Study of Epoxidized-Cardanol Containing Cationic UV Curable Coating Materials

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Abstract

Cationic photopolymerization, thermal and mechanical properties of coating materials containing bio-renewable cashew nutshell oil derivative - epoxidized-cardanol (ECD) were investigated. Higher and more consistent monomer conversion as a function of relative humidity was found for materials containing 10 wt.% ECD and 5 wt.% hydroxy-functional reactive diluents. In addition, ECD imparted unique mechanical and thermal properties to the cationic UV curable materials. ECD showed great potential to be used as a reactive ingredient in cationic UV curable formulations.

1. Introduction

Cycloaliphatic epoxide-based cationic UV curable materials have the advantages of fast cure, low shrinkage, good adhesion, good electrical properties and no oxygen inhibition.[1] Their properties can be further adjusted by the addition of reactive diluents such as oxetanes and polyols to obtain higher monomer conversion and versatile material properties. However, two major factors limiting further development and application of cationic UV curable materials are base (including water) inhibition and higher raw material cost. Cationic photopolymerization was studied as a function of relative humidity and it was found that higher irradiation energy was needed to cure coatings containing a cycloaliphatic epoxide and polyols to a tack-free state under higher relative humidity (RH).[2] A study of the effect of humidity on cationic photopolymerization using real-time FTIR revealed that there exists a system dependent optimal hydroxyl concentration for maximum conversion of epoxide groups.[3] The hydroxyl groups can be provided by either ambient water (humidity) or hydroxyl group-containing compounds such as polyols. As a result of the synergistic interaction between polyols and water, epoxide conversion of the coatings containing polyols passed through a maximum with increasing RH. The fluctuating cure response of cationic UV-curable materials with varying RH is undesired in practical applications, since varying degree of cure will result in inconsistent material properties. Cationic UV curable materials with less hydrophilicity were reported to cure well under higher RH.[4,5] In addition, the authors have proposed and demonstrated that a "humidity blocker" approach, in which 10 wt.% of a hydrophobic epoxy-siloxane monomer ("humidity blocker") in combination with a suitable concentration of hydroxy-functional reactive diluents, succeeded in producing formulations that exhibited higher and more consistent monomer conversion during cationic photopolymerization as a function of varying RH.[6]

Cashew nut shell liquid (CNSL) is an abundant, low cost, bio-renewable material. The use of various derivatives of CNSL in applications such as coatings, adhesives, rubber compounding, plastics materials and additives has been well documented.[7-9] A few publications reported the use of acrylated epoxy CNSL in free radical UV curable coatings.[10,11] However, the utilization of CNSL derivatives in
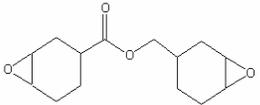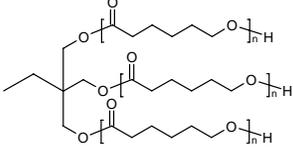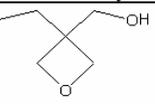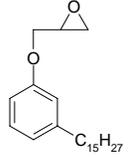
cationic UV curable systems has not been previously studied. It was expected that the use of CNSL derivatives in cationic UV curable formulations could generate lower cost materials with unique properties. In this work, one of the commercially available CNSL derivatives - epoxidized-cardanol (ECD, generic structure shown in Table 1) is of particular interest. ECD can be used as a mono-functional reactive ingredient in cationic formulations due to its epoxy functionality. Also, the combination of the hard aromatic structure and the long flexible alkyl chain of ECD may impart unique properties to the cationic UV cured materials. What's more, ECD possesses higher hydrophobicity because of the long alkyl chain, thus it was hypothesized that ECD will serve as a "humidity blocker" in cationic UV curable formulations, mitigating the interference of humidity with cationic photopolymerization. This report investigated the feasibility of utilizing the low cost, bio-renewable CNSL derivative, ECD, as a "humidity blocking" reactive ingredient to achieve more consistent monomer conversion during cationic photopolymerization at various RH. In addition, the material properties of ECD-based cationic UV curable coatings was investigated.

2. Experimental Part
2.1. Materials used
The chemicals used are listed in Table 1. All materials were used as received.

Table 1. Chemicals used.

Trade Name	Abbreviation	Source	Structure and description
UVI 6974	PI	Dow	mixed triarylsulfonium hexafluoroantimonate salt in propylene carbonate
UVR 6110	ECC	Dow	MW 252, epoxy equivalent weight = 126
Tone 301	PCL	Dow	MW 300, hydroxyl equivalent weight = 100
UVR 6000	OXT	Dow	MW 116, hydroxyl equivalent weight = 116
Cardolite® Lite 2513HP	ECD	Cardolite Corp.	MW 356, epoxy equivalent weight = 356

2.2 Coating formulations

The coating formulations studied are shown in Table 2. Formulations ECD-OXT-x and ECD-PCL-x were made to study the "humidity blocking" effect of ECD with increasing amount of either OXT or PCL, as well as to study the effect of ECD on cationic UV curable material properties. Formulations ECC-OXT-x and ECC-PCL-x were references.

Table 2. Formulations studied (numbers indicates wt. % of the ingredients)

	ECD-OXT-x		ECC-OXT-x			ECD-PCL-x		ECC-PCL-x		
	-5	-10	-5	-10	-15	-5	-10	-5	-10	-15
ECC	80	75	90	85	80	80	75	90	85	80
OXT	5	10	5	10	15	0	0	0	0	0
PCL	0	0	0	0	0	5	10	5	10	15
ECD	10	10	0	0	0	10	10	0	0	0
PI	5									

2.3. Characterization

Real time FTIR (RTIR) provides a straightforward way to examine the photopolymerization behavior of UV curable materials. It is a powerful, commonly used characterization technique in UV curable materials research. In this work, RTIR was used to determine the final monomer conversion of cationic photopolymerization under various RHs. The RTIR experiments were performed using a Nicolet Magna-IR 850 spectrometer Series II with detector type DTGS KBr, with a UV optic fiber mounted in a sample chamber in which the humidity was controlled by using different salt solutions as listed in Table 3. The humidity and temperature inside the sample chamber was monitored using a digital temperature/humidity indicator. The light source was a LESCO Super Spot MK II 100W DC mercury vapor short-arc lamp with a UVA bulb. Such setup directly monitors functional group conversion as the photopolymerization proceeds. Samples were spin-coated onto a KBr plate at 3000 rpm for 30 s to obtain a smooth film with thickness of ~ 6-7 μm. The coated KBr plate was then equilibrated in the sample chamber for 30 s, followed by exposure to UV light in the FTIR beam for 60 s. Spectra were taken over a 120 s period at 2 spectra/s, the resolution was 4 cm^{-1}. The UV source was adjusted to ~ 36 mW/cm^2 (UVA) as measured by UV Power Puck® II from EIT Inc., and the experiments were performed in air at 25 ± 1 ºC. The cycloaliphatic epoxide conversion of ECC was calculated by the percent peak height decrement at 789 cm^{-1}, the oxetane conversion of OXT was calculated by the percent peak height decrement at 976-977 cm^{-1}. The functional group conversion at 120 s was reported and compared.

Table 3. Salts used to obtain different RHs in RTIR experiments.

RH	25	38	50	65	75
Salt used	Environment RH	NaI.2H$_2$O	Ca(NO$_3$)$_2$.4H$_2$O	NH$_4$NO$_3$	NH$_4$Cl

For coating physical property tests, the liquid materials were cast on aluminum panels with a wire-wound drawdown rod to form a ~ 50 um thick coating, followed by UV curing for 60 s using a Dymax light source with a 200 EC silver lamp (UVA, intensity ~ 35 mW/cm^2) in air at RH ~ 25. An automated surface energy measurement unit manufactured by Symyx Discovery Tools, Inc. and First Ten Angstroms was used to measure water contact angle on UV cured coatings. Droplets of water were deposited on the coating surface and a CCD camera imaged the droplets; then automated image analysis

was used to determine the contact angle. Three drops of water were used for each measurement, and the average contact angle values reported.

Hardness testing was performed with a BYK Gardener pendulum hardness tester in König mode; the results are reported in seconds. Methyl ethyl ketone (MEK) double rub experiments were used to assess the solvent resistance of the coatings. A 26 oz hammer with 5 layers of cheesecloth wrapped around the hammerhead was soaked in MEK for rubbing. After 100 double rubs, the cloth was rewet with MEK. The number of double rubs was reported once mar appeared on the film surface, or a maximum of 400 double rubs was recorded. Falling weight direct impact testing was carried out according to ASTM D2794 with a 2 lb weight. The starting height was increased until the film was damaged, and the maximum height at which the film was intact was recorded. The results were reported in lb·inch.

Dynamic mechanical thermal analysis (DMTA) was performed using a TA Instruments Q800 DMA in rectangular tension/compression geometry. Free films of the cured coatings were obtained by removing coatings from the aluminum substrate using a razor blade. Sample size was 10× 5mm and film thickness was measured using a Micromaster® micrometer. The analysis was carried out from – 50 ºC to 200 ºC at a frequency of 1 Hz and a ramp rate of 3 ºC min^{-1}. T_g was obtained from the maximum peak in the tan δ curves. DSC experiments were performed utilizing a TA Instruments Q1000 DSC with a heat-cool-heat cycle. The sample size ranged from 4.5 to 5.5 mg. Temperature was ramped from -50 ºC to 200 ºC at 10 ºC min^{-1} in nitrogen.

3. Results and Discussion

The long, hydrophobic alkyl chain of the ECD was expected to provide a similar "humidity blocking" effect to the epoxy-siloxane during cationic photopolymerization.[6] Formulations containing 10% ECD as the "humidity blocker" and an increasing concentration (5 wt.% and 10 wt.%) of hydroxyl functional reactive diluents were tested and compared with references (formulations contain no ECD but the same amount of hydroxyl-functional reactive diluents, as shown in Table 2). Water contact angle data (shown in Figure 1) were first obtained to examine the hydrophobicity difference for materials with and without ECD. The water contact angles for samples with 10 wt.% ECD were all about 20 degree higher than those without ECD, confirming that ECD did increase the material surface hydrophobicity.
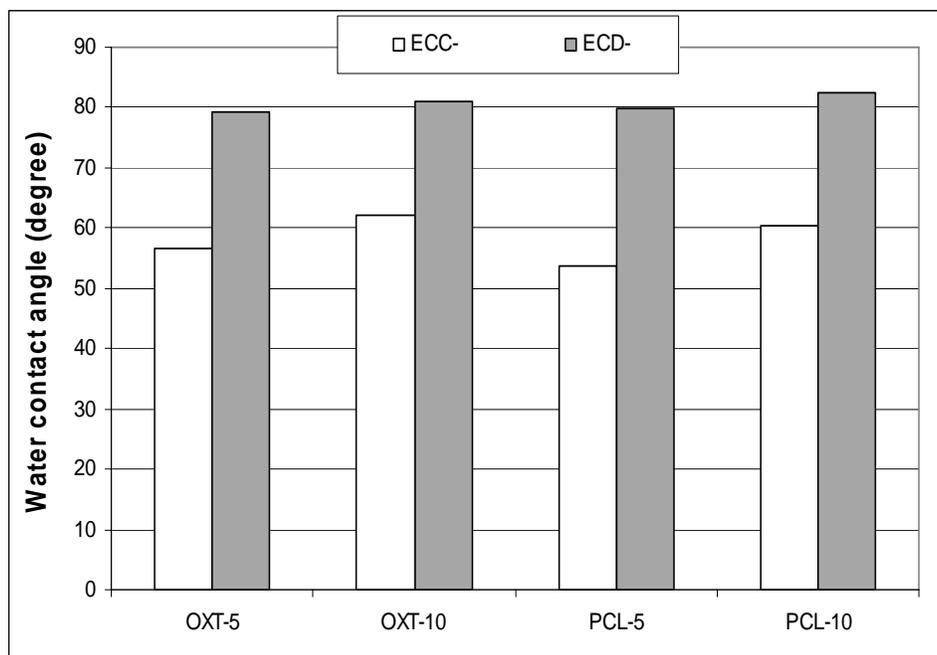
Figure 1. Water contact angle data for coatings studied.

The cationic photopolymerization of ECD-containing UV curable materials were studied as a function of relative humidity. The epoxy and oxetane conversion as a function of RH in OXT added formulations are shown in Figures 2A and 2B, respectively. It can be seen that the cycloaliphatic epoxy conversion for ECD-OXT-5 was high and more consistent at varying RHs compared to other formulations. This was attributed to the ability of the hydrophobic ECD to mitigate the interaction between humidity and the internal hydroxyls, and the optimal internal hydroxyl concentration provided by 5 wt.% OXT.[6] However, with 5 wt.% more hydroxyl-functional OXT in the formulation, as in the case of ECD-OXT-10, the epoxy conversion was much lower at RHs > 50%, especially at RH=75%. The low conversion was attributed to excess interaction of humidity and hydroxyls in the material.[6] As to the reference materials ECC-OXT-5 and ECC-OXT-10, due to the lack of the humidity blocking ECD, the interaction of hydroxyls in the material with humidity is in a less controlled manner, consequently the epoxy conversion for references varied more dramatically. ECC-OXT-5 showed higher epoxy conversion at RH=50% than at RH=25%, probably because at higher RH, more hydroxyls (provided by ambient water, in this case) can be utilized to participate in the chain transfer than those provided by 5 wt.% OXT. But for ECC-OXT-10, the epoxy conversion decreased starting from RH=25%, indicating that 10 wt.% OXT tends to absorb excess ambient water at higher RH thus retarding the cationic photopolymerization. Due to the absence of the "humidity blocking" ECD, both ECC-OXT-5 and ECC-OXT-10 showed very low epoxy conversion at RH=75% as a result of the base inhibition from the excess incoming ambient water into the materials. The above observation can be explained by the proposed "humidity blocker" approach[6] – a humidity blocking compound must be present to mitigate the interference of ambient water with cationic photopolymerization, and an appropriate hydroxyl concentration is necessary to enhance the monomer conversion through chain transfer; but, too much hydroxyl will result in excess interaction with the ambient water thus inhibiting the cationic photopolymerization at high RH.[3,6] With 10 wt.% ECD, 5 wt.% OXT seemed to be providing the optimal hydroxyl concentration in the OXT-containing formulation. The oxetane conversion for OXT-containing formulations followed a similar trend to the epoxy conversion, and the oxetane conversion

for ECD-OXT-5 was high and more consistent as a function of RH when compared to other samples, especially at RH=75%. These conversion data suggest that it is necessary to have both the "humidity blocking" compound and a suitable hydroxyl concentration to obtain reasonable monomer conversion for cationic UV curable materials at varying RH.
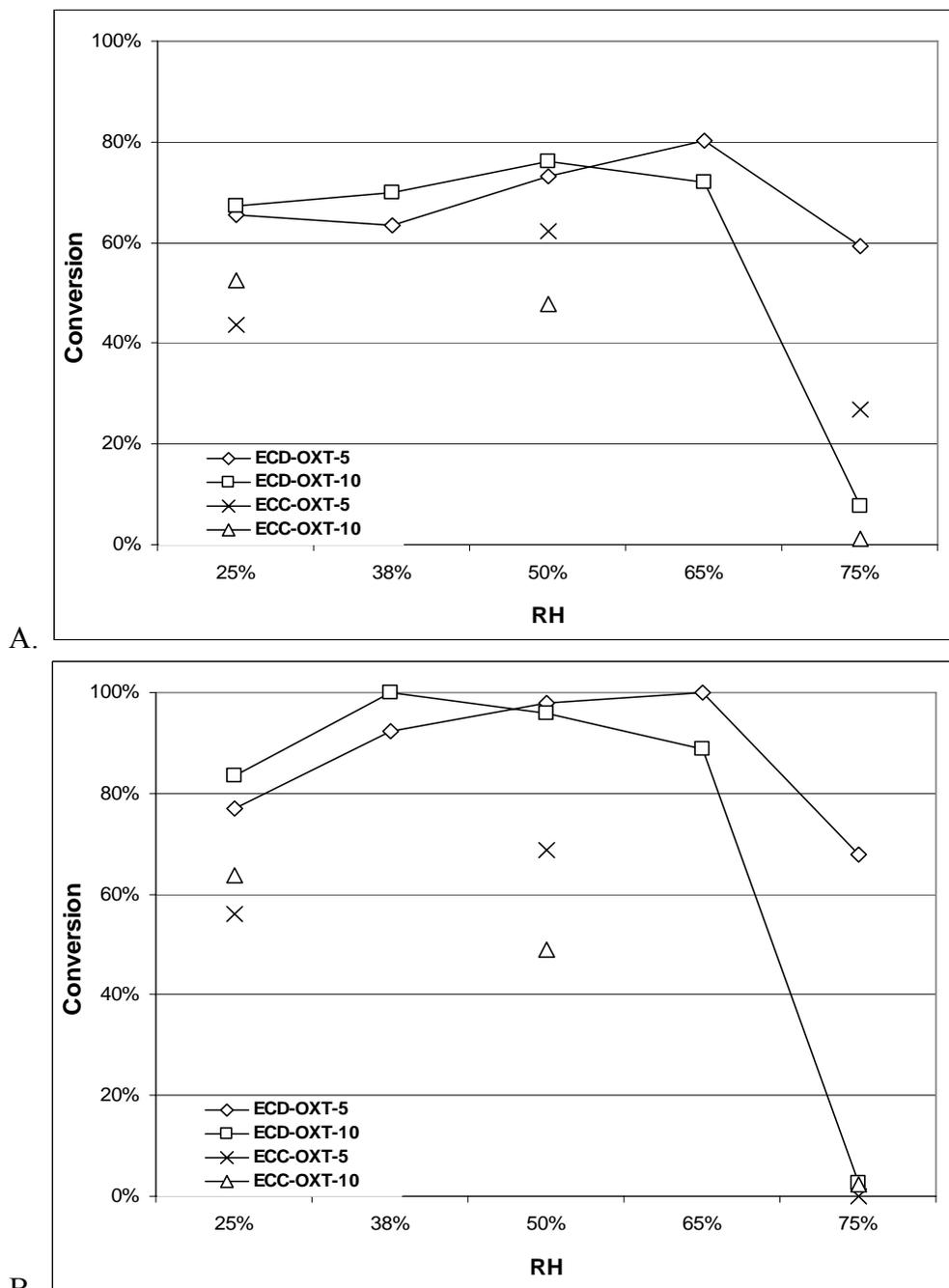

A.

B.

Figure 2. A. Cycloaliphatic epoxide B. oxetane conversion at 120s.

The cycloaliphatic epoxy conversion as a function of RH for PCL-containing materials are shown in Figure 3. Similar to OXT-containing formulations, it was noticed that the combination of 5% PCL and 10% ECD exhibited more consistent conversion with RH. Also, this combination gave higher

functional group conversion at RH=75%. This result suggested that 5% PCL provided an optimal hydroxyl concentration for this particular formulation. The epoxy conversions for ECD-PCL-5 are a little lower than those of ECD-OXT-5 at RH=75%, which may be due to the lower hydroxyl equivalent weight of PCL than OXT, thus excess hydroxyls are present in the formulation to interact with humidity at the same weight percent loading. For ECD-PCL-10, although the epoxy conversion at RHs < 75% were also high and relatively consistent, the 5 wt.% more PCL still resulted in low epoxy conversion at RH=75%. Unlike ECC-OXT-5, the two PCL added reference materials ECC-PCL-5 and ECC-PCL-10 showed decreasing epoxy conversion with increasing RH, which can be explained by the higher hydroxyl content in ECC-PCL-5 and ECC-PCL-10. At RH=75%, the absence of the "humidity blocker" ECD in ECC-PCL-5 and ECC-PCL-10 resulted in inhibition of cationic photopolymerization.
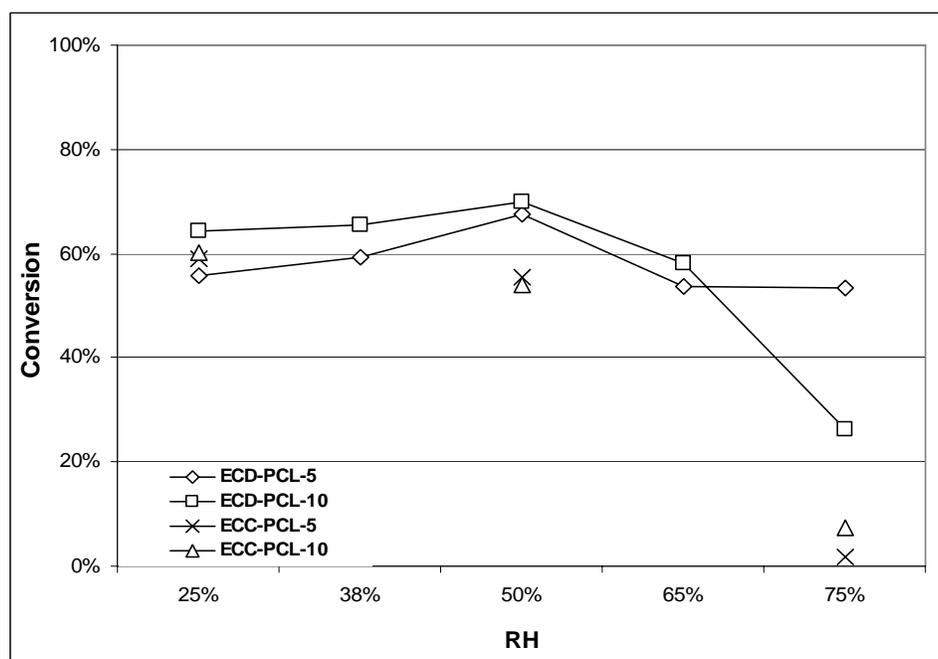

Figure 3. Cycloaliphatic epoxide conversion at 120s.

As a compound with mono epoxy functionality and the long alkyl chain, ECD was expected to function as a reactive diluent/flexibilizer similar to oxetanes or polyols in cationic UV curable formulations. However, UV curing of ECC and 15 – 25 wt.% ECD resulted in wrinkled films. A smooth cured film could only be obtained with the further addition of OXT or PCL, this may be ascribed to the chain transfer induced by the hydroxyls on OXT or PCL. Since the 10 wt.% ECD containing formulations, ECD-OXT-5 and ECD-PCL-5, exhibited more consistent cationic photopolymerization as a function of RH, their coating mechanical and thermal properties were studied and compared to references, ECC-OXT-15 and ECC-PCL-15.

Table 4 summarizes the typical coating properties obtained for 10 wt. % ECD-containing coatings as compared to the references. It can be seen that, after substituting the 10 wt.% OXT or PCL with 10 wt.% of ECD, the hydrophobicity of the coating significantly increased, but other coating properties such as hardness, solvent resistance and impact resistance didn't change. The ECD-containing coatings are hard films with excellent solvent resistance, but, at the same time, the flexibility of the coating films was not sacrificed as evidenced by the impact resistance after replacing OXT or PCL with

ECD. This can be attributed to the unique combination of the hard aromatic structure and the long flexible alkyl chain on ECD molecule. The thermal properties of the same samples were also tested and are listed in Table 5. It was noticed that 10 wt.% ECD containing samples exhibited higher crosslink density than respective references. By substituting the hydroxy-functional OXT or PCL with ECD, the chain transfer induced by hydroxyls during cationic photopolymerization would be reduced. Since the chain transfer will result in networks with lower crosslink density,[1] replacing the OXT or PCL with mono-epoxy functional ECD would consequently generate networks with higher crosslink density. On the other hand, despite the higher crosslink density, ECD-containing coatings possessed lower T_gs. This is probably due to the internal plasticization effect induced by the long flexible alkyl chain on ECD in the crosslinked network.

Table 4. Comparison of coating properties

Formulations	ECC-OXT-15	ECD-OXT-5	ECC-PCL-15	ECD-PCL-5
Pendulum hardness (s)	263	255	260	252
MEK double rubs	>400	>400	>400	>400
Direct impact resistance (lb·inch)	8	8	12	12
Water contact angle (°)	61.92	79.86	64.15	83.56

Table 5. Comparison of coating thermal properties

Formulations		ECC-OXT-15	ECD-OXT-5	ECC-PCL-15	ECD-PCL-5
DSC	T_g (°C)	119.18	110.85	111.71	97.36
DMTA	T_g (°C)	147.76	137.92	121.53	103.88
	ν_e (× mmol/cm^3)	14.47	22.43	6.530	7.843

Conclusions

Cationic photopolymerization of cycloaliphatic epoxy-based cationic UV curable materials containing 10 wt.% hydrophobic ECD and various amounts of OXT and PCL were examined. ECD-containing materials exhibited higher water contact angles. Materials containing 10 wt.% ECD and 5 wt.% either OXT or PCL were found to have more consistent functional group conversion with RH. They also exhibited higher functional group conversion at RH=75%. These results indicated feasibility of utilizing the hydrophobic, bio-renewable CNSL derivative, ECD, as a "humidity blocker" in cationic UV curable formulations to achieve more consistent cationic photopolymerization under various RH.

The substitution of 10 wt.% OXT or PCL with ECD in coating formulations resulted in higher coating hydrophobicity, higher crosslinked density and lower T_g, no change of coating properties such as hardness, solvent resistance and impact resistance was noticed. These results were attributed to the unique molecular structure of ECD.

Acknowledgements

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