The Effect of Amines on the UV-curing of Epoxy Resins

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A B S T R A C T

Epoxies are generally cross-linked by the addition of a hardener, most of the time a diamine such as diamine diphenyl sulphone, oxydianiline or methylene diamine, and then thermocured. These formulations are quite often used, particularly in the aerospace industry for making structural materials, prepregs or composites. In this paper we have investigated the cross-linking reactions of a difunctional cycloaliphatic epoxide monomer 3,4-epoxycyclohexylmethyl-3', 4'-epoxycyclohexane carboxylate initiated by UV-irradiation and compared the kinetics with *N,N*-diglycidyl-4-glycidyloxyaniline (a nitrogen-containing monomer with a functionality of three) and 4,4'-methylenebis (*N,N*-diglycidylaniline) (another nitrogen-containing monomer with a functionality of four). Kinetics is followed using a differential photocalorimetry (DPC) technique. Upon UV irradiation in the presence of cationic photoinitiator, the difunctional cycloaliphatic epoxide monomer shows an exotherm peak whereas for the latter two monomers, no exotherm peaks were observed from the sample as a result of exposure to the UV source. To explain the phenomenon observed, the effect of addition of two amines with wide difference in the basicity of *p*-nitroaniline and pyridine, has been studied on the UV-curing of epoxy resins. It has been found that the presence of amines does retard the rate of photopolymerization and the extent of retardation is dependent on the basicity of the amine. Of the two amines used, pyridine and *p*-nitroaniline, the former is a stronger inhibitor, because of the ready availability of the lone pair of electrons. The results explain the non-reactivity of nitrogen-containing epoxy monomers *N,N*-diglycidyl-4-glycidyloxyaniline and 4,4'-methylenebis (*N,N*-diglycidylaniline) to cationic polymerization upon exposure to UV-radiation.

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INTRODUCTION

Photopolymerization reactions initiated by ultraviolet (UV) light have received considerable industrial and academic attention for rapid and solvent-free curing of polymer films. The solventless process can be performed rapidly at room temperature with a fraction of the energy requirements of thermally cured systems. The recent surge in applications of UV-initiated photopolymerizations has been motivated by at least two factors: environmental concerns about the

production of volatile organic emissions and the need for high-speed reactions to enhance production rates. As a result, UV-initiated photopolymerizations are finding applications in a variety of areas, including coatings, inks, adhesives and electronics [1,2].

UV-Initiated cationic photopolymerization reactions exhibit several advantages compared to free-radical photopolymerization. First, cationic photopolymerization is not inhibited by oxygen [2] and does not require the sample to be cured in the presence of nitrogen. Second, in contrast to the free-radical polymerization where a rapid decrease in rate usually occurs when the UV source is removed (due to radical-radical termination reactions), the cationic reactions proceed long after the irradiation has ceased. This also allows the curing to penetrate recessed areas that the light cannot reach. Finally, the cationic technique is able to polymerize important classes of monomers, including epoxies [1,2,3,4,5] and vinyl ethers [6] which exhibit very low vapour pressures, relatively low viscosities, and negligible toxicity [2]. They typically polymerize very rapidly to form films that exhibit excellent clarity, adhesion, abrasion resistance and chemical resistance.

In our research group, we have concentrated on thermal [7] as well as radiation curing (both E-beam [8] and UV [9,10,11,12] of a number of radiation curable systems: both free radical and cationic induced. Apart from our interest in studying the cure characteristics of such reaction systems, we are interested in the kinetics and structure-property relationships, such as relationship between glass transition temperature and conversion.

Interestingly, although the number of papers reporting the UV-initiated cationic curing of epoxy resins abound, there are not many reports on nitrogen-containing epoxy monomers. The novelty of this work is to understand the kinetics of epoxies and their cross-linking reactions under UV-irradiation and to explain why traditional formulations used for thermal processes do not necessary fit with UV mechanism.

The objective of this investigation is to study the curing characteristics of nitrogen-containing epoxy monomers under UV induced cationic processes and to understand the reason why, these monomers do not respond to polymerization under these reaction conditions.

EXPERIMENTAL

Materials and Experimental Procedures
Monomers
Three epoxy monomers were selected. The difunctional cycloaliphatic epoxide monomer 3,4-epoxycyclohexylmethyl-3', 4'-epoxycyclohexane carboxylate (Cyracure® UVR 6105) (this monomer does not contain nitrogen) was obtained from Union Carbide Asia Pacific, Inc. *N,N*-Diglycidyl-4-glycidyloxyaniline (a nitrogen-containing monomer with a functionality of three) and 4,4'-methylenebis (*N,N*-diglycidylaniline) (another nitrogen-containing monomer with functionality of four) were purchased from Sigma-Aldrich, USA. These two epoxy monomers are widely used in the aerospace industry and are thermally cross-linked in the presence of amines such as hardener.

Photoinitiator
The cationic photoinitiator selected was a mixture (50 wt% solid content with propylene carbonate) of aryl sulphonium antimonate salts (Cyracure® UVI 6974, obtained from Union Carbide, Singapore).

Inhibitors
Two different amines were tested: *p*-Nitroaniline (PNA) and pyridine (Py) that both the amines were purchased from Sigma-Aldrich Ltd, Singapore.

The chemical structures of the epoxy monomers, the cationic photoinitiator as well as the amines used are represented in Figure 1.

Formulation
A uniform measure of 0.25 wt% of the photoinitiator was used for all the three epoxy monomers. The amount of photoinitiator was fixed on the basis of our previous investigations. The amines were added to the mixture of the cycloaliphatic epoxy monomer and the photoinitiator. The weight of amine added was varied in three steps: 5, 10 and 20 wt% (w.r.t. the weight of the photoinitiator). All the formulations containing the epoxy monomer, the photoinitiator and the amine(s) were made by stirring the mixture of components at room temperature. The bottles containing the formulations were carefully wrapped with aluminium foils to prevent exposure to visible light and stored at 0°C.
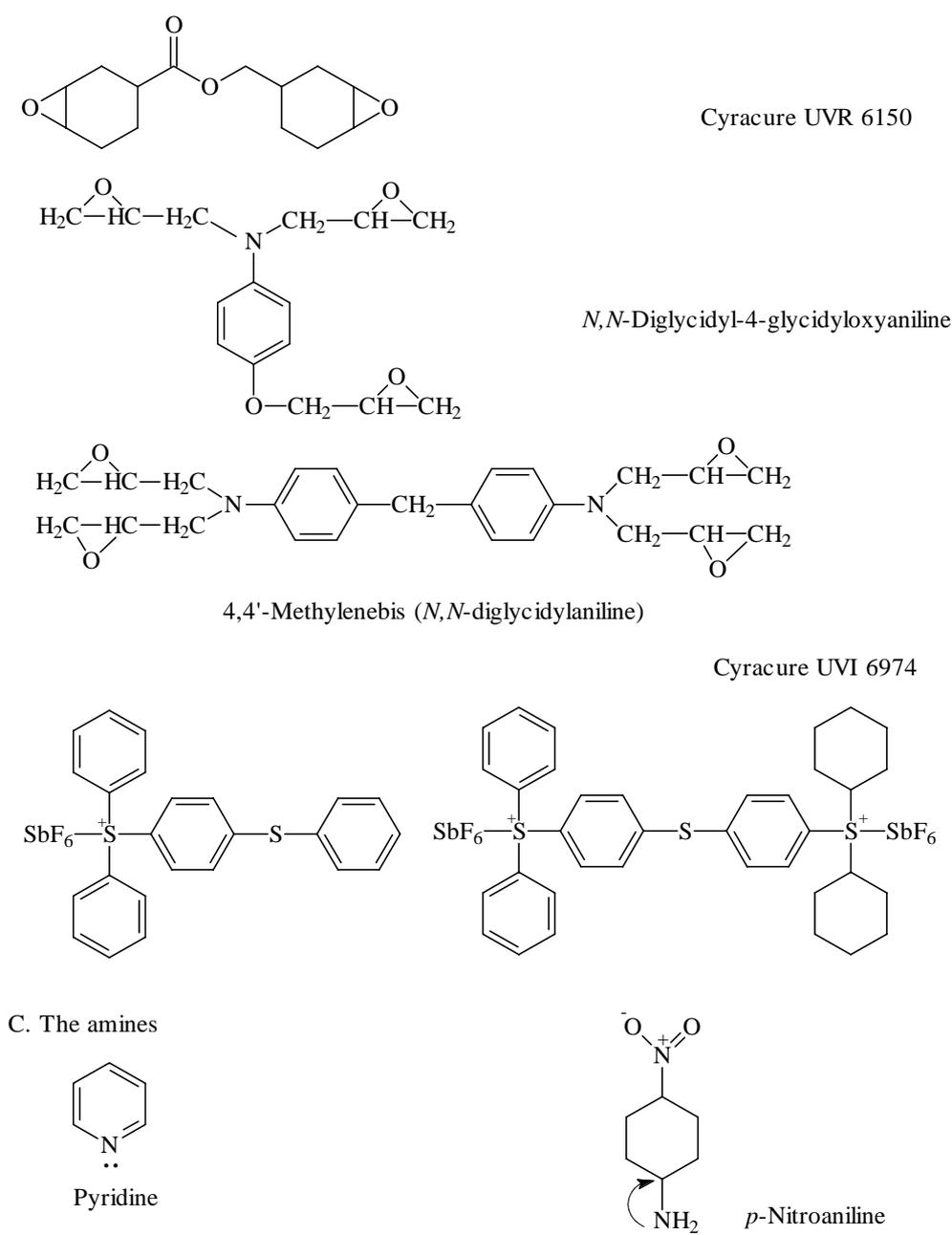
Figure 1. Chemical structures of the materials used.

Kinetics

Reaction kinetics is followed using a differential pho-tocalorimetry (DPC) technique [13]. The UV lamp (280-410 nm) used is integrated with a TA instrument differential scanning calorimeter (DSC). A reference sample (of a fully cured resin) was prepared by expos-ing trimethylol propane triacrylate (TMPTA) with 3 wt% of a radical photoinitiator (Irgacure® 651, from Ciba Geigy). All the samples were subjected to 2 min of isothermal conditioning followed by 5 min of exposure and followed once again by 2 min of isothermal conditioning.

RESULTS AND DISCUSSION

Figure 2 shows the associated exotherm upon expo-sure to UV-radiation for the cycloaliphatic epoxy monomer (Cyracure® UVR 6105) with 0.25 wt% of the sulphonium salt. As observed from the figure, the
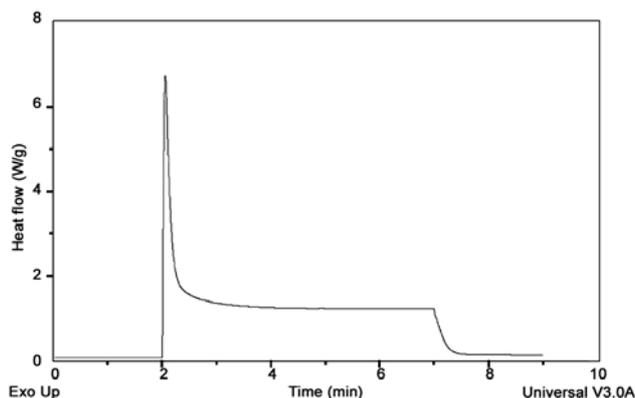
Figure 2. Exotherm associated with the UV exposure (5 min) of cycloaliphatic epoxy resin (Cyracure® UVR 6105) with 0.25 wt% of sulphonium salt (Cyracure® UVI 6974).

baseline is a straight line during the isothermal conditioning period, shoots up with the opening of the shutter, attains a peak maximum and comes down subsequently. This is because of the spontaneous onset of the cationic polymerization of the system. The area of the resulting exotherm is a measure of the extent of curing of the system under UV exposure.

Figure 3 presents the kinetic analysis curve of the resin formulation (referring to the exotherm in Figure 2), which fits with an autocatalytic model. The value of the reaction constant, k, is found to be (4.07 ± 0.72) min^{-1}.

Figures 4 and 5 show the results of the UV exposure, under similar experimental conditions, of the other two epoxy monomers, namely, *N,N*-diglycidyl-4-glycidyloxyaniline (Figure 4) and 4,4'-methylenebis (*N,N*-diglycidylaniline) (Figure 5). As it is observed

clearly, there is no exotherm obtained from the sample as a result of exposure to the UV source. The upward shift in the baseline which comes down to the original position, is due to the residual infrared radiation associated with the UV-radiation, that induces the heat flow into the DSC cell. It may be noted here that this phenomenon was repeatable and observed in every experiment. Our initial suspicion that the photoinitiator might have exceeded its shelf life was verified not to be true, by repeating the experiment with new groups of photoinitiator. Attempts were made to increase the concentration of the photoinitiator, but the anticipated curing exotherm was never observed. The principal objective of this study thus became to investigate the possible reasons behind this difference in the curing characteristics of the two types of monomers. Incidentally, both of the epoxy monomers (exotherms in Figures 4 and 5) contain nitrogen in the basic structural unit, which is not the case for the cycloaliphatic epoxy monomer (Figure 2).

It is known that the UV-curing of epoxy resins in the presence of aryl sulphonium salts proceeds via the cationic initiation mechanism. The cation in the process is a Brönsted acid generated as a result of photodecomposition of the arylsulphonium salt(s), under UV-radiation. The first step of the photoinduced (UV) process is the energy absorption producing an electronically excited triarylsulphonium salt.
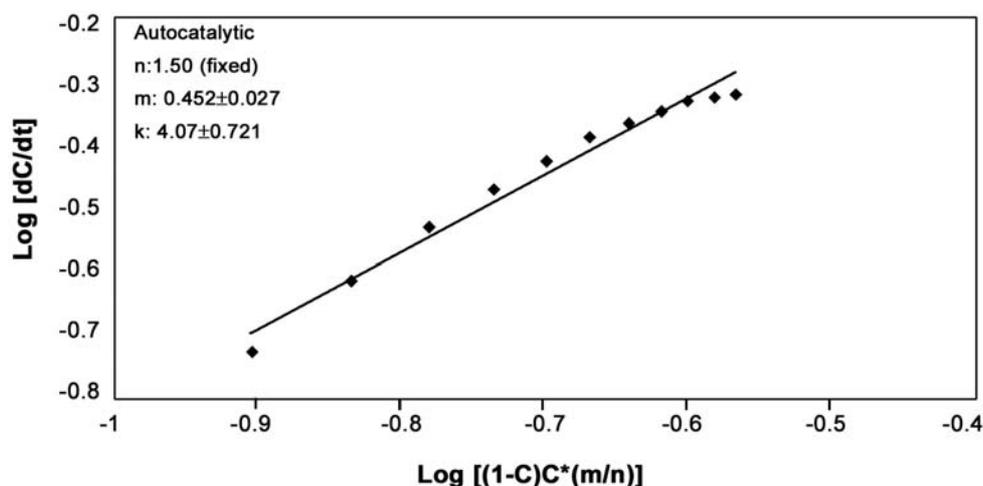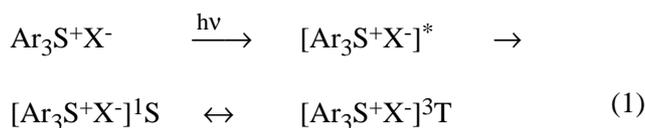
$$Ar_3S^+X^- \xrightarrow{\ h\nu\ } [Ar_3S^+X^-]^* \rightarrow$$

$$[Ar_3S^+X^-]^1S \leftrightarrow [Ar_3S^+X^-]^3T \qquad (1)$$

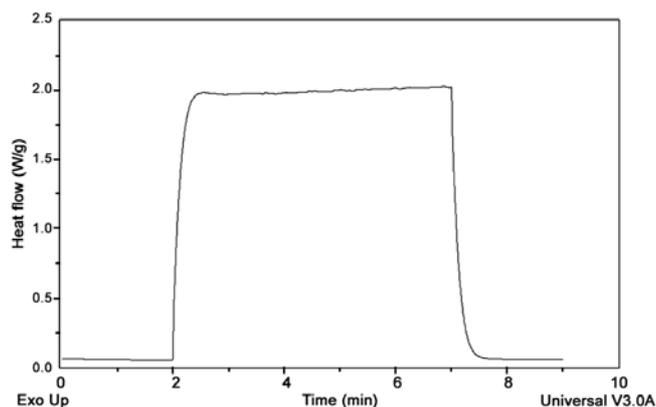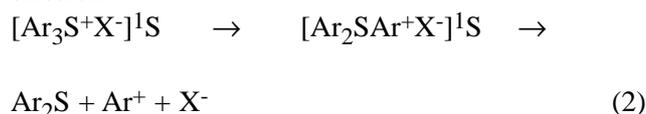**Figure 3.** The application of autocatalytic kinetic model to the reaction exotherm (in Figure 2).
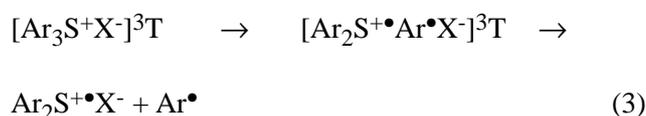
Figure 4. Heat flow curve for *N,N*-diglycidyl-4-glycidy-loxyaniline with 5 wt% of sulphonium salt (Cyracure® UVI 6974).

Subsequent rapid decay of the photo-excited species occurs, with resultant cleavage of the carbon-sulphur bond. This can either be due to heterolytic scission:

$$[Ar_3S^+X^-]^1S \quad \rightarrow \quad [Ar_2SAr^+X^-]^1S \quad \rightarrow$$

$$Ar_2S + Ar^+ + X^- \tag{2}$$

or, by homolytic scission:

$$[Ar_3S^+X^-]^3T \quad \rightarrow \quad [Ar_2S^{+\bullet}Ar^\bullet X^-]^3T \quad \rightarrow$$

$$Ar_2S^{+\bullet}X^- + Ar^\bullet \tag{3}$$

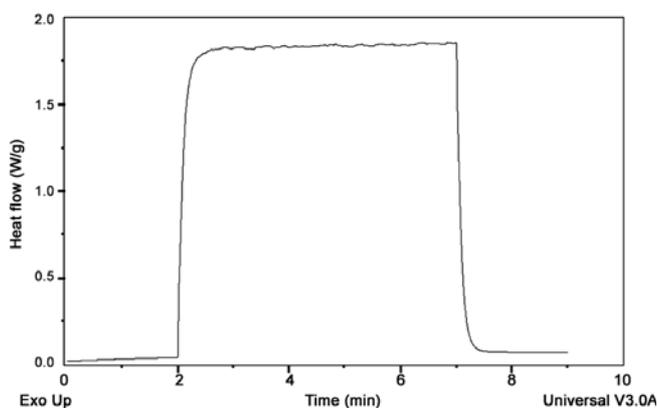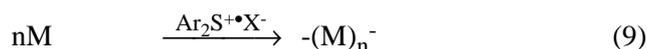giving an arylsulphonium cation-radical and an aryl radical.

Figure 5. Heat flow curve for 4,4'-methylenebis (*N,N*-diglycidylaniline) with 5 wt% of sulphonium salt (Cyracure® UVI 6974).

The cation-radicals are therefore, the species ultimately responsible for initiating cationic polymerization. It has been reported that the resulting cation-radicals react with small amount of protogenic and non-protogenic impurities present in the polymerization media as well as by a variety of chain transfer processes, to give rise to protons, the Brönsted acids, which initiate and propagate the polymerization process.

$$Ar^+ + X^- + RH \quad \rightarrow \quad ArR + H^+X^- \text{ (Minor reaction)} \tag{4}$$

$$Ar_2S^{+\bullet}X^- + RH \rightarrow Ar_2S + R^\bullet + H^+X^- \text{ (Major reaction)} \tag{5}$$

Thus, when a formulation containing a cationic photoinitiator and the monomer(s) is irradiated under UV-radiation, both of the monomers as well as the onium salt absorb the radiation. Since the onium salt concentration is relatively small (typically 1 to 3 wt%), the bulk of energy is absorbed by the monomer, which after excitation transfers the excess energy to the onium salt. A generalized mechanism under radiation induced curing (UV/e-beam), therefore follows:

$$M \quad \rightarrow \quad M^* \tag{6}$$

$$M^* + Ar_3S^+X^- \quad \rightarrow \quad M + [Ar_3S^+X^-]^* \tag{7}$$

$$[Ar_3S^+X^-]^* \quad \rightarrow \quad Ar_2S^{+\bullet}X^- + Ar^\bullet \tag{8}$$

$$nM \quad \xrightarrow{Ar_2S^{+\bullet}X^-} \quad -(M)_n^- \tag{9}$$

Under the present experimental conditions, both the epoxy resins, *N,N*-diglycidyl-4-glycidyloxyaniline and 4,4'-methylenebis (*N,N*-diglycidylaniline), (Figures 4 and 5) do not react to any appreciable extent, even in the presence of excess amount of photoinitiator. This we suspect that is due to the presence of nitrogen in the structural unit of the monomers. The nitrogen atom, which has a lone pair of electrons available in an SP^2 orbital, has the ability to capture the Brönsted acid molecules, and in the process acts as a strongly effective inhibitor of the cationic polymerization process. If this reasoning is assumed to be correct, then any addition of external amine(s) to an epoxy system that is known to react under the UV-radiation, should be significantly affected. In addition,

the effect of the so-added amine should be dependent on the relative strength of *N*-atom in the amine to release the lone pair of electrons.

In view of this fact, two different amines were selected: pyridine (Py) and *p*-nitroaniline (PNA). In case of Py, the lone pair of electrons does not take part in the aromatic structure and is therefore readily available for donation. On the other hand, with PNA, the availability of the electrons is strongly reduced, as a result of the electron-withdrawing inductive effect of the NO_2 group located advantageously in the *para*-position. This explains the strong basicity of Py with respect to PNA (Figure 1).

Keeping this argument in mind, subsequent tests were done with the cycloaliphatic epoxy monomer and the sulphonium salt as photoinitiator, along with the addition of the two amines; Py and PNA in varying proportions. Once again, similar formulations were prepared with the addition of 5, 10 and 20 wt% (w.r.t. the weight of the photoinitiator) of the amines. The formulations were exposed to UV radiation, as described earlier in this article.

Figure 6 shows the original exotherm (of the cycloaliphatic epoxy monomer with 5 wt% of the photoinitiator, without any added amine to the system) as well as those obtained with the addition of varying weight percent of Py in the formulation. As observed in Figure 6, a mere addition of 5 wt% of Py (w.r.t. the sulphonium salt) into the epoxy monomer drastically brings down the exotherm, whereas increasing the same to 20 wt%, more or less eliminates the exotherm altogether.
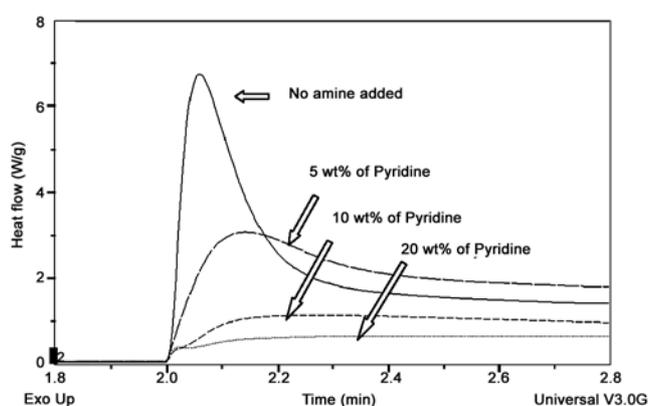
Figure 7 shows similar curves as in Figure 6, but in
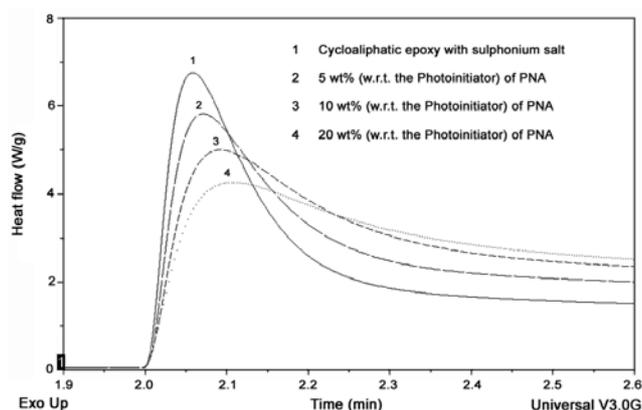

Figure 7. Effect on reaction exotherm by increasing concentrations of *p*-nitroaniline.

this case the added amine was PNA. Once again, a similar trend is very distinctly apparent, although in smaller proportions, vis-à-vis pyridine. Although the exotherm still persists even at 20 wt% addition of PNA the trend is obvious. The effect is less in the case of PNA compared to Py, because the former is a weaker base compared to the latter.

Figure 8 shows the overlaid exotherms of the original formulation, one with 5 wt% of PNA and the other with 5 wt% of Py. The relative difference in the effect of the two amines (thus establishing the relationship to the strength of the amine as a base and hence the ability to capture the Brönsted acid) is quite apparent here.

On the basis of the above findings, we can safely conclude that the presence of amines does in fact affect the course of polymerization reactions, which
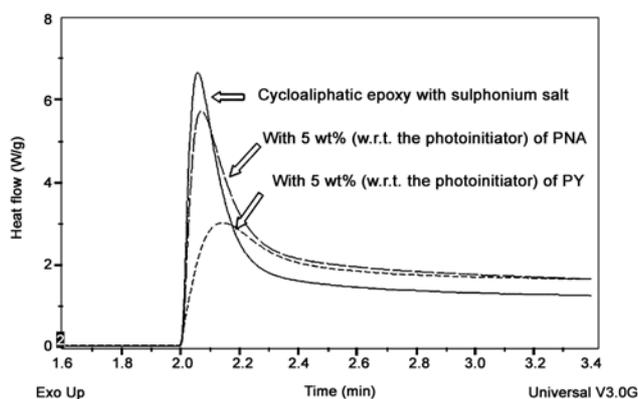

Figure 6. Effect on reaction exotherm by increasing concentrations of pyridine.

Figure 8. Exotherm obtained by exposing 0.25 wt% (sulphonium salt-Cyracure® UVI s6974) formulation of the cycloaliphatic epoxy resin with 5 wt% (w.r.t. the weight of the photoinitiator) of pyridine and *p*-nitroaniline.
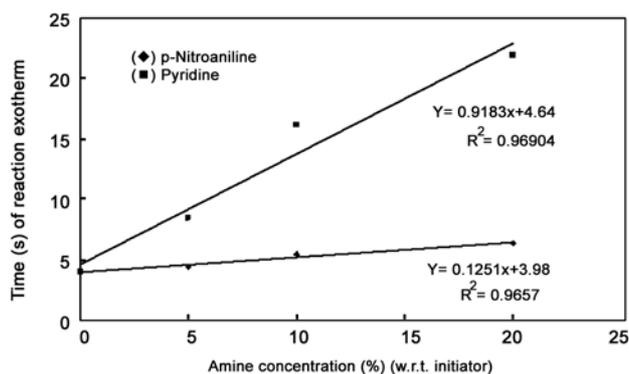
Figure 9. Effect of amine concentration on the occurrence of the peak of the reaction exotherm.

Figure 10. Effect of amine concentration on the reaction constant, k.

must be initiated by a cationic species. The degree of such effect(s) would depend on the readiness of the concerned amine(s) to accept a cationic species, which is a direct consequence of the basicity of the amine.

Figure 9 plots the delay of the peak exotherm (in seconds, as compared to the one without the added amine) with the concentration of the respective amines used. One observes a very clear trend here as well. The peak maximum (of the exotherm) which occurs at 3.6 s for the epoxy and the photoinitiator system does act with delay with an increasing concen-tration of the added amine. And in this case as well, the effect is more apparent in the case of Py than PNA (Py being the stronger of the two amines delays the peak maximum to the maximum extent). Figure 10 plots the reaction constant, k, obtained for each of the formulations containing the amines. Comparing the variation in the magnitude of k with the concentration and the nature of amines, one sees a repeat of the trend in Figure 9, but in the opposite direction. The reaction constant, k, which is a direct measure of the speed of the reaction, shows a falling trend with increasing amine concentration. Again, it can be observed that the stronger amine has a higher tendency towards
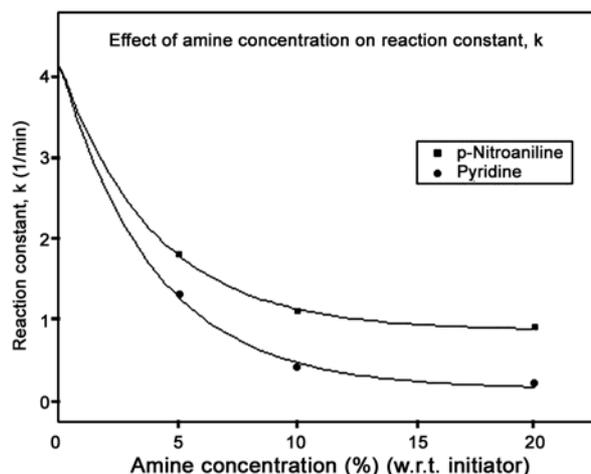
bringing down the reaction constant, k, in line with our argument.

Finally, as a conclusive evidence, a formulation was made of the virgin cycloaliphatic epoxy (Cyracure® UVR 6105) and the photoinitiator system (sulphonium salt Cyracure® UVI 6974) with one of the epoxy monomers that contains nitrogen, but does not react under UV-radiation. The epoxy monomer selected was *N,N*-diglycidyl-4-glycidyloxyaniline (f = 3). The result (Figure 11), once again, follows our line of argument. The epoxy monomer containing nitrogen in its basic structure unit, acts similar to an external amine and inhibits the cationic process, with equal ease.

Based on the findings of this investigation, the general steps involved in a cationic polymerization process which is hindered in the presence of amine(s) may be visualized in Scheme I.

The lone pair of nitrogen which acts as a scavenger for the cationic species is responsible for initiation and propagation of the reaction (step III), competes with steps I and II.
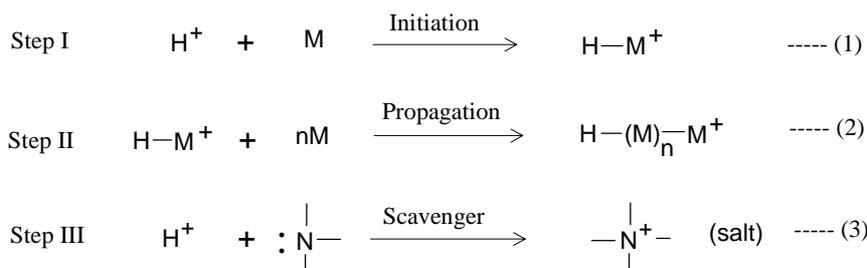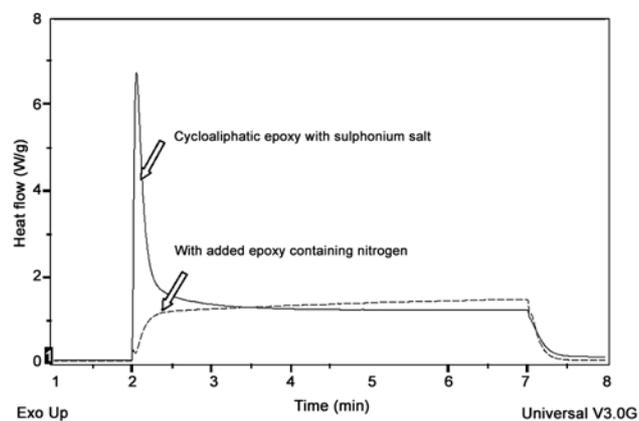

Scheme I.

Figure 11. Effect on the UV exotherm of addition of 5 wt% of *N,N*-diglycidyl-4-glycidyloxyaniline into Cyracure® UVR 6105 (with 0.25 wt% of sulphonium salt-Cyracure® UVI 6974).

CONCLUSION

To cure epoxy resins a variety of coreactants are used either through the epoxide or hydroxyl groups. It is well known that to cure thermally epoxy resins, polyamines as hardener are the most common curing agent with reaction involving ring opening addition of amine. Both primary and secondary amines are used with primary amines being more reactive than secondary amines. Since each nitrogen-hydrogen bond is reactive in the curing reaction, primary and secondary amine groups are bi- and monofunctional, respectively.

Photocuring of epoxy resins can also be achieved by ring opening polymerization of epoxy groups leading to a polyether structure. In this latter case we have demonstrated and shown that the presence of nitrogen in the chemical structure of the epoxy monomer(s) prevent any radiation polymerization or crosslinking reaction. Results of the effect of adding two amines with considerably different basicity have shown that nitrogen group was responsible for this phenomenon and explain the non-reactivity of nitrogen-containing epoxy monomers to cationic polymerization upon exposure to UV-radiation. The degree of retardation depends both on the amount and basicity of the amine concerned.

Therefore formulation of epoxy resins is strongly dependent of the way how it is cured, presence of amine for thermal curing but absence of amine in photocuring process.

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