During the Dispersion

Conductivity measurements during the phase inversion (emulsification) of polyurethane ionomers can be used to determine the end point for the dispersion process. The conductivity of polyurethane ionomers during dispersion, at two dispersing temperatures, are shown in Figure 5. The conductivity increased during the dispersion stage then levelled off. The beginning of the constant conductivity reading was taken as the end point of the dispersion. Conductivity is highly temperature-dependent due to the high mobility of the ions in a low-viscosity medium (Figure 5). At higher dispersion temperatures and higher degrees of neutralisation, water enters more easily into the hard segments. The temperature effect of conductivity can also be explained in terms of hydrogen bonding, which dissociates at 40-60^{0}C[10]. At the dispersion temperature of 50^{0}C most of the hydrogen bonds will be disrupted and more water can enter into the hard segment and increase the ionic mobility and hence the conductivity. The effect of the degree of neutralisation upon the conductivity at the same dispersion temperature was due to the number of ions generated upon neutralisation. It is well known that polymers with bound ions and free counter ions have better conductivity during solvation if sufficient ions are present in the solution[11].

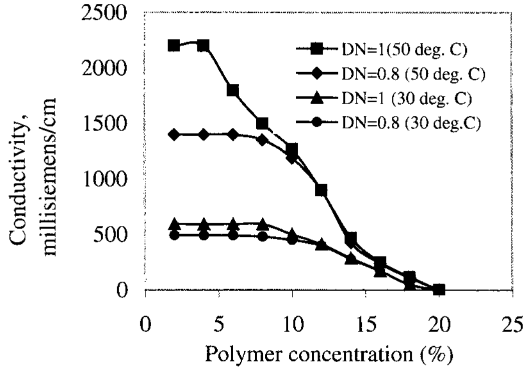

Fig. 5: The effect of dispersion temperature and DN on conductivity of polyurethane ionomers (3.5% ionic)

3.3 Particle-size Control during Dispersion

In polyurethane ionomers, the particle number, particle size and particle-size distribution are directly related to the amount of bound carboxylic acid/ sulphonate groups in the polymer. Dispersion temperature, the ratio of organic solvent to water, the stirrer speed, the NCO/OH ratio (in cases where the prepolymer process is used) have also been cited to contribute to the size of the particles[12]

The neutralising cation has a profound effect on the dispersion and mechanical properties of ionomers. The mechanical properties of the early known ionomers of ethylene and methacrylic acid were strongly dependent upon the neutralising cation[13]. The mechanical properties of polyurethane ionomers neutralised by different metal salts have also been investigated[5]. Whereas the effect of the neutralising cation on the film properties of polyurethane ionomers is well documented, its effect on dispersion properties such as dispersibility, particle-size and dispersion stability has been overlooked.

In this study, phosphated polyurethane resins were neutralised with various neutralising bases. Results of particle sizes are given in Table 2. The phosphated polyurethanes studied had 70% soft segment, 30% hard segment and 4% 2,2-dihydroxymethyl propionic acid, which was fully neutralised.

Table 2: The effect of the neutralising cation on the particle-size and formation of stable dispersions

Neutralising base	**pK_b**	**Particle size (nm)**
Triethylamine	3.24	55
Tripropylamine	3.35	200
Tributylamine	3.11	400 (Dispersible and stable only for 1 day)
Triisobutylamine	3.68	Not dispersible
Tripentylamine	-	Not dispersible
Morpholine	-	62
LiOH	-	40
NaOH	-	45

As seen in the table, the metal cations produced smaller particles than the corresponding ammonium cations. This was due to the ease of hydration during the addition of water. In cases where higher substituted alkyl tertiary amines were used, stable dispersions were not possible. In the extreme cases of triisobutylamine and tripentylamine, the ammonium cations were too hydrophobic to be dispersed in water and no dispersions were possible, irrespective of the amount of the carboxylic acid groups. The smaller particles obtained from the lower alkyl amines seemed to be correlated with their increased water solubility. The short-chain alkyl amines are soluble in water but those amines having more than 5 carbon atoms are insoluble at higher temperatures but sparingly soluble at lower temperatures[14]. To verify the effect of temperature on hydration of the ammonium cations, dispersions were prepared at different temperatures (5^0C-65^0C) for the tributylamine series. As can be seen from Figure 6, the lower temperatures favored dispersibility with lower particle sizes. This result was unexpected, since it has been reported[15] that higher dispersion temperatures disrupt hydrogen bonding and separation of the chains into smaller particles is possible, without considering the effect of the counter ion. The temperature effect of the neutralising amine was very striking especially when considering making paints to be used at higher service temperatures. This is because complete hydrophobicity is obtained, unlike other waterborne systems where blistering due to hydrophilicity is a limiting factor. Though primary particle sizes are smaller for the metal cations in the order of Li < Na < K, the presence of metal cations was not desirable for dispersions intended for use in coatings due to the non-volatility during curing and thus water sensitivity.

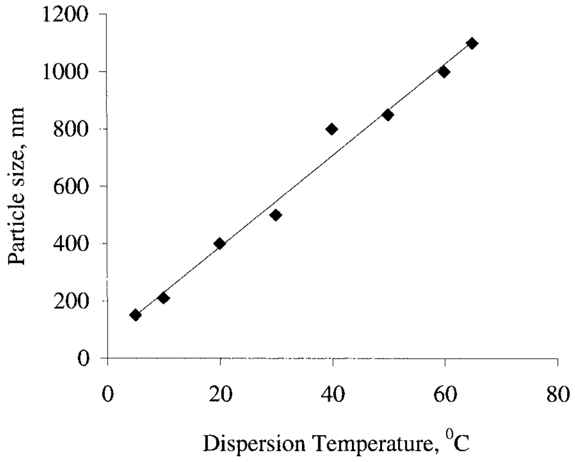

Fig. 6: The effect of temperature on dispersion formation and particle size of the tributylamine- neutralised dispersions

From the range of amines used, morpholine showed a good balance between non-toxicity and dispersibility. It also has a low boiling point (128^0C) and can be easily dissociated upon curing. Morpholine is a secondary amine, which can also react with isocyanates. During this study complete consumption of the charged isocyanate was verified before neutralisation was effected.

3.4 Effects of Ion Concentration on Particle Number

All ion-containing polymers are not water dispersible[16]. A minimum ionic content with choice of favourable counter ions has to be met for water dispersibility and storage stability. While ionic groups associated in polymers in the solid state act as crosslinkers and improve mechanical properties[17], 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, the 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_c, was calculated from the mean particle diameter, D_T (calculated from r_u), obtained from light scattering measurements and using the relationship:

$$N_c = \frac{m_p}{4/3\pi r_u^3 d_p} \tag{2}$$

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.

However, since particles formed from polyurethane dispersions are polydisperse, the calculated value of N_c is smaller than the actual value. A plot of N_c versus concentration of bound stabilisers is shown in Figure 7. 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 amount of ionic groups required for the formation of stable dispersions, below which no stable dispersion could ever be formed. The odd distribution of data points is coincidental and based on experimental deviation.

3.5 Effects of the Degree of Neutralisation (DN) on Particle Size and Particle Number

The degree of neutralisation has a direct effect on the particle size of the dispersions, as shown in Table 3. As the degree of neutralisation increased, particle size decreased, due to the hydrophilicity of the neutralised carboxylate ions, and dispersion viscosity increased due to the hydrodynamic volume of the finer particle size and swelling of the droplets.

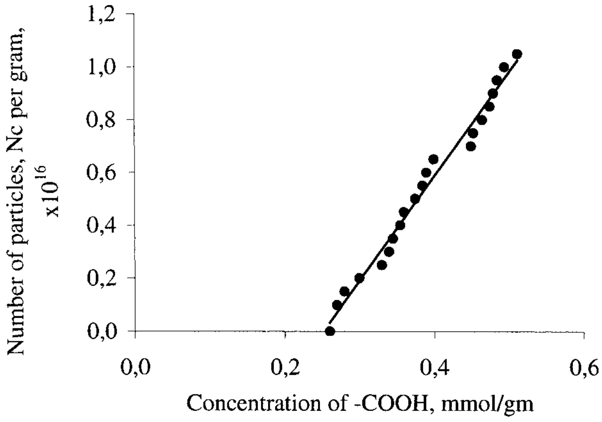

Fig. 7: Number of latex particles, N_c, versus carboxylate ion concentration

Table 3: Variation in particle-size and viscosity of phosphated polyurethane dispersions with the degree of neutralisation

Composition of the ionomer	**Degree of neutralisation** [(a)]	**Particle size, nm**	**Viscosity,** [(b)] **cps**
Phosphated polyester-urethane 70% w/w soft segment and 30% hard segment 0.45mmole g^{-1} COOH	0.70	210	40
	0.80	135	55
	0.85	110	70
	0.90	80	120
	0.95	55	200
	1.00	40	310
	1.20	40	350

(a): triethylamine was used as a neutralising agent; (b): determined with Brookfield viscometer at 20^0C

The effect of the carboxylate ion concentration on the number of particles formed is presented in Table 4. As the concentration of the carboxylate ion increased, the particle number also increased.

3.6 The Effect of the Neutralising Cation on Swelling

The effect of the neutralising base on the water uptake of uncured polyurethane ionomer films has been studied. This study was done on ionomer films cast from butanone. Figure 8 shows that those ionomers neutralised with longer chain amines, which have lower water solubility than short chain amines, had the least water absorption. This was due to the hydrophobic nature of the counter ions. The water swell decreased as we moved from morpholine, to tripropylamine (TPA), tributylamine (TBA), and triisobutylamine (TIBA).

Table 4: Effect of carboxylate ion concentration on the number of particles formed during emulsification

-COOH mmole g^{-1}	Number of Particles x10^{15}
0.27	1.02
0.30	2.22
0.35	3.11
0.40	4.37
0.45	7.83
0.50	9.02
0.55	12.06

There was little change in swelling when N,N-dimethyldodecylamine (DMDDA) was used as the neutralising agent compared with results obtained from the unneutralised film. The use of metal cations resulted in most swelling, increasing in the order of lithium, potassium and sodium.

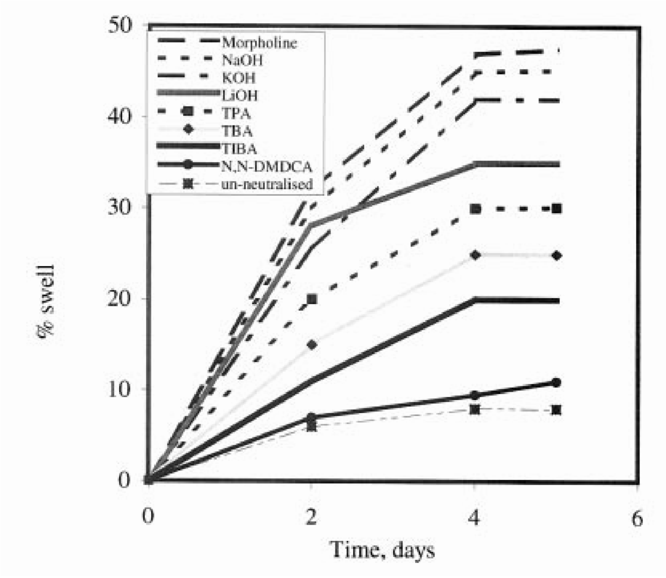

Fig. 8: Effect of the neutralising base on the time-dependent swelling of phosphated polyester-urethane ionomers (70% soft segment, 30% hard segment and 4% DMPA)

4. Conclusions

Phosphate-containing macroglycols have been synthesised from a new phosphate-functional carboxylic acid monomer. The macroglycols were used as a soft segment for the preparation of segmented polyurethane dispersions. Phosphate-containing polyurethane dispersions were made by phase inversion from the organic solvent after the carboxylic acid groups were neutralised. Phase inversion took place in three stages. The first stage was accompanied by a drop in viscosity, the second by a sudden increase in viscosity and the third by turbidity and a drop in viscosity indicating particle formation.

The three stages of the phase inversion of the phosphated polyurethane to form a dispersion were also studied by conductivity measurements during the phase inversion. Results of particle-size analyses and particle-number determinations have indicated that the dispersions were highly dependent on the neutralising base used. It was also shown that the hydration properties of the higher alkyl ammonium cations were reduced as the dispersion temperature was increased.

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