A "Humidity Blocker" Approach to Overcoming the Humidity Interference with Cationic Photopolymerization

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Abstract

A "Humidity Blocker" approach to overcoming the humidity interference with cationic photopolymerization was proposed and validated. Environmental humidity is one of the major interfering factors in cationic photopolymerization, and cationic photopolymerization is found to be inhibited by high humidity. When curing cycloaliphatic epoxide based cationic UV curable materials flexibilized by various reactive diluents under different humidity conditions, it was found that the more hydrophobic materials exhibited higher monomer conversion under higher humidity. In order to obtain cationic UV curable materials that are less influenced by humidity, a "humidity blocker" approach was proposed and monomer conversion of materials containing both hydroxy-functional reactive diluents and epoxy-siloxane were examined using real-time FTIR. The hydroxy-functional reactive diluents act as an internal hydroxyl source that enhances monomer conversion through chain transfer mechanism, and the hydrophobic epoxy-siloxane acts as a "humidity blocker", mitigating the inhibiting effects of humidity. Cationic UV curable materials with an optimized combination of these two components exhibited higher and more consistent monomer conversion under all humidity conditions tested.

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 tailored by the incorporation of reactive diluents such as oxetanes and polyols including diol, triol and hyperbranched polyols.[2] The versatile properties of these materials enable them to find potential applications in coatings, inks,[3] adhesives[4] and microelectronics packaging.[1]

Though not affected by oxygen, one major drawback of cationic photopolymerization is inhibition by bases including water.[5,6] Consequently, environmental humidity significantly affects cationic photopolymerization behavior. Cationic photopolymerization has been studied as a function of humidity. It was found that higher irradiation energy was needed to cure coatings containing cycloaliphatic epoxides and polyols to a tack-free state under higher relative humidity (RH).[6] The cationic photopolymerization of cycloaliphatic epoxide monomers with various structures has been studied using optical pyrometry under high and low RH.[5] An induction period was noticed for all the monomers studied under higher RH (70% - 80%), which was attributed to inhibition by water. At the same time, it was noticed that cationic photopolymerization of cycloaliphatic epoxide monomer with a siloxane backbone (epoxy-siloxane) was less influenced by high RH. This was attributed to the less

hydrophilic siloxane structure in the molecule. A more comprehensive study of the effect of humidity on cationic photopolymerization was carried out using real-time FTIR.[7] Contrary to the common belief that water is detrimental to cationic photopolymerization, it has been suggested that a certain amount of water is needed as a proton carrier and chain transfer agent in the cationic photoinitiation and propagation process, though excess water will capture and terminate the propagating cationic species. The role water played in cationic photopolymerization was further complicated when polyols, which are also effective chain transfer agents, were cured together with cycloaliphatic epoxides. Due to the synergistic effect induced by hydrogen bonding between polyols and water, epoxide conversion of the samples containing polyols passed through a maximum with increasing RH. It was indicated that there was an optimum hydroxyl concentration for obtaining maximum conversion of epoxide groups, and the optimum hydroxyl concentration was system dependent.
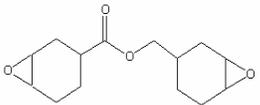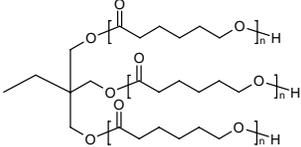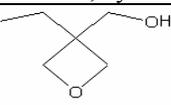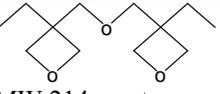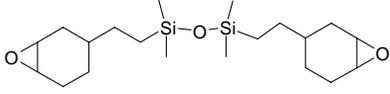
The fluctuating curing response of cationic UV curable materials with varying RH is undesired, since fluctuations result in variations in material properties. Heating samples above a certain temperature was reported to accelerate the UV curing and overcome the effect of ambient moisture.[6,8] In terms of chemical approaches to overcome the influence of humidity, moisture scavengers, such as anhydrides and isocyanates, were investigated but reported to be ineffective.[6] On the other hand, cationic UV curable materials with less hydrophilic structures were reported to be cured well under higher RH.[9] Few other reports can be found on approaches to overcome the effect of humidity on cationic photopolymerization. In an effort to find a chemical approach to overcome the influence of the humidity on cationic photopolymerization, a "humidity blocker" strategy appeared attractive. It is thought that a compound with a hydrophobic backbone added to a cycloaliphatic epoxide based system would migrate to the material – air interface before curing and thereby act as a "humidity blocker", preventing ambient moisture from entering the liquid material. We report on some initial promising results with regard to the "humidity blocker" approach herein.

2. Experimental Part

2.1 Materials used

The chemicals used, abbreviations, and their sources 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	Epoxy equivalent weight = 126
Tone 301	PCL	Dow	MW 300, hydroxyl equivalent weight = 100
UVR 6000	OXT	Dow	MW 116, hydroxyl equivalent weight = 116
OXT 221	DOX	Toagosei Co. Ltd.	MW 214, oxetane equivalent weight = 107
SIB 1092	EP-Si	Gelest Inc.	MW 390, epoxy equivalent weight = 195

2.2 Formulations

The formulations investigated were combinations of PI, ECC and reactive diluents chosen from PCL, OXT, DOX and EP-Si. The amount of PI was 5 wt% for all materials. The amount of reactive diluent and ECC used is indicated by the formulation identification. For example, sample "ECC w/10% OXT & 10% EP-Si" indicates that it is composed of 5 wt% PI, 10 wt% OXT, 10 wt% EP-Si and the remaining is ECC, 75 wt%. All of the samples were clear and homogeneous at room temperature.

2.3 Characterizations

Real time FTIR (RTIR) technique provides a straightforward way to examine the photopolymerization behavior of UV curable materials. It is a powerful and one of the most commonly used characterization techniques in the study of UV curable materials.[10,11] In this work, RTIR was used to determine the final monomer conversion of cationic photopolymerization under various RH. 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 2. 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 20 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 °C. The cycloaliphatic epoxide conversion of ECC was calculated by the percent peak height decrement at 789 cm^{-1}, the oxetane conversion was monitored by the percent peak height decrement at 976-977 cm^{-1}.[1] The functional group conversion at 120 s was reported and compared. To prepare coatings, the liquid formulations were cast on aluminum panels with a wire-wound drawdown rod to form a ~ 50 μm 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 cured material in the form of a coating. 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. 3 drops of water were used for each measurement and the average contact angle reported.

Table 2. Salts used to obtain different RH 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

3. Results and Discussion

The effect of humidity on the cationic photopolymerization of polyol flexibilized cycloaliphatic epoxide-based coating materials was previously studied by Soucek et al.[7] Since oxetanes are also common reactive diluents for cationic systems, it was of interest to study the cationic photopolymerization behavior of oxetane diluted cycloaliphatic epoxide-based materials as well as a polyol diluted system as a function of humidity. Thus, 10 wt.% (a common reactive diluent loading level) of PCL, OXT and DOX were added respectively into the mixture of 5 wt.% PI and 85 wt.% ECC. The cationic photopolymerization of these materials were monitored using RTIR under 5 different RHs and the results compared to the sample containing only 95 wt.% ECC and 5 wt.% PI. The epoxy and oxetane conversion for these samples are shown in Figures 1A and 1B, respectively.

The epoxy conversion data for sample "ECC" under different RH increased with increasing RH until a maximum at RH=65% was reached, then the conversion dropped sharply at RH=75%. This observation can be explained using the proposed model describing the different roles water plays at different RH.[7] When 10 wt.% PCL was added, at RH=25% and 38%, the epoxy conversion was higher than that of "ECC". This was attributed to the flexibilizing effect and chain transfer mechanism imparted by the polyol.^{2} Compared to "ECC", the conversion maximum for sample "ECC w/10% PCL" shifted to lower humidity (RH=38%), after which the epoxy conversion dropped sharply. The shift of the maximum may be due to the synergistic effect between PCL and water as the result of hydrogen bonding, thus the optimum hydroxyl concentration was reached at lower RH.
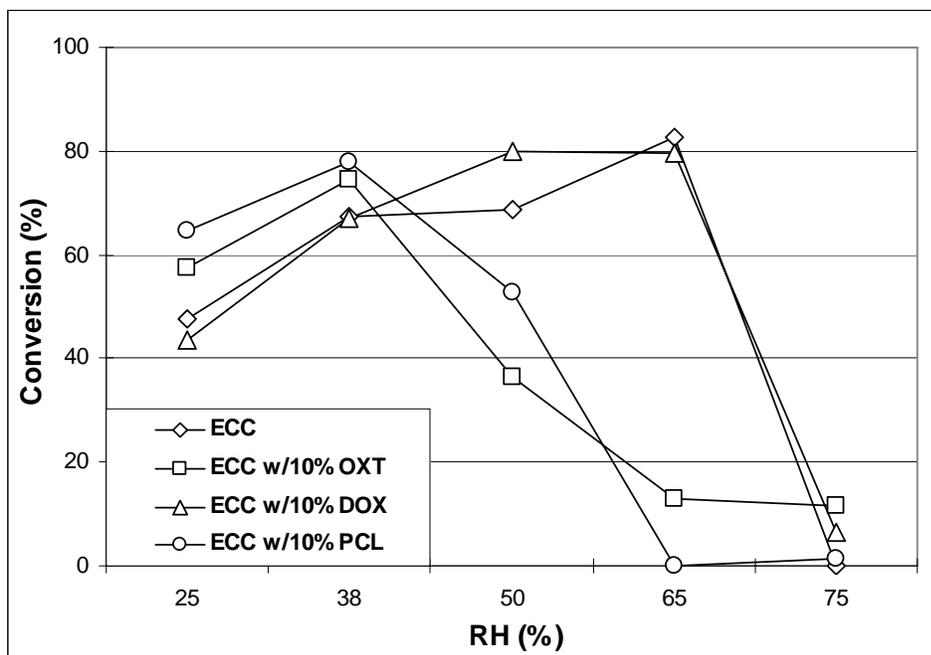
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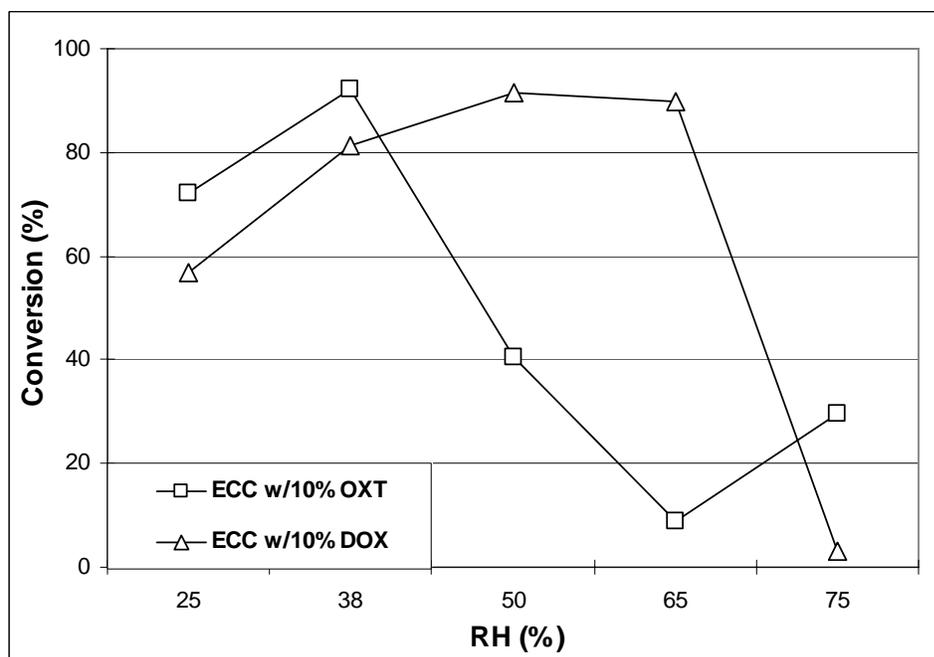
B.

Figure 1. Cycloaliphatic epoxide (A) and oxetane (B) conversion at different RH.

For the OXT diluted sample, the epoxy conversion with increasing RH showed a similar trend to that of the sample diluted by PCL: the maximum appeared at RH=38%, then dropped to very low values at higher RH. The similarity was attributed to the similar hydroxyl equivalent weight for PCL and OXT, consequently the OXT and PCL diluted samples had a similar optimum hydroxyl concentration. Compared to OXT, when the less hydrophilic oxetane DOX was used as a diluent, the epoxy conversion maximum shifted back to the higher humidity (RH=65%). It was apparent that because of the lack of inherent hydroxyl groups, higher humidity was needed to reach the optimum hydroxyl concentration for

this sample. The trend of oxetane conversion maximum was also consistent with epoxy conversion (shown in Figure 1B).

The conversion data in Figure 1 clearly demonstrates the relationship between the hydrophilic/hydrophobic nature of the material and the monomer conversion under different RH. The monomer conversion of a more hydrophilic material (ECC with 10% PCL or OXT) tends to be influenced more by humidity. As a result, the optimum hydroxyl concentration for such material was reached at lower RH, and much lower monomer conversion was found at higher RH since excess water acts as an inhibitor in the cationic photopolymerization process. At the same time, a less hydrophilic material such as "ECC" and "ECC w/10% DOX" showed a more "controlled" interaction with humidity. It is proposed that these materials uptake water in a slower manner, thus the optimum hydroxyl concentration and maximum monomer conversion were reached at much higher RH. However, despite the difference in hydrophilicity of the materials tested, they all showed very low monomer conversion at high humidity (RH=75%).

Since humidity is one of the major inhibiting factors in cationic photopolymerization,[5,8,9] it is desired to have a cationic UV curable material that exhibits consistently high monomer conversion at all humidity levels. As hinted from previous research and results presented in Figure 1, it was hypothesized that a cationic UV curable formulation adapting a "humidity blocker" approach may overcome the negative effect of humidity. Specifically, such a formulation would contain both hydroxy-functional reactive diluents and hydrophobic compounds ("humidity blocker") such as epoxy-siloxane monomers. Coatings containing epoxy-siloxane monomers have been reported to have lower surface energy and higher water contact angle due to the presence of the epoxy-siloxane at the coating surface.[12] Consequently, the more hydrophobic epoxy-siloxane molecules were anticipated to migrate to the liquid material-air interface in order to minimize interfacial energy, forming a hydrophobic, humidity blocking layer, thus mitigating the interaction of ambient water with cationic photopolymerization. At the same time, the hydroxy-functional reactive diluents would act as hydroxyl sources enabling hydrogen abstraction and chain transfer, hence boosting monomer conversion.[13]

In order to explore the "humidity blocker" approach, materials were made that contained 10 wt.% epoxy-siloxane monomer (EP-Si) as the "humidity-blocker", and 5 or 10 wt.% of either PCL or OXT as the internal hydroxyl source. Water contact angle data (shown in Figure 2) were obtained for all the samples after UV curing to examine the change of hydrophobicity after EP-Si addition. It can be seen that with the exception of the DOX containing material, all samples without EP-Si showed higher hydrophilicity. On the other hand, the addition of EP-Si (the "humidity blocker") resulted in increased surface hydrophobicity as indicated by the much higher water contact angles (close to or higher than 90º). The monomer conversion during cationic photopolymerization of these samples as a function of humidity was obtained using RTIR.
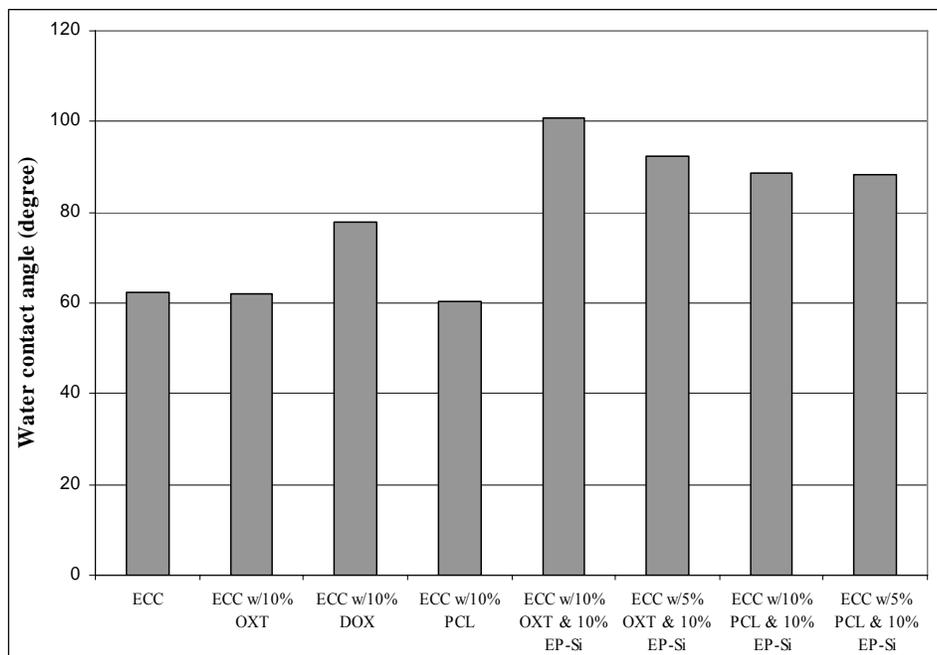
Figure 2. Water contact angle data for cationic UV curable materials studied.

Figures 3A and 3B show the epoxy and oxetane conversion data for OXT diluted materials with and without the "humidity blocker", EP-Si. At lower RH (25% and 38%), all samples had similar epoxy conversion. However, starting from 50% RH, the difference between the materials' capability to interact with ambient water became apparent. Sample "ECC w/10% OXT", had a much lower epoxy conversion than the other three samples, as a result of the hydrophilic hydroxyls on OXT. Such a difference continues at higher humidity until RH=75%, where all the samples except for "ECC w/5% OXT" had low epoxy conversion. This trend was also found in the oxetane conversion shown in Figure 3B. For the other three materials, at RH=65%, the epoxy conversion remained at a reasonably high level. The two samples with OXT and EP-Si had lower epoxy conversion than sample "ECC", which can be attributed to the interaction between the hydroxyl group and water. It was interesting to see that at RH=75%, while the photopolymerization of sample "ECC" was totally inhibited, the samples containing both hydroxy-functional molecules (OXT) and the "humidity blocker" (EP-Si) still had some epoxy and oxetane conversion. It is even noteworthy that the sample containing 5 wt.% OXT and 10 wt.% EP-Si exhibited much higher monomer conversion at RH=75% than all the other samples (the epoxy and oxetane conversion at RH=75% for sample "ECC w/5% OXT" were also obtained and were 27% and 0% respectively). What's more, monomer conversion is much more consistent as a function of RH. This is highly desired in practical applications, since consistent monomer conversion at different RH indicates more consistent cured material properties under a range of ambient conditions. At RH=75%, the monomer conversion difference between samples containing EP-Si and 5% or 10% OXT suggested that the hydroxyl content in the material was critical to obtaining a high conversion at high RH in the "humidity blocker" approach. It was indicated that even with the "humidity blocker" (EP-Si), 10% OXT in the material would still uptake excess water at high humidity, inhibiting the cationic photopolymerization. The results in Figure 3 suggested that the existence of hydrophobic "humidity blocker" and suitable amount of internal hydroxyls are necessary to maintain a high and consistent monomer conversion at different RH; this most probably is due to the synergistic effect between the hydrophobic "humidity blocker" and the internal hydroxyls.
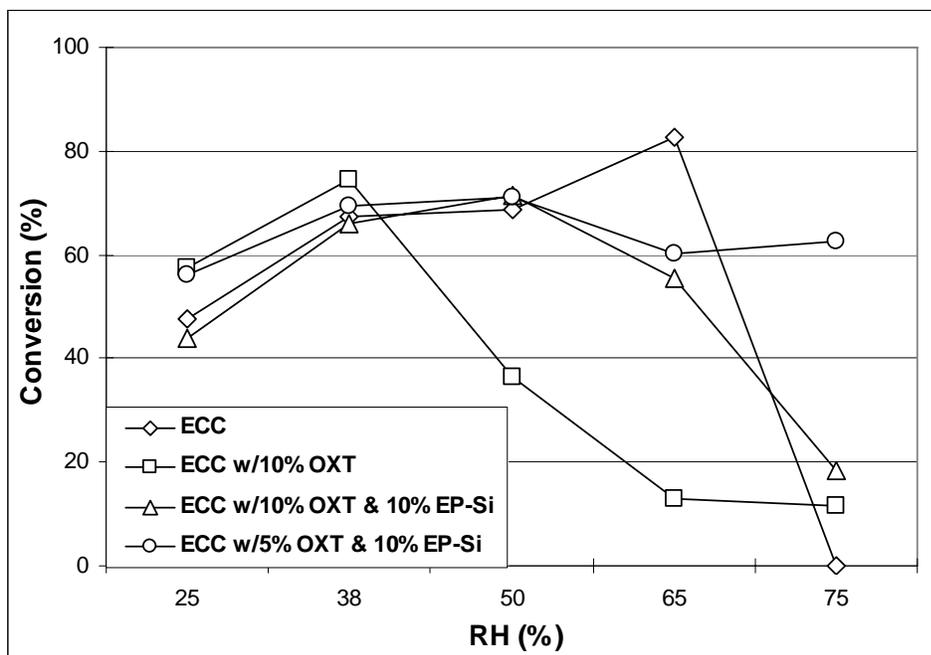
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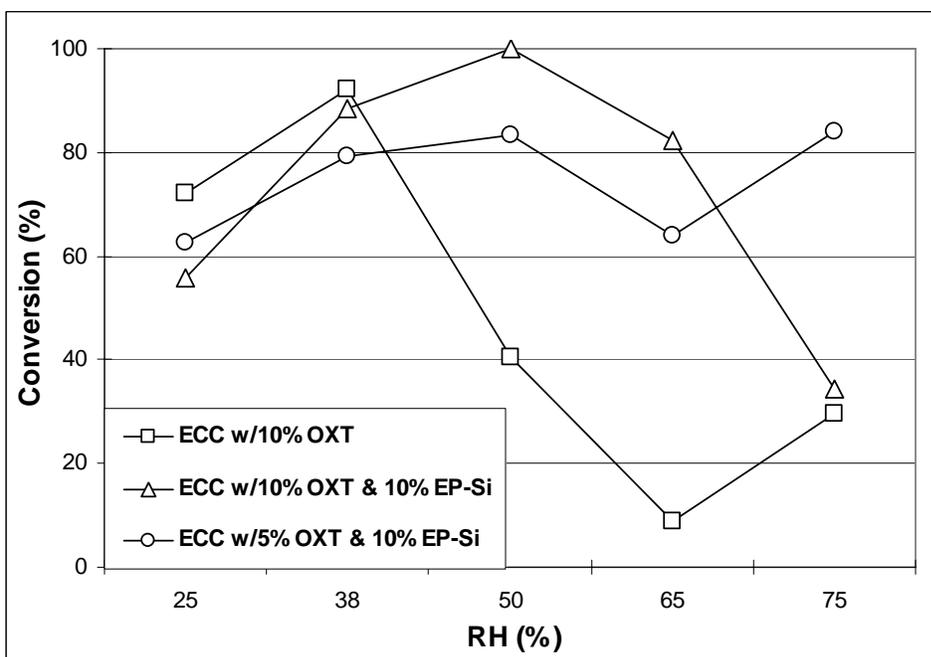
B.

Figure 3. Cycloaliphatic epoxide (A) and oxetane (B) conversion at various RH of OXT containing samples.

The cationic photopolymerization behavior of PCL containing materials showed a similar trend to that of the OXT containing materials, as shown in Figure 4. At lower RH (25% and 38%), sample "ECC w/10% PCL" had the highest epoxy conversion, which was the result of chain transfer induced by PCL[2] and the interaction between PCL and ambient moisture, such that the optimum hydroxyl concentration was reached earlier than with the other samples. The epoxy conversion of sample "ECC w/10% PCL" dropped sharply at higher RH due to the interaction of PCL with excess water, which has a higher basicity/nucleophilicity than polyols such as PCL.[7] Also, the epoxy conversion at RH=75% for

sample ECC w/5% PCL was obtained and was ~ 2% only. In contrast, with the "humidity blocking" effect induced by EP-Si, materials containing both PCL and EP-Si reached the optimum hydroxyl concentration and maximum epoxy conversion at a higher humidity (RH=50%). At even higher RH, the epoxy conversion for these two samples started to decrease. It was noticed that sample "ECC w/10% PCL & 10% EP-Si" had a much faster conversion decrease than sample "ECC w/5% PCL & 10% EP-Si", which maintained a relatively high and more consistent epoxy conversion as a function of RH. This again indicated that, even with the "humidity blocker" (EP-Si), an appropriate hydroxyl concentration was still critical to achieve a reasonable monomer conversion at higher RH.
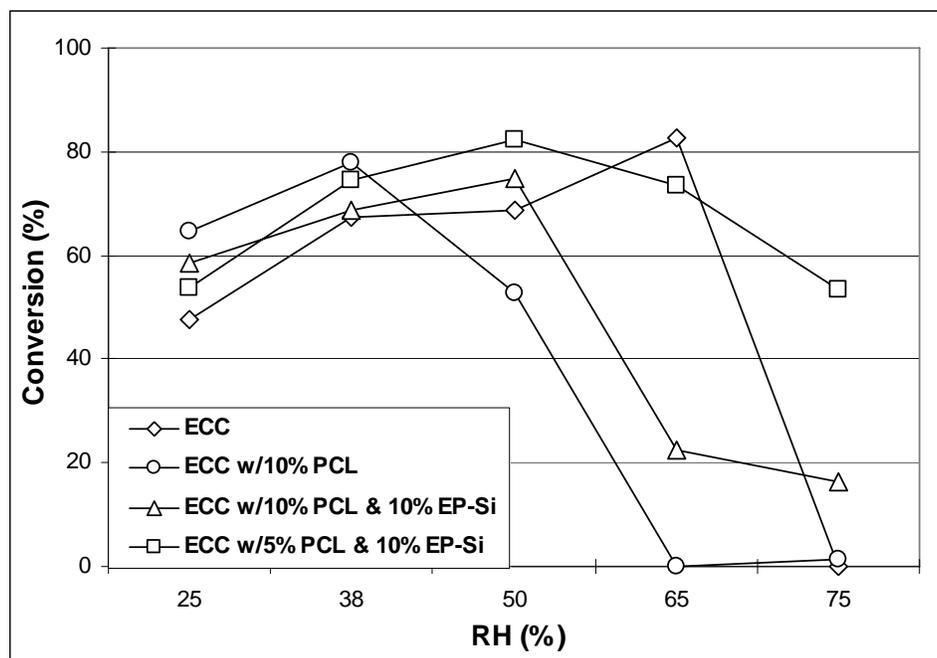

Figure 4. Cycloaliphatic epoxide conversion at different RH of PCL containing samples.

Conclusions

The monomer conversion of cationic UV curable materials with several reactive diluents was studied as a function of RH. It was found that the monomer conversion of more hydrophobic materials was less negatively influenced by varying RH. A "humidity blocker" approach was proposed and verified in order to overcome the negative effect of humidity on cationic photopolymerization. Materials containing the hydrophobic "humidity blocker" (EP-Si) and optimal amount of hydroxy-functional reactive diluents such as OXT and PCL were shown to have higher monomer conversion at higher RH and more consistent monomer conversion a function of RH.

Acknowledgements

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