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UV photo curing of N,N'-bismaleimido-4, 4′-diphenylmethane

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Abstract

The photo curing of a formulation consisting of N,N'-bismaleimido-4, 4′-diphenylmethane (BMI), which is most widely used in commercial thermal curing formulations, was performed. Parameters, such as initiator, co-initiator and temperature, which affect the curing rate and enthalpy, were studied using differential photocalorimeter. BMI undergoes copolymerization with 4-hydroxybutylvinylether (HBVE), when exposed to UV radiation, in presence of the photo initiator, Triphenylphosphine oxide (TPO). Diallylbisphenol A has been observed to be an efficient co-initiator, which improves the reaction rate coefficient and enthalpy of the photo curing process for the system BMI/HBVE/TPO.

Keywords: Photopolymerization; Bismaleimide; Triphenyl phosphine oxide; Diallylbisphenol A; Differential photocalorimetry

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1. Introduction

Bismaleimide (BMI) resins have been finding increasing applications in both aerospace and electronic industries, bridging the gap between relatively low temperature-resistant epoxy systems and the very high temperature resistant polyimides. While having slightly lower glass transition temperatures compared to the latter, BMIs have the advantages of significantly lower moisture absorption, little evolution of volatile gases, better processing properties and lower cost, compared to codensation-type polyimides. Compared to epoxy resins, BMIs have higher tensile strength and modulus, excellent chemical and corrosion resistance, better dimensional stability and good performances at elevated temperature [1]. Brittleness has been a major drawback of BMI based polyimides, due to their aromatic molecular structure. However, this has been overcome in modified BMI resins using various modifiers such as aromatic diamines, diallylbisphenol A (DABA), epoxies, etc. with consequent improvement in plasticity as a result of increase in the distance of cross-links [2].

The major liability while using BMIs as matrix resin, remains its high curing temperature and long cure time [3]. The use of accelerated radiation curing methods, involving UV and electron beam [4,5,7,8], has been shown to resolve this issue for epoxy acrylate systems electron beam curing in particular, occurs typically at room temperature and the whole process takes only a few seconds. This technique has been shown to be effective for acrylate or cycloaliphatic vinyl epoxy systems. It has recently been reported that N-alkylmaleimides homopolymerize in the absence of added photoinitiator, when exposed to UV light in solvents having labile hydrogen [9]. It has also been reported that maleimide/vinyl ether systems can be cured rapidly upon exposure to UV or electron beam source, to form crosslink network [10–12]. The copolymerization between maleimide and vinyl ether takes place via the electron donor/acceptor mechanism, in which maleimide acts as an electron acceptor and vinyl ether acts as an electron donor. The curing mechanism has been schematically illustrated in Fig. 1 [10]. It shows that the labile hydrogen is critical in the photo curing of maleimide/vinyl ether.

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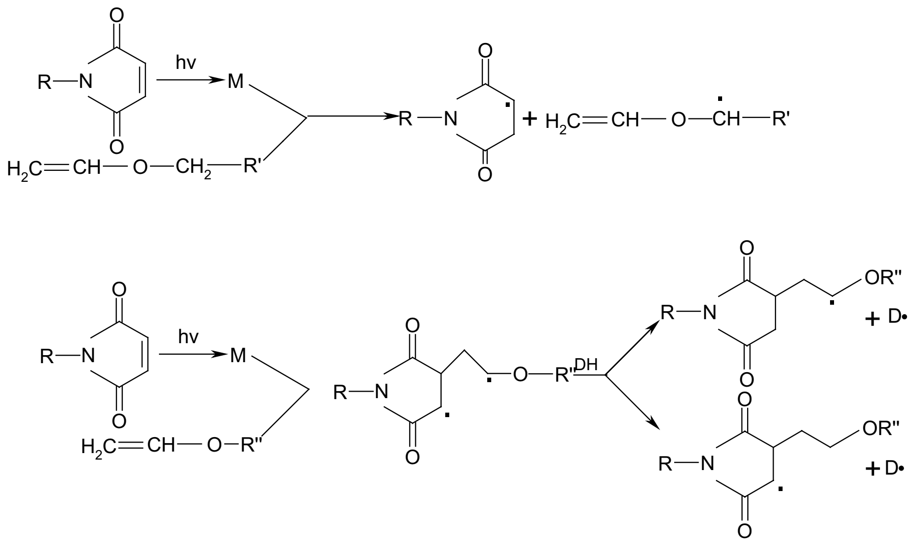


Fig. 1. The reaction between maleimide and vinyl ether.

The maleimide system reported has been the *N*-alkylmaleimides, which undergo radiation curing easily, possibly due to its more flexible chain. The maleimide system which has been frequently used in thermal curing and is the one used in the present investigation, is BMI system [13–15]. This has a molecular structure, which is quite rigid because of the presence of aromatic rings. The presence of the aromatic rings as well as the resultant high crosslinked density during thermal curing, impart the cured product its high heat-resistance, resulting in high T_g and mechanical strength. However, to date, the radiation curing of such a maleimide has not been reported, and therefore forms the basis of this study. In this investigation, UV radiation was used to cure BMI, in the presence of a radical photoinitiator and an added co-initiator.

2. Experimental procedure

2.1. Materials

The materials used in this study were as follows. BMI, 4-hydroxybutylvinylether (HBVE) and DABA, which were used as monomers, were purchased from Aldrich, USA. The photoinitiator used and the respective sources were:- triphenylphosphine oxide (TPO), obtained from BASF, Irgacure® 1700 (IR1700), Irgacure® 651 (IR651) and Irgacure® 4265 (IR4265) obtained from Ciba Geigy as radical generators,

- Cyracure® UVI 6974 (6974) from Union Carbide and Irgacure® 261 (IR261) from Ciba Geigy, as cationic generators.

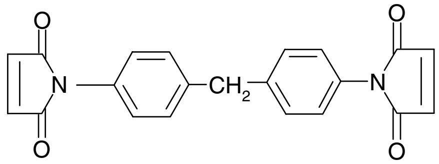
The chemical formulae of the various monomers utilized in this study have been illustrated in Fig. 2.

2.2. Experimental procedure

Cure kinetic analysis was performed using a real time UV curing study using a differential photocalorimeter (DPC). Details of the experimental technique has been described in previous papers [16,17]. The method allows the evaluation of the heat flow from a photosensitive formulation that cures under UV radiation from a UV lamp that operates at an intensity of 0.1–30 mW/cm^2. The formulation of BMI and HBVE was in stoichiometric proportions. About 2 mg of the BMI/HBVE formulation was transferred into the DPC aluminum pan. A polyethyleneterephtalate (Mylar® film) was used to cover the liquid in the DPC pan, so as to prevent atmospheric oxygen from diffusing into the sample. The DPC pan with the sample was placed into the DPC cell and exposed to UV radiation for 5 min. The reaction exotherm was recorded during the process of photo curing. The kinetic parameters were calculated using an autocatalytic model [18,3].

3. Results and discussion

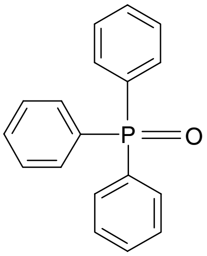
Before attempting the cure of BMI modified with DABA, under exposure to UV radiation, individual components as well as combinations thereof, in presence and absence of the photoinitiators were exposed to the UV source. The results of such tests are presented in Tables 1 and 2 respectively. The results show that the DABA/IR1700 (Table 1) and BMI/HBVE/TPO (Table 2)



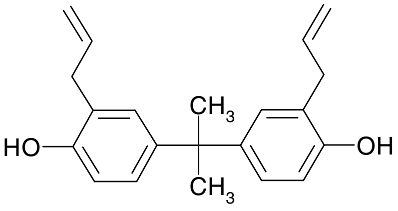
N, N'-Bismaleimido-4, 4'-diphenylmethane (BMI)

$CH_2=CH-O-CH_2-CH_2-CH_2-CH_2-OH$

4-hydroxybutylvinylether (HBVE)



Triphenylphosphine oxide (TPO)



2,2-diallylbisphenol A (DABA)

Fig. 2. Chemical formulae of materials used in the present study.

systems do cure under UV, whereas, BMI/HBVE does not. Both IR1700 and TPO are radical initiators. So either DABA or BMI can only be initiated by radical initiators. The curing reaction mechanism is therefore radical driven.

Table 2
Response of formulations of BMI with HBVE and DABA (in presence and absence of radical photoinitiators), upon exposure to UV radiation

	HBVE	HBVE/ TPO	DABA	DABA/ IR1700
BMI	No[a]	Yes[b]	No	Little[c]

Note: the experimental condition of Tables 1 and 2 is as following: 30 °C, 3% photointiator, 20 mW/cm^2, exposing to UV for 5 min.

[a] There is no exothermic curing peak on the DPC curve.

[b] There is a exothermic curing peak on the DPC curve.

[c] There is a very weak exothermic and relatively flat curing peak on the DPC curve.

From a study of the molecular structure of BMI and *N*-aliphaticmaleimide or *N*-phenylmaleimide, it is clear that the molecular chain of BMI is much more rigid than that of others. Expectedly, its reactivity would be low, because the reactivity of a system is a function of the mobility of reacting segments. Another important factor affecting the reactivity of BMI is the absence of an extractable hydrogen in the molecular structure, which is known to be critical to the reaction between maleimide and vinyl ether. The report by Hoyle and Clark has shown the effect of the structure of maleimide on the curing kinetics [9], with the availability of varying number of extractable hydrogen atoms. Evidently, photo initiators and co-initiators would be required to make the system react under the UV radiation.

Fig. 3 presents a representative DPC exotherm involving the photopolymerization of BMI/HBVE (0.5:1), using TPO as an initiator. The result clearly shows a very sharp exothermic peak occurring during the UV exposure period, confirming that TPO is indeed an effective initiator for the reaction between BMI and HBVE.

In order to investigate the influence of temperature on the reaction, the samples wre exposed to UV light at different temperatures. The results obtained at different temperatures are shown in Fig. 4.

Fig. 4 shows that the rate coefficient and enthalpy increase with increase in temperature upto about 50 °C and decreases with further increase in temperature. This

Table 1
Response of DABA in presence of different initiators (radical/cationic), upon exposure to UV radiation

Initiator	IR1700 radical	6974[a] Cationic	IR1700/6974 radical/cationic	IR261[b] cationic	IR651 radical	IR4265 radical	HBVE	HBVE/TPO radical
DABA	Yes[c]	No[d]	No	No	No	No	No	No

[a] Bronsted acid (H$^+$).

[b] Lewis acid.

[c] There is an exothermic curing peak on the DPC curve.

[d] There is no exothermic curing peak on the DPC curve.

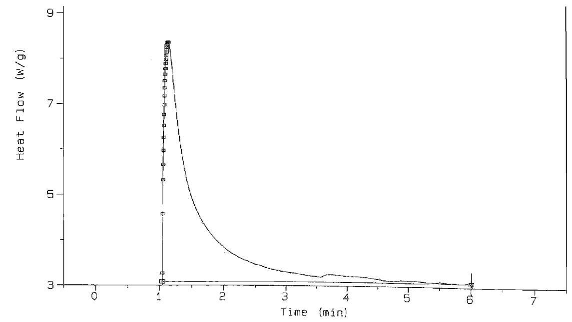


Fig. 3. DPC curve of BMI/HBVE/TPO. BMI : HBVE = 1/2 : 1 mol/mol, 6% TPO. 3 mW/cm^{-2}.

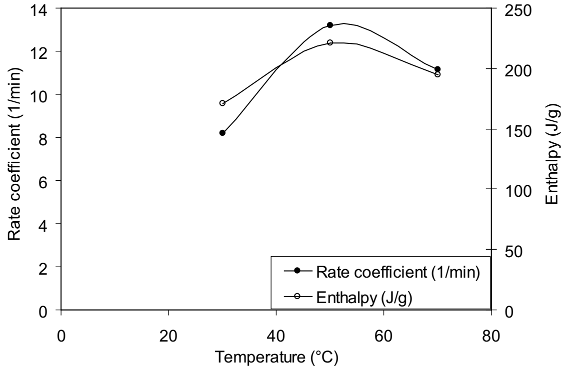


Fig. 4. The influence of temperature on the reaction. Formulation: BMI : HBVE = 1/2 : 1 mol/mol, 6%TPO, 3mW/cm^2.

is because, at high temperature, the radical concentration is high. At one side, high concentration radical will induce the increasing of the initiation rate, but on the other side, it also increases the probability of chain termination. So, there is an optimal temperature to obtain high reaction rate and high enthalpy.

DABA (2,2-diallylbisphenol A) is a common modifier in industrial formulations based on BMI, which helps to increase the toughness of the BMI, although it also lowers the glass transition temperature of the cured product [19,20]. However, our initial studies with DPC showed that DABA did not react with either HBVE or BMI, even in the presence of TPO as a photoinitiator (Tables 1 and 2).

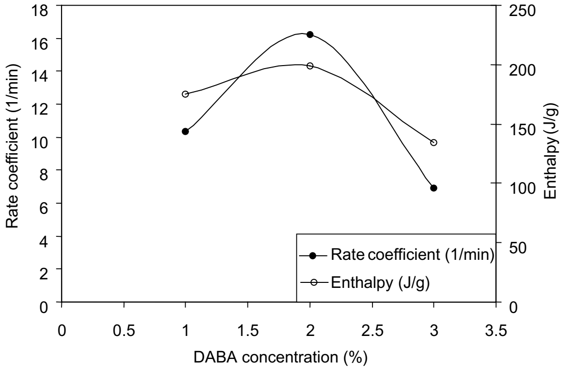


Fig. 5. The influence of DABA concentration on the reaction. Formulation: BMI : HBVE = 1/2 : 1 mol/mol, 6%TPO, 30 °C, 3 mW/cm^{-2}.

Fig. 5 shows the results obtained for the photo curing of the formulation BMI:HBVE (0.5:1), with varying amounts of DABA, at a fixed concentration of the radical photoinitiator (TPO) at 6.00%. It is seen that the kinetic parameters are sensitive to the concentration of DABA. By modifying the concentration from 1% to 3% w/w, the photo crosslinking rate and enthalpy has been observed to increase until a DABA concentration of 2% and decrease for concentrations beyond. This behavior can be explained in two ways. 1. DABA can provide mobile allylic hydrogens, which is beneficial to the initiation of radical chains in the reaction system. 2. DABA, presumably, works as a photosensitizer, which absorbs the radiation and transfers the excess energy to the reacting system.

When the concentration of DABA was increased further, the photo crosslinking rate and enthalpy decrease. This is due to the fact that at high concentrations, DABA absorbs most of the radiation so as to reduce the light intensity obtained by matrix material.

Figs. 6 and 7 show the results of the rate coefficient and the enthalpy in photo curing, as the amount of TPO is varied. The influence of initiator concentration up to 10% w/w is seen to be similar to that of DABA. The optimal amount of TPO for the reaction appears to be about 6%.

Fig. 8 shows the results of the rate constant and enthalpy when the photo curing was performed at

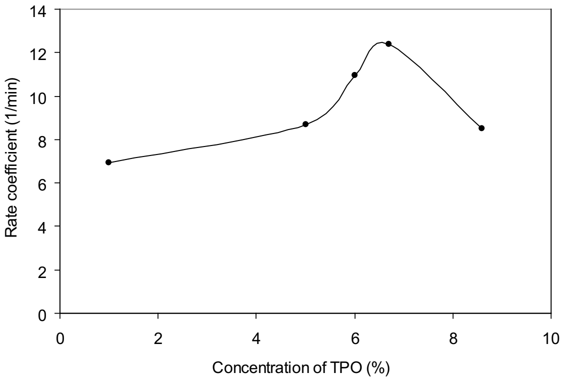


Fig. 6. The influence of TPO concentration on photocuring rate coefficient. Formulation: BMI : HBVE = 1/2 : 1 mol/mol, 2%DABA, 30 °C, 3 mW/cm^{-2}.

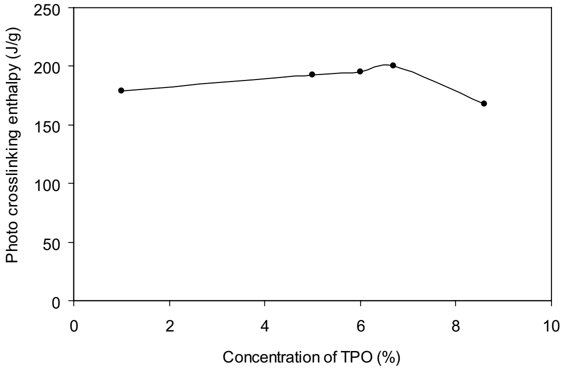


Fig. 7. The influence of TPO concentration on the photocuring enthalpy Formulation: BMI : HBVE = 1/2 : 1 mol/mol, 2% DABA, 30 °C, 3 mW/cm^{-2}.

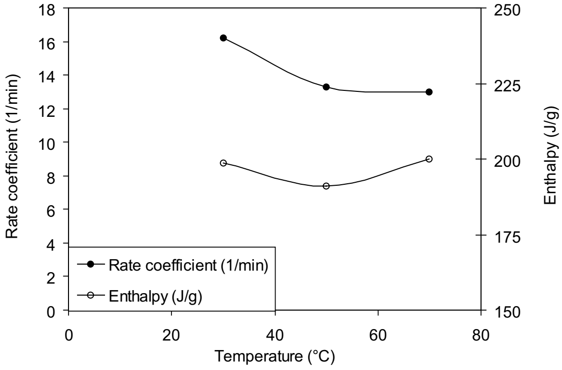


Fig. 8. The influence of temperature on the reaction. Formulation: BMI : HBVE = 1/2 : 1 mol/mol, 2% DABA, 6% TPO, 3 mW/cm^{-2}.

varying temperatures for the system BMI/HBVE/DABA/TPO. The rate constant decreased with temperature increase, but the enthalpy remained more or less constant. This is due to the fact that, at high temperature, the increase of radical concentration makes the rate of chain termination higher than that of the chain initiation rate.

4. Conclusion

BMI, which is most widely used in industrial thermally curable formulations, has been investigated for photo curing. Unlike *N*-alkylmaleimide and *N*-phenylmaleimide, BMI does not react with vinyl ether without photoinitiator. But BMI/HBVE system does polymerize in the presence of photoinitiator TPO. DABA, which is a good property modifier for BMI in thermal curing formulation, does not polymerize with either BMI or HBVE, even in presence of TPO. However, it was observed that DABA works as a coinitiator and speeds up the reaction of BMI/HBVE/TPO. The optical concentration of photoinitiator and coinitiator has been studied. The influence of the temperature on photo curing shows that increasing temperature does increase the polymerization rate and enthalpy. But when the temperature increases up to 70 °C, both the polymerization rate and enthalpy decrease.

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