

# Comparing and contrasting the properties of urethane/acrylic hybrids with those of corresponding blends of urethane dispersions and acrylic emulsions

Richard A. Brown\*, Richard G. Coogan, Dave G. Fortier,  
Michael S. Reeve, Joseph D. Rega

*NeoResins, Inc., 730 Main Street, Wilmington, MA 01887, USA*

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## Abstract

In this work the effect of acrylic emulsion design on polyurethane–acrylic emulsion blend properties has been examined. A series of model acrylic emulsions were prepared and blended with a commercial polyurethane dispersion (PUD). Corresponding polyurethane/acrylic hybrid (U/A) systems were prepared from the same commercial PUD. The acrylic to urethane ratio was kept at 50:50 by weight throughout. The acrylic emulsion parameters varied were: particle size, composition (acid monomer level),  $T_g$  and molecular weight. Modulated DSC was used to qualitatively determine the amount of polyurethane and acrylic polymer in the interphase of the blends and hybrids. Results show that there is approximately 5–20% by weight of each of the acrylic and polyurethane in the interphase in the blends. While in the U/A hybrids there is approximately 20–30% polyurethane and 35–50% of acrylic in the interphase.

The mechanical properties of the dry films were measured by tensile testing. The hybrids were found to compare favorably with, and in some areas exceed, the PUD alone in tensile performance. In contrast the performance of all of the blend systems fell short of the PUD and of the corresponding hybrids. Within the set of blends the best tensile results were achieved using the low  $T_g$ , high molecular weight acrylic emulsions. There were no clear trends with changes in acrylic emulsion particle size or acid content. The difference in performance between blends and hybrids is attributed to the increased phase mixing and the improved dispersion of phase domains in the hybrids.

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## 1. Introduction

In the coatings industry there is a strong commercial need to optimize the performance of water borne systems to replace solvent based coatings as pressures to reduce VOCs increase. Polyurethane dispersions (PUD) are known to offer high performance especially in terms of their combination of toughness, abrasion resistance, mechanical flexibility and chemical resistance. The higher cost of polyurethane dispersions has led some resin suppliers to develop a range of urethane/acrylic hybrid dispersions (U/A) which still maintain an excellent property balance [1,2]. However formulators will still typically blend urethanes and U/A dispersions with acrylic emulsions in a coating package.

In general a blend or mixture of two different polymers will be immiscible in the absence of specific interactions (such as ionic interactions). This is a result of thermo-

dynamic inhibition as the free energy of mixing ( $\Delta G_m$ ) of two polymers is positive for most polymer combinations [3]. In addition the long chain nature of polymers results in slow interdiffusion of polymers relative to monomeric substances such that the kinetics is also prohibitive.

Therefore a physical blend of two aqueous dispersions of different polymers will, in most cases, yield a final film composed of distinct phases of each polymer. Moreover the sizes of the phases will be of the order of the original particles. In an aqueous dispersion the colloid stability of the particles during the film formation process will determine how well dispersed the two phases are in the final dry film. Partial flocculation of particles during film formation results in the formation of large regions of one polymer component in the blend. This in turn will reduce the benefit of dispersing hard polymer regions in a soft matrix (toughening) or soft regions in a hard matrix (impact modifier).

One method of ensuring good dispersion of two polymers in a blend is through mixing via reaction. Here a monomer of polymer 2 is allowed to diffuse into the bulk phase of

\* Corresponding author.

*E-mail address:* richard.brown@neoresins.com (R.A. Brown).

polymer 1. When the monomer is polymerized to give polymer 2 the viscosity rises fast enough to prevent substantial phase separation. This yields an interpenetrating network of polymers 1 and 2 (or more strictly a *semi*-IPN in the absence of crosslinking or grafting). In practice the product of polymerization of acrylic monomers in the presence of pre-made polymer dispersion (such as an acrylic emulsion seed or PUD) is characterized by one of a broad range of multi-phase particles in which partial or complete phase separation has occurred (core/shell, lobed, inverted core/shell, etc.) [4].

Following the work of Satguru et al. [5] the polyurethane particle in an aqueous dispersion is considered to have an 'open', water-swollen structure, while in contrast the acrylic emulsion particle is solid polymer with a surface rich in surfactant, acid and initiator residues. The U/A hybrid particle is considered to be a two phase particle in which the colloid stability is provided by the acid rich, water-swollen polyurethane outer layer. The inner portion of the particle is assumed to contain the acrylic polymer (which has no colloid stabilizing groups). The exact degree of polymer mixing of U and A polymers is the subject of debate (see Fig. 1).

The scope of this investigation was to determine the effect of the design of the acrylic emulsion used in blending with a PUD and to compare with the corresponding hybrid. The PUD used was a commercial product, specifically, *NeoRez R972* (here labelled *PUR*), which is a soft, low  $T_g$  ( $-53^\circ\text{C}$ ) polymer offering good tensile properties. It is characterized by a single, clear glass transition and was considered a good candidate for preparation of hybrids and blends in combination with hard, high  $T_g$  acrylic polymers. The resulting products could then be readily analyzed by thermal methods (showing two clear transitions) and tensile testing (showing clear changes in elongation and modulus). The acrylic emulsions were model latexes which were designed to mimic typical commercial products based on all-acrylic monomers. As close as possible the monomer composition was kept the same for the emulsions and the respective acrylic portion of the hybrids.

Other workers in the field have noted that the properties of U/A hybrids are considerably superior to those of the corresponding blends [6,7]. The purpose of this work was to

examine whether the properties of the blends could be improved relative to the hybrids by modification of the following parameters of the acrylic emulsion: choice of  $T_g$ , acrylic emulsion particle size, acrylic molecular weight or level of acid monomer in the emulsion. Two U/A hybrids were prepared using the *PUR* PUD as a starting point. The ratio of polyurethane to acrylic was 50:50 by weight of polymer, and the acrylic portion was composed of mixtures of methyl methacrylate and *n*-butyl acrylate chosen to give either a low or high  $T_g$  (for convenience they are coded UASoft and UAHard, respectively, see Table 3).

The model acrylic emulsions used in blending with *PUR* were prepared by standard techniques [8,9] using methyl methacrylate, *n*-butyl acrylate and acrylic acid. The latexes fell broadly into two sets; the low  $T_g$  series ( $T_g$ s range from 5 to 15  $^\circ\text{C}$ ) and high  $T_g$  series ( $T_g$ s range from 75 to 85  $^\circ\text{C}$ ), see Table 4 (the samples have been coded for the ease of the reader). Within these two sets the particle size was varied (by adjusting the surfactant level) over a range of about 50–210 nm. An acid monomer free series was made together with a high acid level sample to yield a range from 0 to 10% by weight acrylic acid. Finally the molecular weight was varied by addition of different levels of chain transfer agent to cover the molecular weight range;  $M_w = 14000$ – $150000$  (determined by GPC). All of the model acrylic emulsions were used to prepare blends with *PUR* at a solid weight ratio of 50:50.

## 2. Experimental

### 2.1. Synthesis of the acrylic emulsions

The acrylic emulsions were prepared in a 2l, glass reaction vessel, fitted with a stirrer, nitrogen bleed, thermocouple and feed vessels for initiator and monomers. A semi-continuous method was used to prepare the emulsions. An in-situ seed latex was prepared using a 10% charge of the total monomer, then the remainder of the monomer was fed to the reaction vessel over a 2 h period. A redox couple consisting of *t*-butylHydroperoxide and L-Ascorbic acid was used to remove residual monomer. The final pH of the

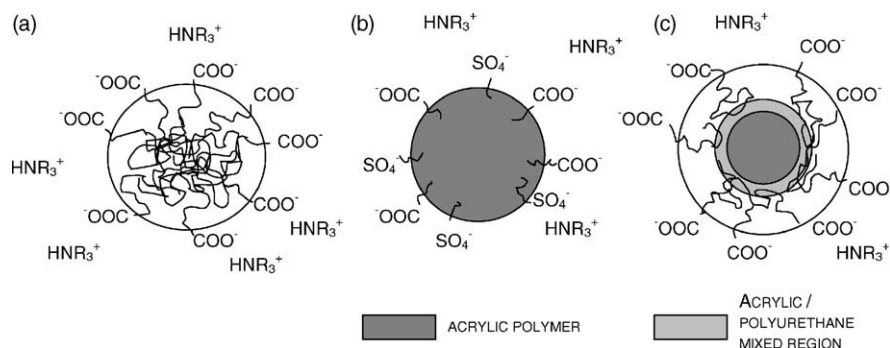


Fig. 1. Diagrammatic representation of a PUD particle (a), an acrylic emulsion particle (b) and a U/A hybrid particle (c).

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