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Selection of coalescing solvents for coatings derived from polyurethane dispersions utilizing high throughput research methods

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ABSTRACT

Reduction of volatile organic compounds (VOCs) in coatings is being driven by regulation and consumer preference. Development of binders that are capable of delivering expected performance at low VOC is a major thrust of coatings research and development. Toward this end, polyurethane dispersions (PUDs) from natural oil polyester polyols (NOPs) have been developed. These hydrophobic NOP-based PUD coatings exhibit exceptional early water resistance and hydrolytic stability, excellent acid resistance, and good toughness & abrasion resistance. Most high performance PUDs require large amounts of solvent to form crack-free films with good properties. However, with the right choice of process and solvent parameters, PUDs have been shown to require reduced amounts of coalescing solvents to yield the desirable array of end-user properties with ambient temperature drying. High-throughput research (HTR) was used as a means to accelerate formulation and product development of PUDs. Rapid formulation and testing allows for probing of interactions between variables in greater depth and breadth than conventional formulation techniques, leading to rapid development of robust products and formulations. The HTR methods for coatings applications include the use of specially designed experiments, robotic formulation, coating, and characterization tools as well as informatics for data visualization, extraction, and modeling. This paper details the use of HTR capability to explore the effect of cosolvents on end-use properties of NOP based PUD coatings as well as the proposed mechanisms of film formation in NOP-PUDs. The results provide a basis for guidelines for selection of cosolvents for PUD coatings with high performance and low VOC (<100 g/L VOC).

1. Introduction

Waterborne polyurethane dispersions (PUDs) are a rapidly growing segment of the polyurethane coating market. Such rapid growth is primarily driven by environmental regulations to reduce volatile organic compounds (VOCs) and technological advances resulting in improved properties and performance. Due to their attributes, PUDs have become effective substitutes for solvent-based counterparts in various coating applications including wood and concrete coatings [1,2]. PUDs derived from natural oil polyester polyols (NOPs) have been developed. Coatings made from the NOP-based PUDs have good toughness, abrasion resistance, hydrolytic stability, and acid resistance. They also exhibit superior water uptake (less) relative to competitive PUDs, due to the hydrophobic nature of NOPs [3–5].

Water-based solvents are often used in preparation and formulation of PUDs. In the "prepolymer mixing process", isocyanate-inert, water-miscible, high boiling point solvents are used to facilitate prepolymer synthesis [6]. The solvents include N-methylpyrrolidone (NMP) as well as PROGLYDE^{TM} DMM (DMM) and N-methylpyrrolidone [7]. These solvents remain in the PUDs, enhancing film formation as coalescing aids, but contribute to VOCs (>15%, corresponding to >200 g/L VOC). Furthermore, the presence of NMP or DMM in PUDs limits the formulators' options in balancing VOC level and coating properties. NMP and DMM are excellent solvents for synthesis of PU prepolymer, but there are better coalescing solvents.

VOC regulation scaling for < 100 g/L limit for industrial coatings, such as the South Coast Air Quality Management District (SCAQMD) exerts a continuous pressure on coatings manufacturers. To meet the requirements, PUD producers are utilizing acetone and methyl ethyl ketone (MEK) for prepolymer synthesis, followed by solvent stripping in order to provide solvent-free PUDs (USP 4,820,762). The recent availability of solvent-free PUDs including solvent-free versions of NOP based PUDs presents an opportunity for new options in the selection of cosolvent in order to minimize total VOC while achieving good film formation and coating properties. Better understanding of cosolvents versus end-user properties

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will lead to the selection of the best cosolvents for the development and commercialization of high performance NOP-PUDs with low VOC.

Today's coatings market exerts multiple pressures to successfully develop and introduce new coating products. Improving the environmental profile of these new products is a major driver that often requires significantly different formulation strategies. These complex coating formulations offer an excellent opportunity to use the strengths of high-throughput research (HTR) to understand how interactions between coating components affect final properties [8–10]. Not only in the area of coatings and formulations, but also in a broad variety of areas including catalysis, materials, genomics, protein assay, pharmacology, and pathology, HTR approach has been utilized for screening and development of new materials [11–13]. Compared to conventional bench-top research, such broad appeal to the establishment of HTR is attributed to the fact that HTR offers multiple and timely solutions by rapid screening of broad range of materials and parameters using robot-driven automation and software-supported models.

This paper describes the effect of cosolvents on end-use properties of NOP-PUD coatings using HTR methods. The central idea of the project is to select cosolvents that can reduce VOC level as well as improve end-use properties. In order to explore resulting coating properties, zero-VOC NOP-PUDs (formed using an MEK process followed by solvent stripping) were formulated with glycol solvents as well as NMP as a control. The resulting coatings were tested for minimum film formation temperature (MFFT), early water resistance, impact resistance, and pendulum hardness. In addition, the results from combined bench-top experiments and analytical methods allowed for better understanding of potential mechanisms of film formation and coalescence in terms of the distribution of hard domains in soft matrix in NOP-PUDs.

1.1. HTR capabilities for development of coating formulations

HTR is an integrated set of advanced capabilities in hardware and software that allow many more experimental variables to be explored and understood than could be achieved with traditional approaches. Hardware includes material handing robots as well as automated stations for measuring key properties of intermediates and final products to provide the key information for identifying promising products. Software includes HT experimental design, robotic control, data collection, processing, storage, visualization, analysis, and modeling.

In coatings, the basic steps are to formulate the materials, make the coatings, and test the dried films. The formulation capabilities cover most coating materials including solids and liquids over a broad range of viscosities. Each coating is coated on various substrates including Leneta paper, steel, aluminum, and wood that are placed in a substrate holder and tracked based on a unique experimental ID attached to the substrate holder via a barcode. The dried films are tested using automated HTR tools, including color, gloss, thickness, tack, friction, scrub resistance, stain resistance, block resistance, and low temperature coalescence. In addition, wet formulations are tested for pH, colloidal stability, freeze–thaw stability, viscosity, and rheology.

1.2. PUDs derived from bio-renewable NOPs

NOPs are prepared from chemically modified fatty acid methyl esters (FAMEs) derived from soy oil. The FAMEs are hydroformylated to the corresponding aldehyde intermediates and subsequently hydrogenated to the primary hydroxyl groups. The soy monomers are transesterified with a suitable glycol to increase molecular weight and generate the NOPs. The NOPs used in this study possess an average hydroxy functionality of two.

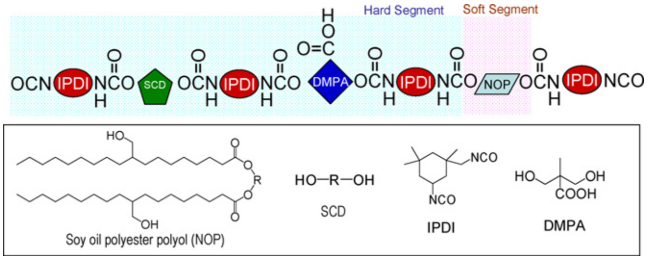

Fig. 1. Schematic illustration of structure of NOP-PUDs.

PUDs derived from NOPs are prepared by polycondensation reactions of polyisocyanates and polyols. Fig. 1 illustrates the structure of NOP-PUDs. Polyols include NOPs, acid-containing diols such as 2,2-bis(hydroxymethyl)propionic acid (DMPA), and optionally short chain diols (SCDs) to enhance the hard segments. To facilitate PU prepolymer synthesis, high boiling point solvents such as DMM and NMP or low boiling point solvents such as ketones are often used. They can reduce the viscosity of PU prepolymers and dissolve solid DMPA in reaction mixtures. Sequential steps including neutralization, dispersion, and chain extension yield stable NOP-PUDs with a diameter of 50–150 nm.

2. Experimental

2.1. Solvent-free NOP-PUDs (SF-NOP-PUDs) using MEK process

SF-NOP-PUDs were prepared by the MEK process. Briefly, NOP-based PU prepolymers were first synthesized from polyols including NOPs, DMPA, optionally SCDs, and MEK charged in a round-bottom flask under nitrogen. The mixture was immersed in an oil-bath preset at 70 °C. When the reaction temperature reached 55–60 °C, polyisocyanates were slowly added using a dropping funnel. The mixture was then stirred for 4–5 h. Samples were taken periodically to measure %NCO and COOH level. When the target values were reached, triethylamine (TEA) was added to neutralize COOH groups of PU prepolymers. The resulting PU prepolymers were dispersed in water under high shear, yielding a stable dispersion of PU prepolymers. Chain extender was added and then MEK was stripped off under vacuum at 50–55 °C.

2.2. Glycol solvents and NMP

Table 1 summarizes glycol solvents whose structures are classified into three groups; ethylene glycols (EGs), propylene glycols (PGs), and EGs and PGs of diether (PEGR). For comparison, NMP is included as a control.

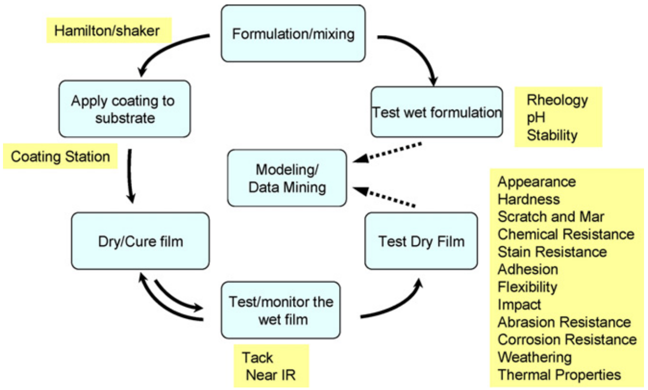

Fig. 2. HTR workflow used in the experiment.