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ARTICLE

NEW ADVANCES IN HYBRID TECHNOLOGY FOR FLOOR COATINGS



New Advances in Hybrid Technology for Floor Coatings

By marrying reactive surfactant technology with solvent-free waterborne hybrid resin technology, coating formulations of which total VOC is less than 50 g/L can be developed. Urethane-acrylic hybrid polymer dispersions (HPDs) can offer cost/performance advantages over common 1K coating materials such as PUDs, acrylic emulsions, and blends thereof. Although both the PUDs and the HPDs provide many benefits, one disadvantage is the inclusion of N-methyl pyrrolidone (NMP) solvent, which is commonly a necessary process solvent included at levels ranging from about 3 to 15%. Due to new regulations, it has become desirable to eliminate NMP from these products.

Consequently, solvent-free versions of HPDs have now been developed that, despite the lack of NMP used in their preparation, have been found to perform favourably compared to analogous solvent-containing polymers. By using this technology, several starting-point coating formulations with total VOC of less than 50 g/L have been developed.

Thermoplastic polyurethanes are well known for their excellent balance of mechanical toughness and chemical resistance. Unfortunately, the solvent-based versions require exceedingly high levels of VOC for application by conventional coating techniques.

Technical work

The waterborne versions (polyurethane dispersions or PUDs) require significantly lower VOC and are, therefore, becoming increasingly popular choices as binders for a variety of one-component coatings for wood (floors and furniture), plastic (business machine housings), leather, metal, and concrete. Their superior physical and chemical properties have been attributed to a combination of their molecular structure and hard/soft domain morphology. In general, PUDs are prepared by reacting an excess of di-isocyanate with a polyol, dispersing the resulting pre-polymer in water, and completing the reaction

by adding a water-soluble diamine to chain extend the pre-polymer to a high molecular weight. The dispersed PUD particles are usually anionically stabilised, which is commonly accomplished by incorporating dimethylol propionic acid (DMPA, a carboxylic acid-functional diol) into the backbone of the polyurethane and neutralising the acid groups with a tertiary amine. Thus, in many cases, no external surfactants are present to contribute adversely to water sensitivity of PUD-based coatings.

PUDs are available in both aromatic and aliphatic varieties. The aromatic versions provide better hardness and chemical resistance than their aliphatic counterparts. However, because they are based on aromatic di-isocyanates, the aromatic PUDs undergo a photochemical transformation when exposed to sunlight that generates a strong yellow chromophore. For applications requiring light stability, aliphatic PUDs must be employed.

One of the main disadvantages of aliphatic PUDs is their relatively high cost. As a result, formulators have sought ways to reduce the cost of their aliphatic PUD-based coatings. The most popular strategy is to blend the PUD with acrylic polymer emulsions, which generally cost less than one-half that of standard aliphatic PUDs. Although the acrylics reduce the system cost, they also reduce the overall performance of the binder. The reduction in performance can be lower than what would be predicted from an arithmetic rule of mixtures. One possible reason for this behaviour is that, on a molecular level, the acrylic polymers are not soluble in the polyurethane polymers. Therefore, the polymers remain phase-separated during film formation. The resultant phase morphology is probably at least partly responsible for this diminished performance behaviour.

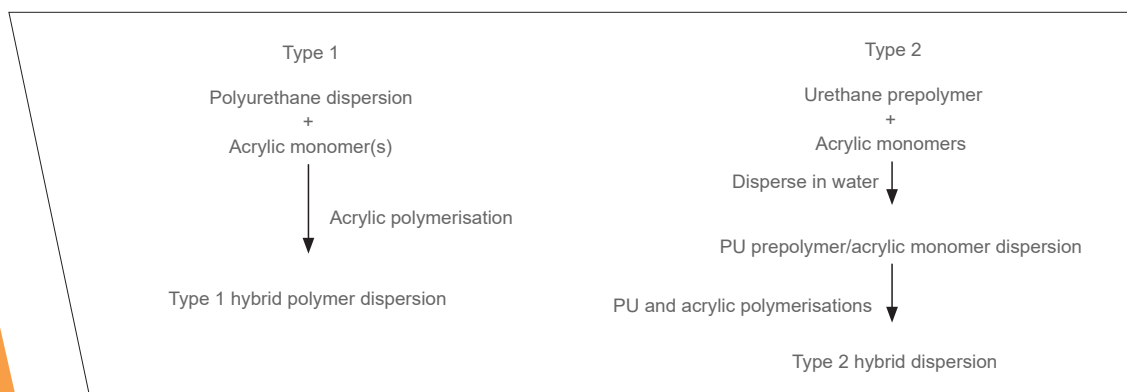
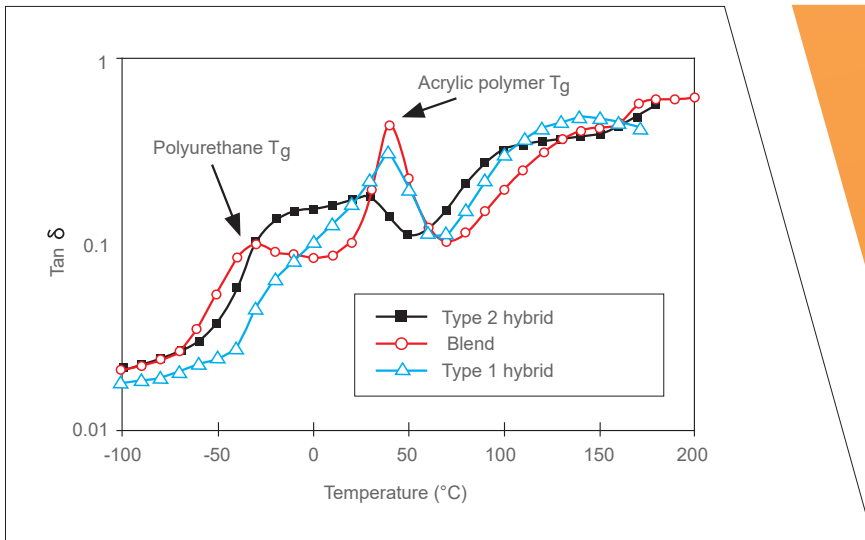


Figure 1: Simplified process flow of two methods for preparing HPDs (Type 1 and Type 2)



2:HPDs

Figure 2: DMA data comparing a simple blend with HPDs

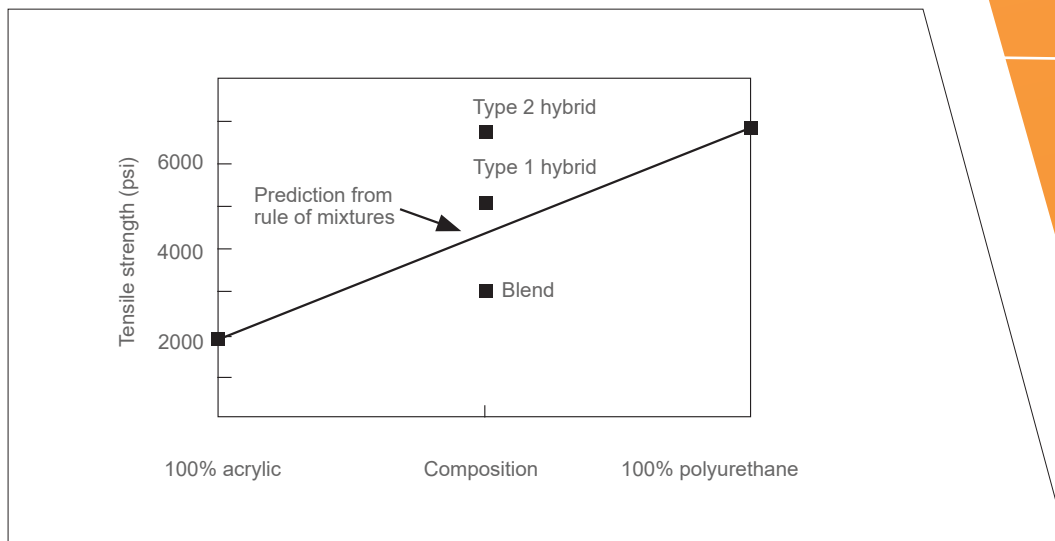


Figure 3: Tensile strengths of free films prepared from a simple blend and HPDs [11~12]

In order to take advantage of the potential cost reduction afforded by the acrylics and maintain a greater share of the advantageous PUD properties, the so-called "hybrid" systems were developed. The hybrids incorporate both the urethane and the acrylic polymers into the same dispersion. As outlined in the simplified process flow (Figure 1), there are generally two methods for preparing HPDs (Type 1 and Type 2). For Type 1 hybrids, a PUD is first prepared, acrylic monomers are added to the PUD, and the acrylic polymer is formed in the presence of the PUD. To prepare Type 2 hybrids, a polyurethane prepolymer is

formed, the acrylic monomers are added to the pre polymer, the mixture is dispersed in water, and the urethane and acrylic polymerisations are completed concurrently.

The urethane and acrylic polymers in HPDs exhibit improved molecular compatibility versus simple blending, but the degree of compatibility is highly dependent on the process of manufacture, as demonstrated by the dynamic mechanical analysis (DMA) data that are shown in Figure 2. In all of these samples, the polyurethane and acrylic compositions are essentially identical. The simple blend has 2 distinct tan delta ($\tan \delta$) peaks, which correspond to the glass transition temperatures (T_g) for the phase-separated urethane and acrylic polymers. The hybrid prepared from the first method described above also shows 2 T_g peaks, but the peaks have become somewhat broader, which is indicative of some limited molecular mixing. In contrast, a Type 2 hybrid, in which the urethane pre polymer and acrylic monomers are homogeneously mixed prior to dispersion and subsequent polymerisation, exhibits only a single, very broad $\tan \delta$ peak. The single peak, which spans the temperature range between the theoretical T_g s of the urethane and acrylic polymers, is strong evidence for a significant amount of polymer-polymer mixing, in which, presumably, the different polymer molecules are intertwined in a form of interpenetrating network (IPN) (Figure 2).

As mentioned previously, the rationale for preparing the hybrids was to improve performance relative to a simple blend. In Figure 3, the tensile strengths of films prepared from the individual polymers (i. e., a blend) and the 2 hybrid types are compared to that predicted by a linear rule of mixtures. The blend and the hybrids contain equal amounts of the same urethane and acrylic polymers. As expected, the urethane polymer had a significantly higher tensile strength than the acrylic polymer. Interestingly, the tensile strength of the blend was found to be lower than that predicted by the simple averaging rule. On the other hand, the hybrid systems show higher tensile strengths than predicted. Remarkably, the Type 2 hybrid was found to have a tensile strength approximately equal to that of the polyurethane. This evidence strongly suggests that the phase morphology of a urethane/ acrylic polymer system has a significant influence on the ultimate performance.

Typically, PUDs and HPDs contain a polar, aprotic solvent such as N-methyl pyrrolidone (NMP). The NMP is required in the polyurethane pre polymer step to dissolve the DMPA, which is a crystalline material that is virtually insoluble in the polyol-di isocyanate mixture that reacts to form the urethane pre polymer. Being a relatively high boiling solvent, NMP cannot be readily removed from the process and remains in the final dispersion product. Although the amount of NMP can vary according to the product, typical

NMP levels are 10% to 15% for PUDs and 3% to 8% for hybrids, based on total dispersion weight. In a final formulated product such as a coating, NMP is beneficial as a coalescing solvent for film formation. Conversely, NMP and high levels of residual acrylic monomers are undesired due to their odor and, in the case of NMP, its regulatory status (e.g., inclusion on California's Proposition 65). Therefore, there is a market need for NMP-free, low residual monomer HPDs that meet these regulatory requirements and still provide the outstanding performance that is expected of their NMP-containing counterparts.

There continues to be strong regulatory demand to reduce the amount of Volatile Organic Content (VOC) in paints and coatings.

The VOC of most of conventional PUDs and HPDs which are currently being used for the industrial coatings is at least 160 g/L because typical NMP levels are 10% to 15% for PUDs and 3% to 8% for hybrids. Those polymer dispersions can't be used to formulate coatings with a VOC less than 50 g/L.

The purpose of this study was to develop waterborne coating formulations based on new NMP and solvent-free HPDs that would have the performance required in many coatings applications while limiting added coalescing solvent.

With no solvent, it has normally been found that the level of coalescence will be insufficient to meet the performance requirements of a good coating material. Therefore, additional ingredient must be necessary to increase the coalescence. It is known that surfactants can reduce the minimum film-forming temperature (MFFT), thereby improving coalescence. This product recipe calls for reactive surfactants (surfmers) and hydrophobic monomers. This low VOC, formaldehyde free acrylic nano polymer shows very high hardness, water resistance, blushing resistance, hot tire resistance, wet look and chemical resistance (gasoline, brake fluid, sulfuric acid 25 %, etc).



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