Development of Interpenetrating Network (IPN) Hybrid Composite for Thin Film Protection

G.L. Seah [1], V. Yu. Voytekunas [2] & M.J.M. Abadie [1, 2]

[1] School of Materials Science & Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

[2] Laboratory of Polymer Science/Advanced Organic Materials – LEMP/MAO, University Montpellier 2, S.T.L., Place Bataillon, Montpellier Cedex 34095, France

Abstract

Conventional production of polymer composite is a time consuming process which involves a long thermal curing step of the monomers into thermosets. An attractive cost saving and environmentally friendly alternative is to perform curing via UV radiation. It shortens the curing time from hours to minutes, lowers the curing temperature and requires little or no solvent. Thus it is increasingly popular in the coating and microelectronic industries. Acrylates and other radical initiated monomers are widely studied and among the more popular monomers used in the industry. However, they are highly sensitive to oxygen and have poor adhesion on many surfaces, making them poor coatings. On the contrary, epoxides are more stable in oxygen and have good adhesion properties, establishing them as good coatings for many surfaces. Unfortunately, they are not well studied and hence not widely used. It is desired to create an IPN of both epoxides and acrylates to retain the advantages of individual polymers while increasing the hardness, impact strength and chemical resistance to produce high performing coating. DPC was used to carry out the curing with the analysis of curing kinetics and photoreactivity simultaneously. In this study, TMPTA, TMPT(EO)A and Epolam® 5015 were used in the investigation of the formation of simultaneous IPNs with TMPT(EO)A as the most reactive monomer within the three. The effects of composition of individual monomers and temperature were investigated under optimum photoinitiator concentration of 3 weight percent. The highest percentage conversion and rate of reaction is the highest when the experiment was conducted at 70 ˚C with the highest triacrylates proportion. The activation energies of the IPNs were found to be either between or lower than that of the monomers.

1. Introduction

UV curing of polymers is popular in various industries like coating and microelectronics in the last few decades due to its fast and simple process under ambient condition [1-5]. The absence of gel time during curing [1] allows the formation of thin film coating on different substrates with good finish, wear, abrasion and chemical resistance [3, 4]. It is an environmentally friendly technology with low Volatile Organic Compound (VOC) emission and energy consumption [1, 3-4].

The common monomers that are used in photopolymerization are acrylates, epoxides and vinyl ethers [2, 5]. Acrylates, which are sensitive to radicals, are the most extensively studied monomers in this area due to availability of a number of photoinitiators and a great variety of monomers and oligomers. However, acrylate monomers are volatile and highly sensitive to oxygen when polymerized; the oligomers have high viscosity and presence of residual functionalities in 3D matrices after curing. Also, volume shrinkage during polymerization causes poor adhesion on many substrates [2-5].

Epoxides, which are sensitive to cationic reactions, are opposite of acrylates and capable of undergoing dark curing with a cationic photoinitiator to generate reactive electrophiles. This is of advantage as even after UV exposure is ceased, the electrophiles generated can continue the reaction. This also allows shorter UV exposure times and reduces production cost. In addition, any portions of the resin inaccessible to UV exposure can be polymerised even after UV exposure. The epoxy coatings produced have high mechanical properties and excellent adhesion on many substrates [2-6].

The two ways to combine two monomers of opposite characteristics are by chemical and physical means. To chemically combine two or more different types of multifunctional monomers, the monomers (eg. acylates and/or vinyls) have to react by the same mechanism to form random copolymers or eventually alternating copolymers. However, if these different types of multifunctional monomers cure through different mechanisms, they will cure individually with their own type of monomers. This will form a blend with two physically intertwined homopolymer networks, also known as an Interpenetrating Network (IPN) as in Figure 1a. As in the case of mixing acrylate and epoxide, acrylate polymerizes by radical mechanism and epoxide by cationic mechanism, polymerizing the mixture allows the attainment of a thermosetting blend of polyacrylate and polyepoxide. An IPN allows two polymers of different properties to exist in the same medium to form a high performance coating. In this project, the monomers were polymerized simultaneously to form a simultaneous IPN [7]. Figure 1b shows the formation of a semi-IPN (sIPN) where a thermosetting polymer is entangled with chains of thermoplastic.
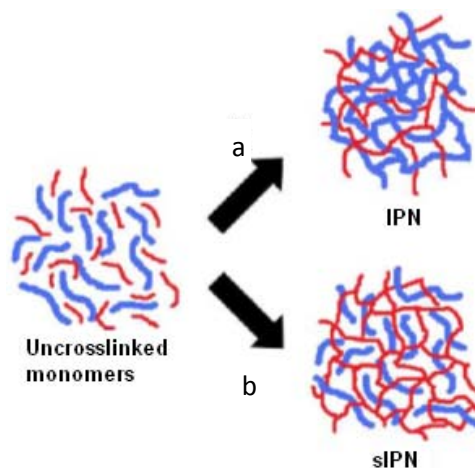
Figure 1: Formation of (a) IPN and (b) semi-IPN

Differential Photo Calorimetry (DPC) was used in this study to perform in-situ analysis of photo-reaction and its kinetics as it is equipped with a UV lamp for photocuring while measuring the heat flow using Differential Scanning Calorimetry (DSC). The sample and reference were exposed to UV light simultaneously and the polymerization exotherm of the sample is recorded as a function of time [1-3, 5-6].

The objective of this paper is to study the curing kinetics and photoreactivity of monomers, TMPTA, TMPT(EO) and Epolam® 5015, and formulate IPNs from these monomers to produce coatings for thin film antiscratch purposes.

2. Experimental

2.1 Materials
The two different triacrylate monomers used were trimethylolpropane triacrylate (TMPTA) (Figure 2a) and trimethylolpropane tri(ethyleneoxide) acrylate (TMPT(EO)A) (Figure 2b) obtained from Sartomer USA, LLC. Epolam® 5015 (Bisphenol-F-epichlorhydrine) (Figure 2c) obtained from Axson Techonologies.

The radical photoinitiator (RPI) used for the curing of triacrylate monomers was Ciba Darocur® 1173 (2-hydroxy-2-methyl-1-phenyl-propan-1-one) (Figure 2d), which when exposed to UV light gives radicals. The cationic PI (CPI) for diepoxide curing was Cyracure® UVI-6976, consisting a mixture of dihexafluoroantimonate of S,S,S',S',-tetraphenylthiobis (4,1-phenyllene) disulfonium and hexafluoroantimonate of diphenyl (4-phenylthiophenyl) sulfonium (50 wt.% solid in propylene carbonate) (Figure 2e). Figure 2f shows the photolytic cleavage of triarylsulfonium salts [8], giving rise to protons as well as radicals. All the monomers and PIs were used as received.
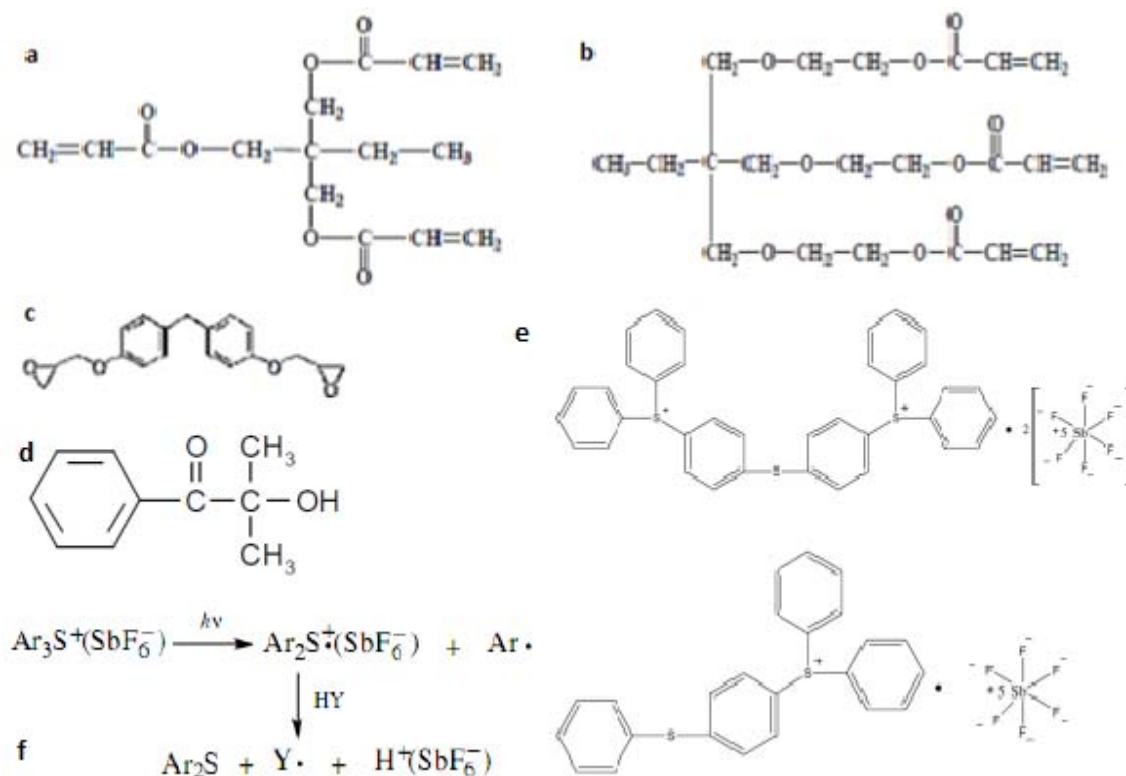
Figure 2 : Chemical structure of monomers and photoinitiators(a-e): (a) Trimethylolpropane triacrylate (TMPTA). (b) Trimethylolpropane tri(ethyleneoxide) acrylate (TMPT(EO)A). (c) Epolam® 5015 (Bisphenol-F-epichlorhydrine). (d) Darocur® 1173 (2-hydroxy-2-methyl-1-phenyl-propan-1-one). (e) Cyracure® UVI-6976, consisting a mixture of dihexafluoroantimonate of S,S,S',S',-tetraphenylthiobis (4,1-phenyllene) disulfonium and hexafluoroantimonate of diphenyl (4-phenylthiophenyl) sulfonium (50wt% solid in propylene carbonate). (f) Photolytic cleavage of triarylsulfonium salts [1]

2.2 Differential Photo Calorimetry (DPC)

Kinetic parameters of the monomers used and the resultant interpenetrating network (IPN) had been obtained using TA Instrument 912, MDSC 2920 Model Differential Photo Calorimeter. A high pressure mercury lamp emitting light of wavelength range 285-440 nm and an intensity of 30 mW/cm^2 was used throughout the entire study.

Aluminium standard pans were used for all thermal studies. The reference pan was filled with resin and fully cured for 20 min under UV exposure. The sample pans were filled with resin weighing 2.0 ± 0.1 mg with PET film covering the sample.

The samples underwent 1 min of isothermal conditioning, 5 min of UV exposure and finally 1 min of isothermal conditioning. The isothermal UV exposure was carried out at 30, 40, 50, 60 and 70 ^{o}C.

2.3 Kinetic Model and Calculations

TA Advantage Specialty Specialty Lib software was employed to perform kinetic calculation based on Sestak and Berggren equation [2, 4-5] :

$$R_p = \left(\frac{d\alpha}{dt}\right)_{t,T} = k(T)a^m(1-a)^n[-ln(1-a)]^p \tag{1}$$

where : α = degree of conversion; k is the rate coefficient; m, n and p are the order of initiation, propagation and termination respectively.

Assuming the termination reaction begins significantly later after the initiation of UV exposure, p was taken as 0 when the autocatalytic model was used [2, 4-6] :

$$R_p = \left(\frac{d\alpha}{dt}\right)_{t,T} = k(T)a^m(1-a)^n \tag{2}$$

The rate of change of conversion could be calculated by Equation 3 and its integral gives Equation 4 [1, 4] :

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_T} \tag{3}$$

$$\alpha_t = \frac{\Delta H_{exp,t}}{\Delta H_T} \tag{4}$$

where: $\frac{d\alpha}{dt}$ = conversion rate; $\frac{dH}{dt}$ or $\Delta H_{exp,t}$ = experimental enthalpy at time t; ΔH_T = theoretical enthalpy; α_t = degree of conversion at time t.

The theoretical enthalpy can be calculated by the below Equation 5 [4] :

$$\Delta H_T = \left(\frac{\Delta H_{Tf}}{M}\right)f \tag{5}$$

where f = functionality of monomer; ΔH_{Tf} = theoretical enthalpy if one reacted functional group (J/mol); M = molar mass of the monomer (g).

The theoretical enthalpy of TMPTA, TMPT(EO)A and Epolam® 5015 are calculated as 813.31 J/g, 562.46 J/g and 605.44 J/g respectively from Equation 5.

Activation energies of the monomer or IPN systems were defined by the Arrhenius equation [3-4, 6] :

$$k = Ae^{-\frac{Ea}{RT}} \tag{6}$$

where: A is the collision factor; Ea is the activation energy of the system (J/mol); R is the ideal gas constant (8.314 J/mol.K); T is temperature (K).

3. **Results and Discussion**

3.1 Monomers

In this section, the effects of changing the PI concentration, temperature and the chemical structure of monomers on the polymerization of the monomers were studied. Figure 3 shows the heat flow-time profile of the three monomers at 30 ˚C. The curing commenced when the UV lamp was activated, as represented by the sharp increase in the heat flow at the first minute. The heat flow profile was sharper and higher for the acrylates (radical mechanism) whereas compared to the epoxides (cationic mechanism) which were lower and broader.
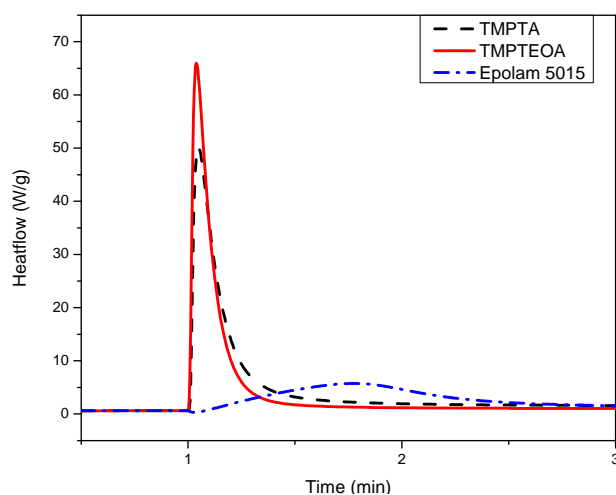

Figure 3 : Heat flow-time profile of TMPTA, TMPT(EO)A and Epolam 5015 at 30 ˚C

3.1.1 Effect of Photoinitiator Concentration on Photopolymerization

In order to find the optimum PI concentration, all three monomers were studied using different PI concentration, ranging from 0.5-5 wt.%. The conversion of the monomers with respect to the different PI concentrations at 30 ⁰C, are shown in Figure 4. The percentage conversion of all monomers increases with PI concentration and reaches a maximum at 3-5 wt.% PI concentration. Additional PI up to 5 wt.% did not raise the percentage conversion significantly. Also, the increase in percentage conversion appears not to improve beyond 80-85 % conversion for TMPTA, 90-95 % for TMPT(EO)A and 55-60 % for Epolam® 5015. Therefore, we established the optimum PI concentration for radical and cationic mechanism at 3 wt.% for further experiments discussed below, at 30 mW/cm² UV intensity. In addition, it is inferred that TMPTA and TMPT(EO)A had a higher percentage conversion, since acrylates are more reactive and less viscous than epoxides, as evident in Figure 3.
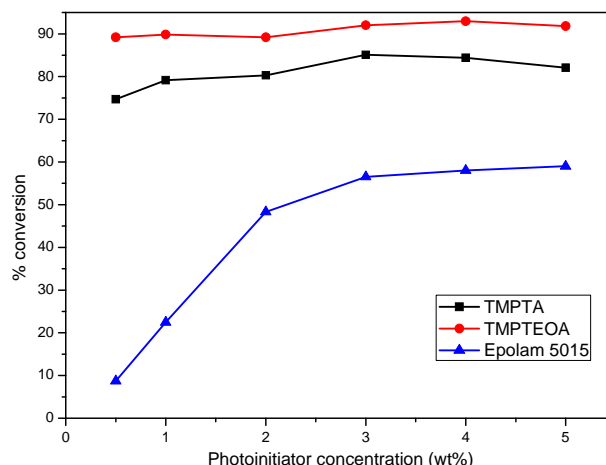
Figure 4 : Percentage conversion-PI concentration curve of the monomers at 30°C

3.1.2 Effect of Temperature on the Kinetics of Photopolymerization

Table 1 represents the kinetics calculated using Equation 2 and 3. (Percentage Resin reacted at peak maximum is abbreviated as RPM; Induction time (in s) is the time required for 1 % monomer conversion; and Peak Maximum is the time (in s) when the peak maximum is reached).

Table 1 : Kinetic analysis results for the photo-curing of TMPTA, TMPT(EO)A by RPI and Epolam® 5015 by CPI in the presence of 3 wt.% PI from 30-70 °C

T(°C)	TMPTA					TMPT(EO)A					Epolam 5015				
	$\Delta H_{exp,T}$ (J/g)	RPM (%)	k (1/min)	induction time	peak max	$\Delta H_{exp,T}$ (J/g)	RPM (%)	k (1/min)	induction time	peak max	$\Delta H_{exp,T}$ (J/g)	RPM (%)	k (1/min)	induction time	peak max
30	481.82	16.2	11.1 +/- 1.7	0.60	4	461.77	17.9	20.1 +/- 3.5	0.67	4	259.47	41.7	1.48 +/- 0.010	5.42	64
40	495.17	16.1	13.3 +/- 2.0	0.80	4	463.69	18.9	21.4 +/- 2.3	0.47	3	308.21	31.0	2.70 +/- 0.021	3.17	32
50	538.50	16.9	13.8 +/- 2.1	0.85	4	468.27	19.2	22.6 +/- 2.5	0.64	4	358.08	28.6	3.84 +/- 0.034	2.58	25
60	536.39	17.1	14.6 +/- 2.2	0.72	4	450.44	18.3	22.8 +/- 2.5	0.53	3	397.09	25.7	4.83 +/- 0.065	2.38	20
70	535.18	17.4	15.0 +/- 2.1	0.72	4	490.11	19.3	25.6 +/- 3.2	0.90	4	428.88	22.0	5.80 +/- 0.13	1.82	15

In general, it is observed that with an increase of operating temperature for curing, both the rate of polymerization and the rate coefficient increased, for each monomer as indicated in Table 1. This is resultant of increased thermal energy with increased temperature, in improvement of the molecular mobility of the reaction species. [4] Also, the $\Delta H_{exp,t}$ of the monomer, resin reacted at RPM and the final percentage conversion increased when the polymerization rate increased. This increase is accompanied by a reduction of induction time and peak maximum. We noted at a higher temperature, the induction time and peak maximum were less significant, as reported in literature. [6] Table 1 also show that TMPT(EO)A had the highest rate coefficient, followed by TMPTA and Epolam® 5015.

The rate of polymerization versus time for TMPTA with variation of temperature from 30-70 °C, was plotted in Figure 5a, indicating an increase in polymerization rate with temperature. Temperature has a larger influence in cationic than radical photopolymerization [4]. This is apparent in Figure 5b for the UV curing of Epolam® 5015, that the percentage conversion increases significantly from 55-90 % from 30-70 °C. The conversion rate increased rapidly when the UV lamp was on but the increase slowed down quickly 1 min later for all monomers.
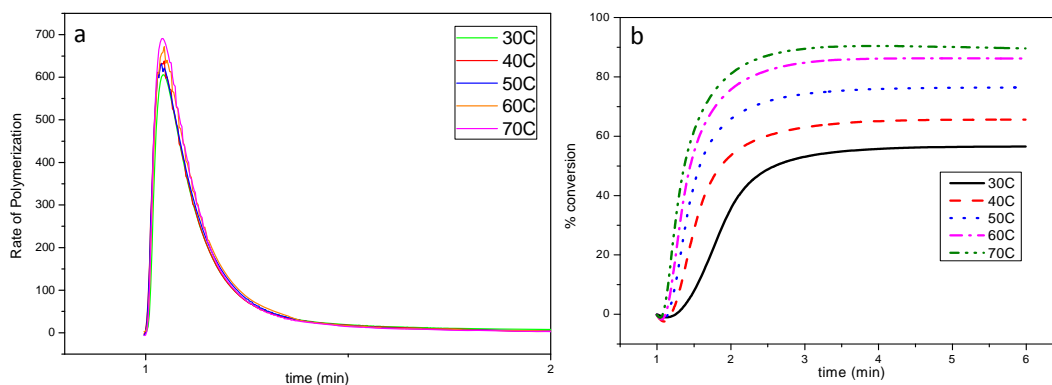

Figure 5 : (a) Rate of polymerization-time curve for TMPTA from 30-70 °C. (b) Percentage conversion of Epolam® 5015 from 30-70 °C

3.1.3 Effect of Chemical Structure of Monomer on Photopolymerization

As compared to TMPTA, TMPT(EO)A is more reactive, which is evident in Figures 3 and 4 and Table 1. This is due to the presence of the oxygen atom in the -O-CH$_2$-CH$_2$- structure linked to each acrylate function which gives the molecular chain in TMPT(EO)A more flexibility and hence higher reactivity [5-6]. This hypothesis is further supported by Figure 6a. In addition, Figure 5a shows that Epolam® 5015 has a much lower polymerization rate and hence lower reactivity than the triacrylates due to the less reactive nature of the glycidyl group.

Ln k versus 1/T graphs of the three monomers were plotted in Figure 6b with their respective activation energies and the collision factors calculated using Equation 5. The data is presented in Table 2 with TMPT(EO)A having the lowest Ea and Epolam® 5015 having the highest Ea. It can then be concluded that TMPT(EO)A is slightly more reactive than TMPTA and polymerizes six times faster than Epolam® 5015.
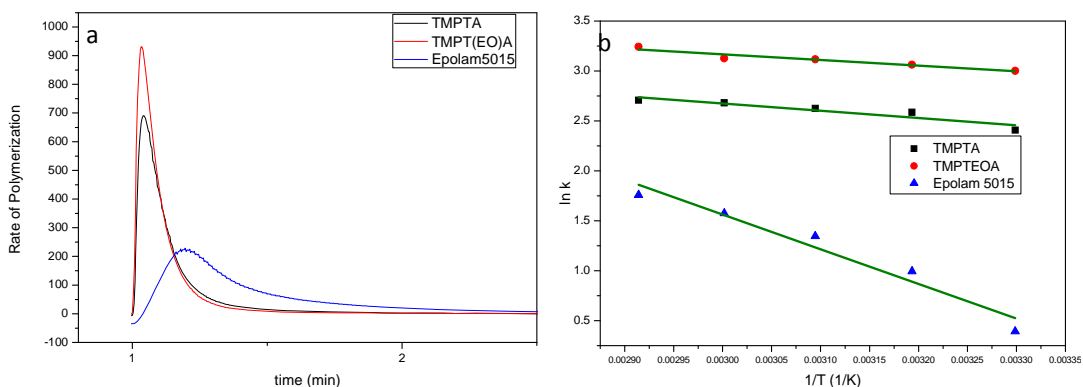
Figure 6 : (a) Rate of polymerization-time curve for the monomers at 70 °C. (b) ln k- 1/T graphs for the monomers from 30-70 °C

Table 2 : Activation energies and the collision factors of the three monomers

Monomer	E_a (kJ/mol)	A
TMPTA	6.09 ± 0.07	130
TMPT(EO)A	4.71 ± 0.05	131
Epolam® 5015 Resin	28.89 ± 0.25	1,606,809

3.2 Interpenetration Network (IPN)

Two different types of IPN systems were created by mixing TMPT(EO)A with Epolam® 5015 and TMPTA with Epolam® 5015. The composition of the different IPNs and their respective theoretical enthalpies are calculated using Equation 5, as shown in Table 3.

Table 3 : Composition of the different IPNs and their respective theoretical enthalpies

	IPN A		IPN B	
Epolam® 5015 (wt.%)	**TMPTA (wt.%)**	**ΔHT (J/g)**	**TMPT(EO)A (wt.%)**	**ΔHT (J/g)**
20	80	771.74	80	571.05
35	65	740.56	65	577.50
50	50	709.38	50	583.95
65	35	678.19	35	590.40
80	20	647.01	20	596.84

3.2.1 Effect of Composition on the Kinetics of Photopolymerization

Figures 7a and 7b illustrates the heat flow-time curve of the two different sets of IPNs. All the heatflow curves shown depict the characteristics of the curing of triacrylates and diepoxide. Each curve can be split into 2 portions : the first, would be the sharp peak near the 1st min contributed by the polymerization of triacrylates; the second would be the broad hump after the sharp triacrylate curing peaks. In comparison to the polymerization of pure triacrylates, the IPN curing peaks were shorter and broadened, with the diepoxide monomers curing together with triacrylate monomers. The broad hump of the diepoxide

monomer had shifted to the left and spread over a shorter period of time, due to the reduced amount of Epolam® 5015 monomers in the IPN formulation.

When the composition ratio of the triacrylates in their respective IPNs were increased, the triacrylate curing peaks are more dominant, with the maximum height increased and became relatively narrower. The broad hump had a reduced presence with decreased proportion of Epolam® 5015 used. On the other hand, as the Epolam® 5015 composition increased, the narrow peak decreased in height and became relatively broader, accompanied by the presence of a shoulder peak. The rate of polymerization for both sets of IPN were the highest when the composition of triacrylates were the highest, since acrylate has a higher reactivity as shown in Figures 7c and 7d.
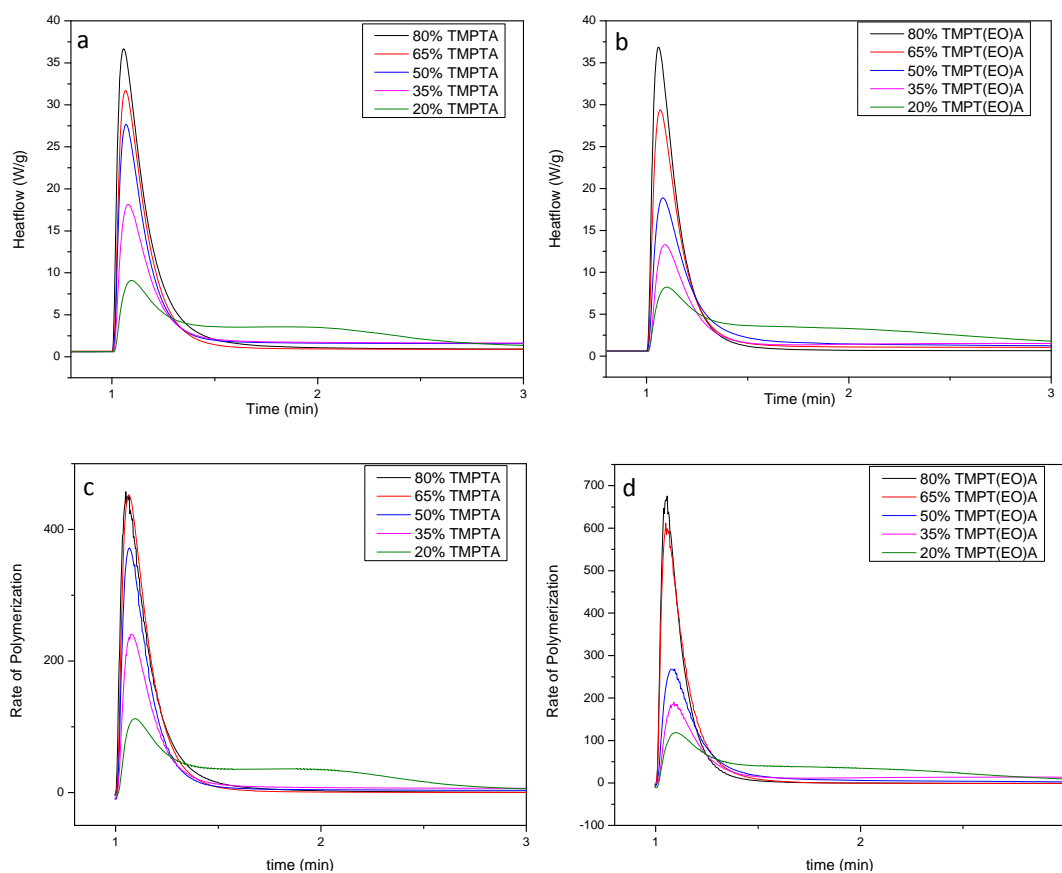

Figure 7: (a & b) Heat flow-time curve of IPN A & B respectively. (c & d) Rate of polymerization of IPN A & B respectively

A decrease in triacrylates composition led to a percentage drop in conversion to a minimum at 35 wt.% TMPTA for IPN A and a 50 wt.% TMPT(EO)A for IPN B as shown in Figures 8. This percentage conversion increases again when the proportion of TMPTA drops from 35-20 wt.%, and 50-20 wt.% for TMPT(EO)A. This suggests that the conversion is better when the triacrylate monomers are higher in proportion over the diepoxides and have an increased proximity to each other at the molecular level. The converse would be true when the diepoxide compositional proportion is higher over the triacrylates.
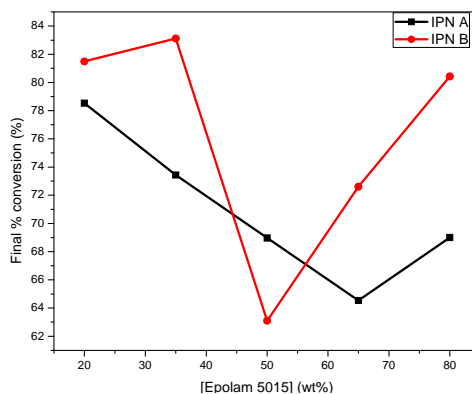
Figure 8 : Final percentage conversion of IPN A & B

3.2.3 Effect of Temperature on the Kinetics of Photopolymerization

The effect of temperature on the IPNs was similar to effect of temperature when the individual monomers were cured independently. For each composition, the kinetic parameters were studied by varying the temperature when the experiment is carried out. Through this, ln k versus 1/T of the ten IPNs are plotted in Figures 9a and 9b. The activation energies of the IPNs in Table 4 were either between or lower than that of the monomers. This implied that the rate coefficient of all IPNs were higher than that of Epolam® 5015. Also, between 35-65 wt.% Epolam® 5015, the rate coefficient is slightly dependent on temperature. This could be a result of larger molecular distance between two epoxy or two acrylate groups when the weight proportions of the monomers were comparable This caused an increase in molecular mobility with the effect of temperature to be less significant in this case.
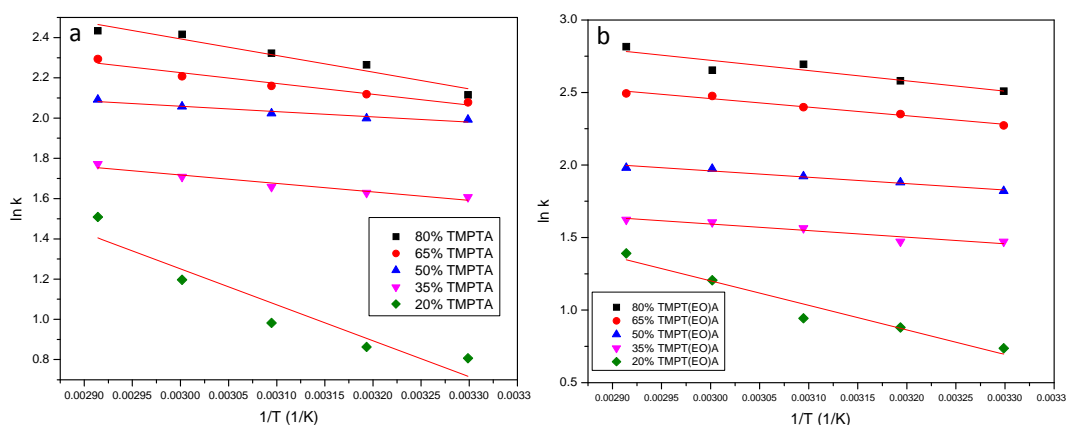

Figure 9 : (a & b) ln k-1/T for IPN A & B respectively from 30-70 $^{\circ}$C

Table 4 : Activation energies and the collision factors of IPN A & B

	IPN A			IPN B		
Epolam® 5015 (wt.%)	**TMPTA (wt.%)**	**Ea (kJ/mol)**	**A**	**TMPT(EO)A (wt.%)**	**Ea (kJ/mol)**	**A**

20	80	6.87 ± 0.55	808	80	5.91 ± 0.50	128
35	65	4.47 ± 0.42	46	65	4.91 ± 0.41	69
50	50	2.19 ± 0.20	17	50	3.63 ± 0.40	26
65	35	3.49 ± 0.32	19	35	3.76 ± 0.29	19
80	20	14.86 ± 0.90	744	20	14.05 ± 0.84	529

4. Conclusion

The photoreactivity and cure kinetics of TMPTA, TMPT(EO)A, Epolam® 5015, IPN A (TMPTA/Epolam® 5015) and IPN B (TMPT(EO)A/Epolam® 5015) were studied with the help of a Differential Photocalorimetry. By using the autocatalytic model, this allowed the quantification of significant parameters such as k, $\Delta H_{exp,t}$, resin RPM, induction time and peak maximum.

We examined the effects of PI concentration, temperature and chemical structure of monomers on the kinetics of polymerisation of the homopolymers. This included the k, $\Delta H_{exp,t}$, resin RPM, induction time, peak maximum, rate of polymerization and the percentage of conversion. It was found that TMPT(EO)A had the highest reaction rate because of its flexible chains and acrylate functional groups. It was further shown that the Ea of TMPT(EO)A was calculated to be the lowest and one sixth that of Epolam® 5015.

The effect of composition and temperature were also studied for 2 sets of IPN systems differing in the use of TMPTA and TMPT(EO)A. The heat flow-time profile of both IPN systems show the initial curing of acrylates (TMPTA and TMPT(EO)A) followed by Epolam® 5015. The rate of conversion was the highest when the composition of the acrylates was at the maximum. For both IPN A and B, the percentage conversion decreased with the proportion of acrylates to a minimum and then increased with the proportion of Epolam® 5015. The effect of temperature on the curing of IPNs was similar of just curing monomers alone. Ea of IPNs was found to be either between or lower than that of the monomers.

Further mechanical tests can be done in future work to quantify the mechanical properties of the above studied IPNs to conclude their suitability for application as coatings on different substrates.

5. Reference

[1] V. Y. Voytekunas-Abadie and F. L. Ng, "Alternative Curing Methods for Structural Epoxy Resins", SIMTech technical reports, Apr-Jun 2010, Vol. 11, No. 2, Pg 53-58.

[2] V. Y. Voytekunas-Abadie, F. L. Ng and X. C. Shan, "Designing of UV Exposure Process in R2R UV Embossing of Microlenses", Proceedings of the 12th Electronics Packaging Technology Conference, December 9-10, 2010, Singapore 2010, Pg 819-824.

[3] V. Y. Voytekunas-Abadie, F. L. Ng, Koh Chai Ling and M. J. M. Abadie, "Kinetic Analysis of UV-curable Epoxy Resins for Micromachining Applications", Advanced Materials Research, 2009, Vol. 74, Pg 299-302.

[4] V. Y. Voytekunas-Abadie, F. L. Ng and M. J. M. Abadie, "Kinetics Study of UV-Initiated Cationic Polymerization of Cycloaliphatic Diepoxide Resins", European Polymer Journal, 2008, Vol. 44, Pg 3640-3649.

[5] M. J. M. Abadie and V. Y. Voytekunas-Abadie, "New Trends in UV Curing", Eurasian Chem Tech Journal, 2004, Vol 6, Pg 67-77.

[6] A. K. Diby, V. Yu. Voytekunas and M. J. M. Abadie, "Kinetic Study of Negative Dry-Film Photoresists", eXPRESS Polymer Letters, 2007, Vol. 1, No. 10, Pg 673-680.

[7] Richard R. Roesler, "An Interpenetrating Polymer Network", RADCURE'86, Baltimore Maryland, September 1986, 8-11, Pg 16-13 – 16-28.

[8] J. V. Crivello, "Cationic Polymerization - Iodonium and Sulfonium Salt Photinitiators", Advances in Polymer Science, 1984, Vol. 62.