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Development of water-soluble, metal-based catalysts for polyurethane coating applications

As regulatory changes continue to restrict the use of volatile organic compounds (VOCs) as well as traditionally used polyurethane catalysts, such as dibutyltin dilaurate (DBTL), in polyurethane (PU) coating applications the demand for the development of new two-component, waterborne polyurethane (2K WB PU) coating formulations and suitable waterborne PU catalysts has emerged. While the use of waterborne coating formulations may address many of the VOC concerns, the design of water-soluble, hydrolytically stable PU catalysts that exhibit performance matching that of DBTL in aqueous environments remains a challenge. The shortcomings of typical PU catalysts like DBTL in waterborne formulations, where factors such as temperature, relative humidity, hydrolytic stability, NCO/OH selectivity, and catalyst shelf life are of paramount importance, have become more evident as the usage of 2K WB PU coatings has increased. This work showcases several novel, water-soluble organotin-, Bi-, and Zn-based catalysts that exhibit excellent reactivity in several 2K waterborne and solventborne coating applications. The catalysts also demonstrate exceptional gloss/color, hardness, and chemical resistance development in addition to other related physical properties. Furthermore, WS-Sn 1 displays enhanced reactivity under high levels of relative humidity when compared to that of DBTL and a high level of selectivity towards the NCO/OH reaction over the undesired NCO/H₂O side-reaction. Given the exceptional reactivity, selectivity, and stability that this series of water-soluble catalysts display, they offer promising alternatives to DBTL and other traditional PU catalysts in 2K WB PU coating applications.

1 Background

While traditional organotin-based catalysts, such as dibutyltin dilaurate (DBTL), have been widely used in PU-based applications, recent regulatory changes have restricted their sustainability and driven a demand for environmentally friendlier versions of current products and practical non-organotin replacements [1]. Catalysts based on inorganic Sn, Bi, Zn, and Zr have been viewed as promising replacements since they possess lower toxicity levels, high catalytic activity, and greater levels of NCO/OH selectivity [1 – 3].

In PU applications a versatile catalyst that provides a high level of reactivity, long-term stability, and a high level of selectivity towards the NCO/OH reaction is often desired, however, this “universal catalyst” has eluded researchers for many years and no suitable material has yet been identified [4].

While DBTL is frequently considered the most versatile PU catalyst, it suffers from several drawbacks including poor catalyst stability upon exposure to water and low NCO/OH selectivity. As the use of 2K WB PU coating applications continues to grow, the shortcomings of DBTL and related catalysts have become more apparent. The undesired NCO/H₂O side reaction (fig. 1) can be extremely detrimental to 2K WB PU coatings as it often results in gassing/CO₂ generation, pinhole formation, low gloss, and other film defects. Moreover, undesired reactivity between the isocyanate and water may also result in reduced pot-life.

Solventborne coatings also suffer from reduced NCO/OH selectivity as a result of residual water introduced by additives, solvents, or atmospheric humidity. However, selection of the appropriate catalyst may greatly reduce CO₂ generation as a result of improved NCO/OH selectivity while increasing drying speed and pot-life [3, 5].

The development of stable catalysts with improved shelf lives and enhanced hydrolytic stability in aqueous environments places a greater demand for high performance catalysts that meet all of the desired requirements. In an effort to address this demand for viable DBTL substitutes and waterborne PU catalysts this study showcases the utility of a variety of water-soluble, organotin-, Bi-, and Zn-based catalysts in 2K WB and solventborne polyurethane coating formulations.

2 Experimental

2.1 Investigated catalysts

Several commercial and experimental water-soluble organotin-, Bi-, and Zn-based catalysts were utilized in this study. Commercially available dibutyltin dilaurate (DBTL) was used for comparison.

2.2 Two-component waterborne polyurethane (2K WB PU) coating formulations

Waterborne coating formulation A was prepared using a hydroxyl-bearing, polyester polyl dispersion (205.5 g), rutile TiO₂ pig-
ment (65.3 g), defoamer (3.8 g), dispersant (2.3 g), flow modifier (3.4 g), rheological modifier (0.9 g) and a 3:1 mixture of a water-dispersible aliphatic polyisocyanate and ethyl-3-ethoxypropionate (9.0 g) to achieve a 1.1 NCO/OH ratio. Catalysts were added to achieve a final catalyst concentration of 0.1 wt% on resin solids.

Waterborne coating formulation B was prepared using a water-reducible polyester polyol (295.6 g), silicone-based substrate wetting agent (4.4 g), 10 % aqueous ammonia solution (23.4 g), water-dispersible polyisocyanate based on hexamethylene diisocyanate (HDI) (462.0 g), and water (641.3 g) to achieve a 1.4 – 1.5 NCO/OH ratio. Catalysts were added to achieve a final catalyst concentration of 0.2 or 0.4 wt% on resin solids.

Waterborne coating formulation C was prepared with a urethane modified polyester polyol (25.0 g), water-dispersible polyisocyanate based on hexamethylene diisocyanate (HDI) (10.0 g), and a water letdown (6.7 g) to achieve a 2.0 NCO/OH ratio. Catalysts were added to achieve a final metal concentration of 0.1 wt%.

2.3 Two-component solventborne polyurethane coating formulation

The solventborne polyester urethane coating formulation was prepared using a branched hydroxyl-bearing polyester polyol dispersion (58.6 g), an aliphatic polysiocyanate resin based on hexamethylene diisocyanate (HDI) (12.7 – 13.3 g), rutile TiO2 pigments (38.0 g), dispersant (1.42 g), flow modifier (2.36 g), ethyl-3-ethoxypropionate (71.2 g), and 1-methoxy-2-propanol acetate (18.22 g) to achieve a 1.1 – 1.2 NCO/OH ratio. Catalysts were added to achieve a final catalyst concentration of 0.1 wt% on resin solids.

2.4 Determination of NCO/OH selectivity using FT-IR ATR

The determination of NCO/OH selectivity was performed using Fourier transform infrared (FTIR) spectroscopy (Jasco FT/IR-4100). Waterborne coating formulation A was drawn down onto aluminum foil to provide a thickness of ca. 2 mm and aluminum stripes were removed for analysis after a set amount of time. Disappearance of the NCO peak (2,270 cm⁻¹) was monitored over time and compared against an internal C-H reference peak (2,935 cm⁻¹) to compensate for wavelength film penetration as the refractive index of the material changed during curing. The relative reaction rates of 1-butanol and water were then determined based on the disappearance of isocyanate.

2.5 Coating physical property determination

Pot-life was determined by measuring 60° gloss as a function of time after mixing using a gloss meter in accordance with ASTM D523. Dry time was determined following ASTM D5895. Coating hardness was determined using pencil hardness as described in ASTM D3363 while solvent resistance (MEK double-rub) was determined as described in ASTM D4752. Coating adhesion was measured according to ASTM D3359 method B using the cross-cut tape adhesion test.

3 Results and discussion

We evaluated the new series of water-soluble catalysts in two separate 2K WB PU coating formulations. In waterborne formulation A the catalysts WS-Sn 1, WS-Bi 2, and DBTL demonstrated the highest levels of reactivity (fig. 2) with DBTL being the overall most reactive material of the group. WS-Zn, WS-Bi 1, and the control (no catalyst) displayed slightly lower levels of reactivity. However, WS-Bi 1, WS-Bi 2, and WS-Zn demonstrated far better pot-lives than DBTL. As previously mentioned, one of the drawbacks of DBTL is the shortened pot-life that the catalyst often demonstrates in waterborne systems. While all the new water-soluble catalysts demonstrated very comparable curing profiles to that of DBTL, each material provided an extended pot-life. It is particularly interesting to see that WS-Sn 1 possessed a faster set-to-touch time than DBTL while still providing a longer pot-life.
In addition to investigating the curing profiles we also evaluated the formulation’s physical property development (tab. 1). WS-Bi 2 provided the highest hardness value followed by WS-Bi 1. The remaining catalysts demonstrated similar hardness values with WS-Sn 1 resulting in a slightly softer coating. WS-Bi 1 and WS-Bi 2 showed considerably better solvent resistance when compared to that of DBTL and the control whereas WS-Sn 1, WS-Sn 2, and WS-Zn afforded only slightly better solvent resistance than DBTL.

The effect of catalyst selection on color and gloss development was also studied (tab. 2). Each catalyst afforded a glossy white industrial coating with gloss levels greater than 78 gloss units at 60° in addition to good color development. While color and gloss development is often highly dependent on the composition and additives of the formulation it should be noted that the utilized catalysts showed no detrimental effects and resulted in excellent film properties.

Waterborne formulation B was utilized to evaluate the effect of catalyst loading on the curing profiles (fig. 3). In general, the higher catalyst loadings (0.4 wt%) demonstrated faster overall curing than the lower loadings (0.2 wt%) of the same catalyst. In this formulation WS-Sn 1 and WS-Sn 2 were more reactive than DBTL at 0.2 wt% loading. However, DBTL did possess a much quicker dry through time than WS-Sn 1 and WS-Sn 2. Both bismuth catalysts (WS-Bi 1 and WS-Bi 2) showed slightly slower rates of curing, however, it is interesting to note that using 0.4 wt% provided very similar curing profiles to that of DBTL at a loading of 0.2 wt%, suggesting that using a slightly higher loading of either bismuth catalyst may act as a “drop-in” replacement for DBTL. The WS-Zn catalyst showed reduced reactivity when compared to the other materials, however, the curing times were still superior to that of the control (while not shown the control required >6.5 h to even achieve set-to-touch).

The reactivity of the catalysts in a solvent borne coating formulation (fig. 4) was investigated next. WS-Sn 2 and DBTL both demonstrated very fast curing while WS-Bi 2 provided slightly slower rates of curing, however, all catalysts showed superior reactivity compared to that of the control sample.

In addition to investigating the curing speed and property development in several water-
borne and solventborne coating formulations. We also were interested in the effect that relative humidity has on catalyst activity. Figure 5 examines the curing profiles of waterborne formulation A using WS-Sn 1 and DBTL under elevated levels of relative humidity. The data show that while both catalysts exhibited elongated drying times under higher levels of relative humidity, WS-Sn 1 provided faster curing at all levels of humidity and demonstrated less “drop-off” in reactivity at higher humidity levels than DBTL. In order to begin to explain the observed increased reactivity of WS-Sn 1 at higher levels of humidity we elected to study the NCO/OH selectivity of WS-Sn 1.

In order to determine the selectivity of WS-Sn 1 towards the NCO/OH reaction the reaction rates of 1-butanol and water in waterborne formulation C (Fig. 6) were determined. The data revealed that the reaction rate of 1-butanol is nearly seven-fold ($K_{\text{rel}} = 6.7$) faster than that of water, demonstrating that the NCO/OH reaction is highly favored over the NCO/H$_2$O side-reaction and CO$_2$ formation are problematic.

4 Conclusions

This work showcases a series of novel, water-soluble, hydrolytically stable organotin-, Bi-, and Zn-based catalysts that exhibit exceptional catalytic activity, physical property development, and color/gloss development in both 2K waterborne and solventborne coating formulations. WS-Sn 1 was found to display enhanced reactivity under high levels of relative humidity when compared to that of DBTL, which may be a result of its high level of selectivity towards the NCO/OH reaction. Consequently, this work has demonstrated the importance of selecting the appropriate catalyst for both 2K waterborne and solventborne applications and as regulatory restrictions on commonly used organotin-based catalysts tighten, a number of Bi- and Zn-based catalysts have shown tremendous potential as viable DBTL alternatives in both waterborne and solventborne coating formulations.

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