Perfect partners

Urethane/acrylic hybrids marry low VOCs to excellent physical properties.
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Ways to synthesise hybrid dispersions, which contain acrylic and urethane polymers in the same particles, are described. These resins can offer the best properties of waterborne polyurethanes at an optimum cost/performance balance. VOCs can be eliminated by utilising part of the acrylate starting materials to replace solvent in the urethane polymer synthesis.

Environmental and legislative pressures have driven the surface coating industry to concentrate on waterborne polymers. Advances in design and development have yielded coatings with properties that frequently match and sometimes exceed those provided by solventborne systems. Two major classes of waterborne polymers are in use:
- Aqueous polymer dispersions prepared in the waterborne state by emulsion polymerisation, such as acrylic polymers;
- Aqueous dispersions of pre-formed polymers which are subsequently dispersed in water, such as waterborne polyurethanes.

Acrylic emulsion polymers will readily copolymerise, giving economical systems that exhibit reasonable film properties. Polyurethanes, though, can yield excellent mechanical properties, which are ideally suited to high performance surface coating applications.

Technical advancement in both these areas has been very well documented in both academic and industrial research [1-4]. In an attempt to provide the best of both these technologies, a useful class of material which has recently emerged is the combination of urethane and acrylic polymers in one polymer colloid, usually known as urethane/acrylic hybrids or composites. The key factors required for a useful surface coating of this type are highlighted.

Designing waterborne coating polymers
Key requirements for a useful surface coating are to be able to provide a defect-free and coherent film on the substrate and develop mechanical and resistance properties. In the case of solventborne polymers, film formation is readily achieved through the unhindered mobility of low molecular weight polymer chains in solvent media.

The situation with a dispersed waterborne polymer system, however, is entirely different. Here, in general, high molecular weight polymer chains are contained within particles. On film formation, the particles need to deform effectively and then coalesce in order to attain efficient interpenetration of the chains and yield a coherent film. This process is recognised to be difficult, and the design of such particulate systems thus becomes critical. The mode of synthesis of aqueous polyurethane dispersions typically results in particles which are polydisperse in terms of size and swollen in terms of their internal particle morphology [5]. In fact, the particles behave as a collection of large macromolecular chains held together by intermolecular interactions. In general the particle size is small, in the region of 60 - 150 nm, and the size distribution is broad. This dispersion morphology clearly derives from the nature of the synthesis, which is based on step growth polymerisation followed by emulsionification. Additionally, evidence from fluorescence and small angle neutron scattering measurements suggests that the internal particle morphology is swollen via plasticisation by water molecules [5]. These features allow polyurethane particles to achieve excellent film formation [6].

The polymer chain makeup of a typical polyurethane commonly contains soft and hard segments [7]. Soft segments mainly arise from high molecular weight polylol components, while the hard segment contribution arises from disiocyanates, low molecular weight diols and urethane or urea bond sequences. The hard domains provide both physical interaction sites via hydrogen bonding and filler-like reinforcement to the soft segment matrix. Coating film properties are also dependent on the phase mixing or de-mixing (via hydrogen bonding) of the soft and hard segments [8]. Polyurethane dispersions are therefore employed in a wide variety of surface coating applications where mechanical properties are key requirements. Superior toughness, elongation, mar and scratch resistance properties are typical. The raw material cost is higher than for a typical acrylic emulsion. Polyurethane dispersions are often combined with less expensive polymers to reduce costs. More often than not however, simple physical blending of the polymers does not achieve the required property/cost balance.

Two-stage synthesis improves binder properties
A more elegant solution is to synthesise a urethane(acrylate (U/A) hybrid polymer, which contains both urethane and acrylic phases in the same composite particle. Mechanical and tensile properties in particular have been shown to be significantly better for hybrid systems than for blends of the same components [9, 10]. Important factors include the ability to produce small phase sizes and thus create large interfaces between the urethane and acrylic phases leading to interpenetrating network formation, and/or grafting [11] between the urethane and acrylic phases. Properties will clearly depend on the synthetic route, selection of optimum backbone and compatibility/interaction of the different phases.

A typical urethane/acrylic hybrid is prepared by carrying out a free radical polymerisation of acrylic monomers in the presence of a urethane dispersion. Since the urethane polymer is frequently the stabiliser for the acrylic particles, it must be envisaged that the acrylic phase will usually reside in the core of the composite particle. Amongst several available routes, the acrylic polymerisation can be conducted either by feeding the monomer continuously to the urethane dispersion or via a batch process. In the latter case, the monomer is allowed to swell in the urethane dispersion for a specific period of time before effecting polymerisation. This process was employed for the studies described here.

The batch process offers very fast polymerisation kinetics, leading to relatively monodisperse composite particles. A transmission electron micrograph of a typical urethane/acrylic dispersion prepared via batch process is shown in Figure 1; this exhibits true hybrid particle morphology with both the urtd and polyurethane dispersions present within the same composite particle. This feature, together with the fast reaction kinetics, provides qualitative evidence for nucleation within monomer-swollen urethane particles, a situation which parallels some of the characteristics of conventional mini-emulsion polymerisation [12].

Factors affecting hybrid properties
The particle and film morphology of a U/A system is directly dependent on the choice of the backbone types. The choice
The essential step of regulating the prepolymer viscosity is stage, resulting in a high molecular weight polyurethane and transferred to water, where spontaneous particle such a manner that the isocyanate terminated prepolymer (isocyanate: hydroxyl ratio) of the reaction is maintained in the process required to produce an anionic polyurethane dispersed in water [13, 14]. A schematic representation of polyols are reacted with diisocyanates and subsequently conventional polyurethane synthesis in which diols or

A common feature of all routes for the synthesis of hybrids can eliminate solvent from PUD production

Conformity to environmental and legislative regulations is fast becoming of paramount importance in the surface coating industry. Although polymers supplied in water attempt to satisfy this need, there remain a number of issues where less desirable chemicals are used either in their synthesis or in the subsequent formulation. With respect to urethane/acrylic polymers, two issues must be considered:

- Removal of NMP
- Lowering the concentration of other volatile organics.

A common feature of all routes for the synthesis of polyurethane dispersions is that the first step is a conventional polyurethane synthesis in which diols or polyols are reacted with diisocyanates and subsequently dispersed in water [13, 14]. A schematic representation of the process required to produce an anionic polyurethane dispersion is shown in Figure 3.

In the prepolymer mixing process the stoichiometry (isocyanate: hydroxyl ratio) of the reaction is maintained in such a manner that the isocyanate terminated prepolymer has a workable viscosity/molecular weight, to facilitate the aqueous dispersion step. The prepolymer is then neutralised and transferred to water, where spontaneous particle formation occurs. Chain extension is carried out at this stage, resulting in a high molecular weight polyurethane dispersion.

The essential step of regulating the prepolymer viscosity is generally achieved by using a diluent, which ultimately remains in the final dispersion and contributes to its VOC content. NMP is commonly used for this purpose. Because of concerns over the presence of NMP [15], worldwide legislation now stipulates labelling of products containing it. Polyurethane manufacturers are therefore seeking either to reduce or eliminate NMP. However, in general, alternative diluents either do not have the solvating and viscosity regulation power of NMP or they are more expensive.

The urethane/acrylic hybrid polymerisation is, however ideally suited to overcoming this problem. Part of the acrylic monomer can be employed as diluent during the prepolymer reaction. After the dispersion and chain extension steps, the rest of the monomer is added, followed by acrylic polymerisation. This route not only avoids the use of NMP or any other solvent but also does not contribute to VOCs. By suitable process design, the colloidal and film properties of these NMP-free urethane/acrylic hybrid polymers can be made equal to or even better than those of NMP-containing dispersions.

A hybrid polymer without NMP

Two 50/50 U/A hybrids (U/A-1 and U/A-3) were synthesised from the same urethane and acrylic compositions as described above. The urethane prepolymer and thus the dispersion of U/A-1 contained NMP as diluent. However, in the urethane part of U/A-3, NMP was replaced by the same weight of a monomer mixture based on methyl methacrylate. After the dispersion and chain extension steps, U-1 and U-3 were converted to U/A-1 and U/A-3 hybrid polymers respectively at an overall U/A ratio of 50/50.

In the case of U/A-1, all monomers, and in the case of U/A-3 the remaining monomers, were added to the dispersion. After a swelling period of 0.5h, free radical polymerisation was effected to provide the hybrid polymers. Colloidal and film property results are shown in Table 1 and DMTA plots are also presented in Figure 2.

It can be seen from Table 1 that the average particle size of U/A-1 is larger than that of U/A-3, most probably because the NMP swells the particles. The minimum film forming temperature (MFFT) of both polymers are low despite the 50% content and high Tg (50°C) of the acrylic phase. This result suggests that the soft urethane phase in the film behaves as the continuous phase and is essentially present as a shell in the composite particle.

Although the strain at break for both samples is similar, a significant difference in stress at break or tensile strength is evident. The low tensile strength for U/A-1 is most likely due to the plasticising effect of NMP and its possible retention in the film. In the case of U/A-3, however, the hybrid develops its true tensile strength. Tand plots shown in Figure 2 indicate the general phase behaviour of both systems to be essentially similar.

No coalescents required

An additional source of VOCs is the use of coalescing solvents to aid film formation. Ways to drastically reduce the required level of coalescent are being actively pursued. It remains important to provide a balance of properties such as film formation at low temperatures in the absence, or presence of a minimum level, of coalescent while maintaining excellent hardness, tensile properties and chemical resistance.

U/A hybrid systems are well suited to achieving the required property balances due to their inherent hard and soft segmentation, and excellent properties can be obtained without the need for coalescent. It is noteworthy that, in the absence of coalescent, film formation on a micro scale is difficult to achieve unless suitably designed, and so chemical resistance is generally compromised. This situation is more noticeable in the case of NMP-free
urethanes and urethane/acrylics where NMP is replaced by acrylic monomer as discussed earlier.

An example of this is shown in Figure 4, where the surface morphology of an NMP-free urethane/acrylic film is compared to the clearly more uniform appearance of the same film annealed at higher temperature. A useful way to overcome this in a urethane/acrylic system is to design the urethane with a high level of soft segment content to effect micro film formation.

Hybrids bring together the best of both technologies

The advantages and the wide design scope available within waterborne urethane/acrylic hybrid technology have been highlighted. Careful synthetic and morphological considerations can produce tailor made products to meet specific application needs. Urethane/acrylic hybrid technology is well placed to achieve the best of both worlds in providing high performance and environmentally friendly surface coatings.

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References


Results at a glance

- Waterborne polyurethane dispersions can provide coatings with high mechanical strength combined with good chemical resistance.
- Their relatively high raw material costs can be overcome by urethane/acrylic hybrid technology which combines urethane and acrylic polymers within one particle.
- Using hybrids, it is possible to eliminate the N-methyl pyrrolidone normally used in PUDs by using acrylic monomers as the ‘solvent/diluent’ in urethane polymerisation then polymerising them later.
- By careful design of these hybrid polymers, it can also be possible to eliminate, or significantly reduce cosolvents from coating formulations.
Figure 1: Electron micrograph of a urethane/ acrylic hybrid dispersion coating prepared by the batch process.

Figure 2: Dynamic mechanical thermal analyses (DMTA) of the hybrid samples U/A-1, U/A-2, U/A-3 and the parent urethane U-1. Frequency 10 Hz, heating rate 3°C/min. Black curves: storage modulus $E'$, red curves: loss modulus $E''$, blue curves: loss factor $\tan \delta = \frac{E''}{E'}$. 
Figure 3: Schematic representation of the synthetic steps of the polymer mixing process to produce an anionic dispersion.

Figure 4: Atomic force images of the surface morphology of an NMP-free hybrid dispersion before (left) and after heating (right). Measured in height mode, z-range: 28.1 nm.
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<thead>
<tr>
<th>Property</th>
<th>U/A-1</th>
<th>U/A-3</th>
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<tbody>
<tr>
<td>Average particle size (nm)</td>
<td>145</td>
<td>88</td>
</tr>
<tr>
<td>MFFT (°C)</td>
<td>&lt;5</td>
<td>&lt;5</td>
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<tr>
<td>Stress at break (MPa)</td>
<td>1.8</td>
<td>14</td>
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<tr>
<td>Strain at break (%)</td>
<td>741</td>
<td>715</td>
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