Characterization of low-*k* benzocyclobutene dielectric thin film

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Abstract
This paper reports the characterization of a photosensitive benzocyclobutene (BCB), a low dielectric constant spin-on polymer for use as interlayer dielectric in the microelectronics industry. Research work is divided into three main sections. First, BCB thin film characterization was done to investigate the effects of curing conditions on BCB film thickness, dielectric properties, optical properties and extent of cure. Thermal stability of BCB was then evaluated using thermogravimetric analysis (TGA) to detect weight loss during thermal curing and degradation. Finally, curing kinetics study was conducted using both differential scanning calorimetry (DSC) dynamic (American Society for Testing and Materials method) and isothermal approaches.
The first study shows that determination of vitrification point during thermal curing of BCB is crucial to predict film properties. By curing to just before vitrification, lowest refractive index, hence dielectric constant, could be obtained.

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Introduction

The growth of integrated circuit (IC) technology is primarily based on the continued scaling of devices to even smaller dimensions. Smaller devices give higher packing density as well as higher operating speed. In the ultra large scale integration (ULSI) era, the millions, and soon to be billions, of transistors on a chip must be interconnected to give desired functions. As a result, interconnect technology is getting more complicated with each device generation. For advanced logic chips, it is now the interconnect rather than the transistors that is limiting the packing density and operating speed (Peters, 1998; Ting and Seidel, 1995).

As the critical dimensions of ICs continue to shrink, performance and reliability requirements for interconnect systems are becoming more stringent. This has resulted in a need for interlayer dielectric (ILD) with low dielectric constant (k) together with high conductivity metal, to lower the RC (resistance $\times$ capacitance) delay for high performance interconnect.

Low-k dielectrics not only lower line-to-line capacitance, but also reduce cross-talk noise in the interconnect and lower power dissipation; while high conductivity metals reduce resistance. Currently, there exist quite a number of candidates with dielectric constants in the low-k region ($k = 2.5$-3.0). In order to be useful, new low-k dielectric materials must be carefully characterized for their electrical, chemical, thermal and mechanical properties (Ting and Seidel, 1995).

The effectiveness of a non-conductor (dielectric) at storing electrical potential energy under the influence of an electric field is measured in its permittivity or dielectric constant (k). The lowest attainable k is 1.0, that of air. The value of k depends on film chemistry and deposition method. The best low-k dielectrics should perform reliably upon integration with the manufacturing process, exhibiting good thermal stability (up to 425°C), mechanical stability and compatibility with etching, stripping, cleaning and polishing processes (Chiu *et al.*, 2001).

The greatest amount of competition among low-k candidates exists in the $k = 2.5$ arena. Thermal stability, adhesion and mechanical strength of low-k candidates are particularly important. Promising spin-on candidates at $k = 2.5$-2.8 include organic polymers such as divinyl siloxane benzocyclobutene (DVS-BCB), a silicon-based polymer with high organic content and poly(arylene)ethers (PAE), both of which are highly aromatic.

Most spin-on polymers (SOP) are significantly different from spin-on glasses in that moisture is not evolved during curing, and due to superior crack resistance, single layer deposition is usually possible. However, adhesion promoters are usually required to enhance the adhesion between the SOP and underlying film. Factors responsible for polymer properties include the backbone chemical structure, polymer backbone rigidity and mobility, and effects of deposition, curing and annealing. Polymer curing is often performed in an inert environment to prevent the breaking of polymer bonds at high temperatures (Peters, 1998).

Therefore, it is of current research interest to carry out in-depth study of the curing characteristics of low-k spin-on polymeric thin films. In this study, BCB thin films were processed and characterized to better understand the curing kinetics and how different curing conditions affected its properties.

Experimental

Thin film characterisation

Shrinkage and refractive index vs extent of cure study

Film thickness of interlayer dielectric (ILD) is of great importance, as it affects the optical, dielectric, thermal and mechanical properties. In this evaluation, the effect of cure temperature and durations on the shrinkage and refractive index was investigated.

The BCB thin films were prepared by spin coating Dow Chemical Cyclotene™ 4024-40 solution onto 8 inch silicon wafers at a spin speed of 2,500 rpm. The spin-coated wafers were soft baked at 70°C for 90 s. The BCB films were subsequently cured at different temperatures for different durations to study the effects of curing conditions on film properties. The temperatures investigated were 180, 200, 220, 240, 250, 260, 280 and 300°C. Films were held at each temperature for different durations of 15, 30, 45 and 60 min. The recommended cure profile for BCB is curing at 250°C for 60 min. It has been reported that BCB curing is initiated at around 200°C (Chan *et al.*, 2001), and full cure can be achieved in minutes by curing at 300°C (Strandjord *et al.*, 1997).

Figure 1 shows the cure profile used. All curing processes were conducted in nitrogen atmosphere since BCB is susceptible to oxidation at elevated temperature. Both heating and cooling rates were programmed at 10°C/min. Temperature was first ramped from 25 to 150°C, then soaked for 15 min, after which, again ramped up to the desired cure temperature and held for the duration under investigation.

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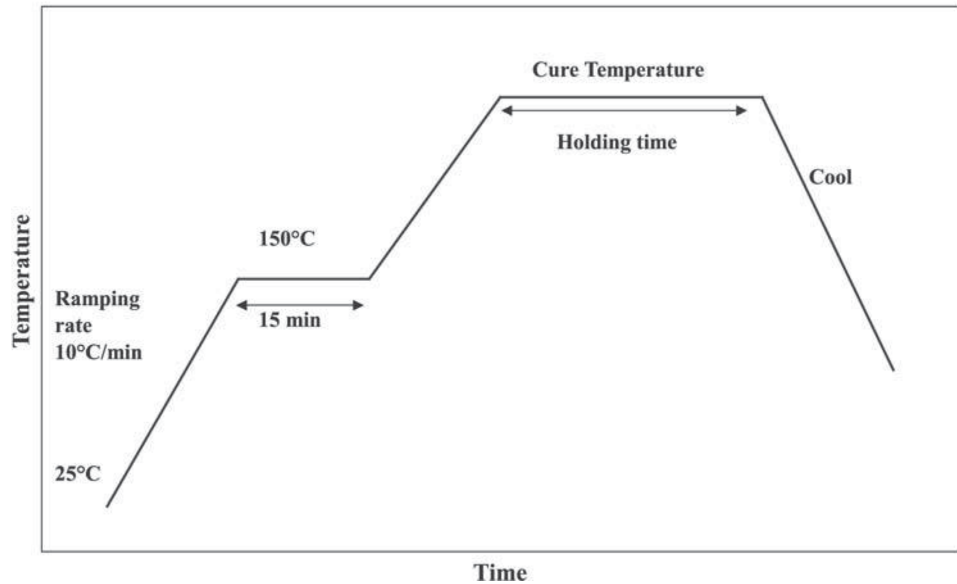
Figure 1
Cure profile for BCB films



Cured films were then cooled to below 150°C before removal from the nitrogen atmosphere.

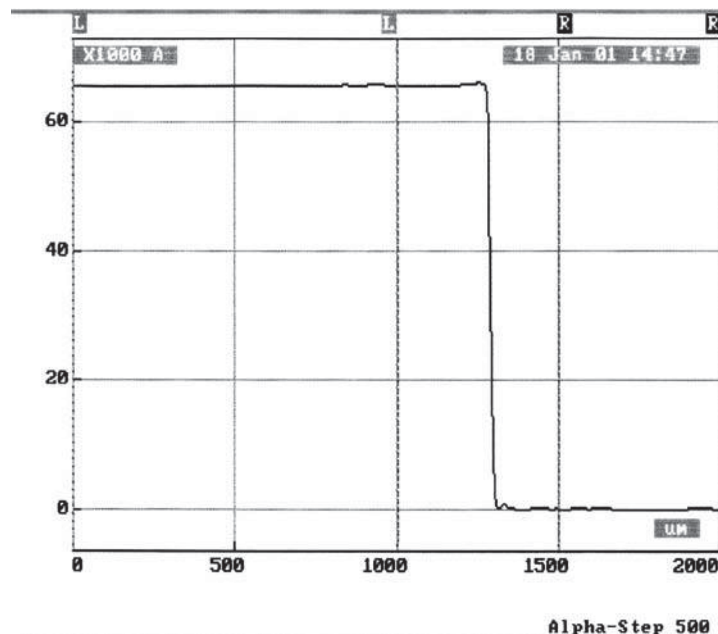
The film thickness measurements were performed on the Alpha Step 500 Surface Profiler, using a scan length of 2,000 μm, scan speed of 200 μm/s and a stylus force between 4.0 and 5.0 mg. The stylus force was controlled at appropriate level to avoid damage to the soft polymeric films.

Prior to measurements, a portion of each film sample had to be scrapped off using a razor blade to create a region of bare silicon wafer without any coating. This region serves as a reference level so that the film thickness can be measured when the stylus scans across the step. A typical scan profile is shown in Figure 2, where the drop in height indicates the film thickness. Film thickness measurements were done both before and after cure on the same sample to monitor changes in thickness due to curing. The difference of the film measurements indicates the shrinkage values. Three readings were taken for each sample, and the average was taken as the film thickness.

Refractive index measurements for cured films were conducted on the Shimadzu UV-Visible Light Recording Spectrophotometer, UV-2501 PC. Measurements were taken within the wavelength range of 500-800 cm^{-1}, using thickness obtained from the surface profiler.

The extent of cure of the BCB thin films was determined using transmission mode Fourier transform infrared (FTIR) spectroscopy. FTIR spectra were recorded in the range

Figure 2
Typical scan profile for thickness measurements



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400-4,000 cm^{-1} at a resolution of 2 cm^{-1}. Each spectrum represents the average of 64 scans. The extent of cure can be estimated by the following equation:

$$\text{Degree of cure} = \frac{100[A(\text{softbake}) - A(985)n]}{A(\text{softbake})} \quad (1)$$

The softbake condition of BCB was assumed to be in 0 per cent cure condition.

$A(1254)$ is the reference peak for normalization (rocking mode of methyl group attached to Si atom), $A(985)$ is the BCB reactant group (out-of-plane bending mode of the vinyl moiety), $A(985)n$ is the ratio of $A(985)/A(1254)$, $A(\text{softbake})$ is the ratio of $A(985)/A(1254)$ at softbake condition.

Cumulative curing time study

The effect of cumulative curing time on the BCB shrinkage and refractive index was further quantified at 220°C. The cumulative curing time study uses the same sample, which is subjected to multiple curing steps at the same cure temperature, with the total cure duration at any step equal to the sum of all previous incremental curing time. By using the same sample throughout, random errors due to inconsistencies between samples could be reduced. The cure temperature chosen was 220°C since the curing rate at this temperature is reasonable, reaching close to 90 per cent degree of cure only after 60 min (from the Results section). Moreover, from the characterization results, this temperature is just below the transition where shrinkage and refractive index started levelling off. Below 220°C, curing rate is too slow and may be too time consuming to achieve a reasonable degree of cure. At 240°C and higher temperatures, curing rate is too fast for any significant change to be detected. The total cure duration planned was 150 min with the incremental times shown in Table I. This duration is more than twice that for previous work done where films were cured to a maximum of 60 min. The longer cure duration was proposed in the hope of detecting a certain trend of film properties with an increase in curing time.

After each curing step, thin film characterization was carried out through film thickness measurements, refractive index measurements and extent of cure analysis as done previously.

Thermal stability evaluation

A low dielectric material is of no use if it has a low thermal stability temperature. Thermal stability evaluation was investigated with thermogravimetric analysis (TGA). The model of TGA used was TA Instruments 2950. TGA provides the measurement of minute changes in sample mass during thermal curing. This helps to detect any outgassing during cure and determine the degradation temperature of BCB.

Soft baked BCB film sample was scrapped off from the silicon wafer using a razor blade. Care was taken to avoid scrapping silicon off together with the BCB sample. A sample size close to 15 mg was collected. Since the sample was very light and may get blown into the TGA chamber during run, it was pressed into pellet form before run. TGA study was conducted by ramping at 10-600°C/min in nitrogen atmosphere.

Curing kinetics study

Curing kinetics study was investigated with differential scanning calorimetry (DSC). The model of DSC was TA Instruments 2010. Both dynamic (ASTM E698 method) and isothermal heating experiments were conducted. In all runs, the DSC cell was purged with nitrogen gas.

Samples for curing kinetics study were obtained from soft baked BCB film samples by scrapping the film off the silicon substrate using a razor blade. Samples of size more than 5 mg were collected and sealed using DSC normal aluminium pans. It is important that the weight of each DSC sample is determined accurately.

For dynamic heating experiments, DSC runs were conducted by ramping from 30 to 375°C at different ramping rates of 2.5, 5, 7.5 and 10°C/min.

For isothermal experiments, the DSC cell was first heated to the desired temperature using the "initial temperature" program segment. The cell was then rapidly opened, the sample loaded and the cell closed. When the temperature was within 4°C of the desired temperature, data collection was initiated. The temperatures investigated were 180, 200, 220, 240, 250, 260, 280 and 300°C, similar to that for thin film characterization. All isothermal runs were done for 60 min. Subsequently after each run, the DSC cell was cooled down and the same sample ramped at 10°C/min from 30 to 375°C to investigate the residual cure of the sample after isothermal curing. The degrees of cure predicted by these two methods and that from FTIR were then compared.

Results and discussions

Thin film characterisation

Shrinkage and refractive index vs extent of cure study

Results obtained showed that before cure, film thickness was between 7.1 and 7.6 μm. After cure, shrinkage was observed for all cure profiles, with thickness decreasing to between 6.5 and 7.0 μm. For both cases, standard deviations of less than 0.07 μm were observed. This indicates good thickness uniformity for the BCB films.

Shrinkage observed after cure ranged from 4.5 to 11.2 per cent. Figure 3 shows the trend of percentage shrinkage with curing condition. Generally, shrinkage decreased with cure temperature. However, above 240°C, shrinkage did not decrease much with cure temperature. Not much correlation could be seen with curing time.

The results suggest that curing at high temperatures produce thicker films. Assuming that the lateral dimension of BCB film is restricted by the Si substrate, the film thickness change is directly related to change in film volume and density. Therefore, high temperature curing gives less dense BCB films, associated with more free volume.

Refractive indices obtained over the different curing conditions ranged from 1.61 to 1.68, approximately 4 per cent difference. Figure 4 shows the refractive index of cured BCB films as a function of curing condition. As with percentage shrinkage observed, refractive index also showed a general decreasing trend with cure temperature, and started to level off above 240°C. Little correlation could be seen with curing time.

Therefore, higher cure temperatures produce BCB films with lower refractive index. Since the dielectric constant, k is approximately square of refractive index at optical frequencies (Siew *et al.*, 2000), this suggests that lower k value can be obtained by curing at higher temperatures.

Results also indicate that changes in refractive index followed the same trend as that of percentage shrinkage with curing condition. This is so since refractive index is related to dielectric constant, which is in turn related to film volume and density. With increased film volume or decreased density at higher temperatures, both percentage shrinkage and refractive index will drop. In both cases, cure temperature is a more significant process parameter compared to curing time.

The random crosslinking process due to faster reaction rate could explain this increase in free volume at higher cure temperatures. At high temperatures, crosslinking occurs too rapidly, leading to non-selective reactions between the reactive sites on the monomers. This prevents the formation of a big network structure. Instead, many small clusters of oligomers form with dangling bonds left behind. For crosslinking to continue, these dangling bonds have to

Table I
Incremental times for cumulative curing time study

Cure duration (min)	0	10	20	30	45	65	95	150
Incremental time (min)	–	10	10	10	15	20	30	55

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Figure 3
Percentage shrinkage as a function of curing condition

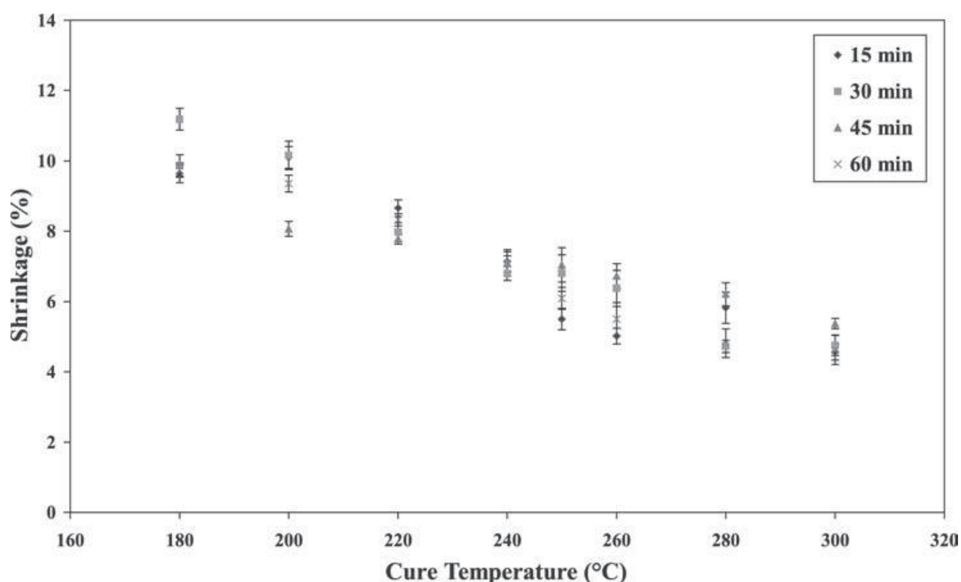
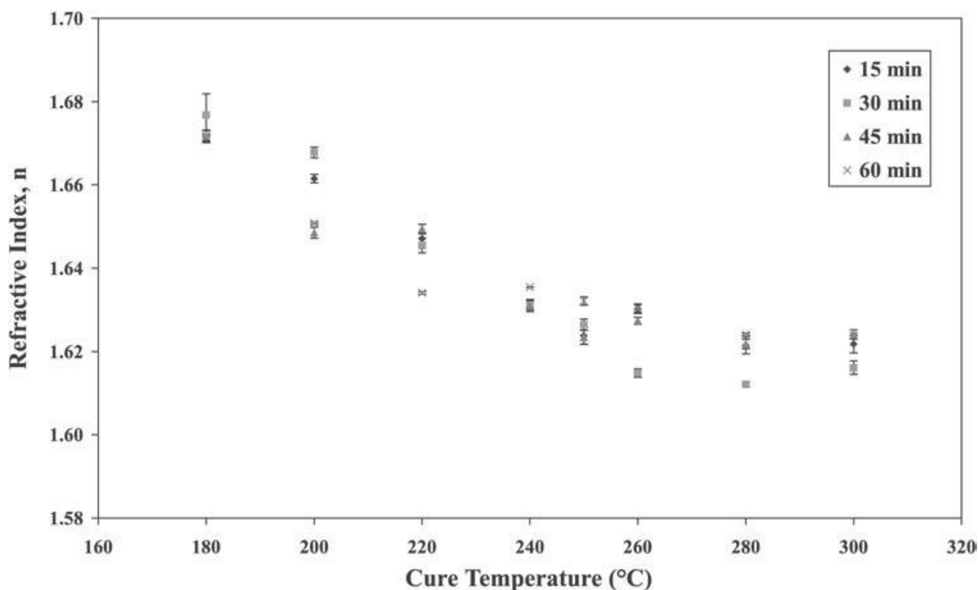


Figure 4
Refractive Index as a function of curing condition



be aligned to react. Hence, rotation of bonds within each cluster causes free volume to increase.

Results from both percentage shrinkage and refractive index measurements showed a certain amount of deviations with curing time. This could be attributed to random errors due to inconsistencies from sample to sample. Special effort had been taken to reduce these errors by using samples from the same wafer, and determining shrinkage by measuring film thickness on the same sample before and after cure. However, uniformity between samples cannot be guaranteed as each sample is from different parts of the wafer. Another possible reason is that the curing time investigated is too short to detect any trend.

On the degree of cure on the BCB thin films, several changes could be observed from FTIR spectra obtained before and after thermal curing of BCB. The few peaks that are related to the extent of cure occur at wavelengths of 1,498, 1,472, 1,194 and 985 cm^{-1}. The peak at 1,498 cm^{-1} is associated with the vibration of the tetrahydronapthalene polymerization product being formed, and grow with increase extent of cure. The amplitude of the 1,472 cm^{-1} peak is associated with the ring-bending mode of the BCB reactant group being consumed. The 1,194 cm^{-1} peak is associated with vibration of the BCB reactant group and the 985 cm^{-1} peak represents the out-of-plane bending mode of the vinyl moiety. All these three peaks are associated with the reactant group, hence get depleted with curing. By quantifying the growth or depletion of these peaks, the extent of cure can be determined. A strong absorption at 1,254 cm^{-1} associated with the rocking mode of the methyl groups attached to the silicon atoms can be used for normalization since these bonds are nearly unaffected by the polymerization (Dow, 1995; Stokich *et al.*, 1991).

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It has been reported that all FTIR transmission measurements for BCB should be done at Brewster's angle to eliminate interference fringes. These interference fringes can obscure low intensity peaks in the spectrum and affect quantitative analysis of peak area (Dow, 1995). Figure 5 shows the typical spectra obtained at normal incidence and at Brewster's angle.

However, our lab does not have the Brewster's angle accessories. Hence, FTIR could only be done at normal incidence. Peaks at 1,498, 1,472 and 1,194 cm^{-1} were difficult to quantify due to interference fringes present nearby. Even by increasing the number of scans to more than 200, not much improvement in the spectra could be seen. Therefore, the extent of cure was analysed by following the depletion of the 985 cm^{-1} peak as shown in Figure 6.

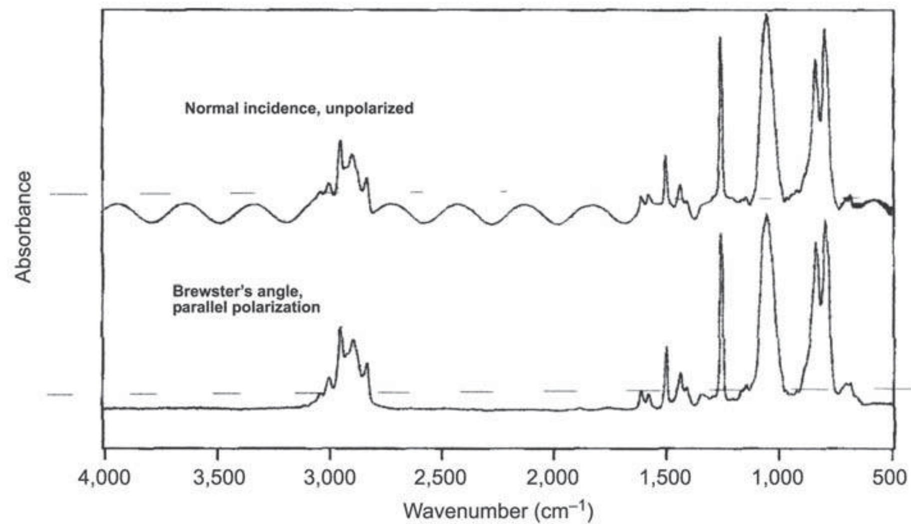
Figure 7 shows the degree of cure as a function of curing condition. Results show that degree of cure increases with both cure temperature and duration. Similar to percentage shrinkage and refractive index results, degree of cure started to level off above 240°C.

At cure temperatures of 180 and 200°C, less than 60 per cent degree of cure was achieved even after 60 min. Curing at 220°C for 15-60 min gave degrees of cure ranging from 68 to 87 per cent. Degree of cure more than 90 per cent was attained within 15 min with cure temperatures above 240°C. Hence all films cured above 240°C were vitrified.

Cumulative curing time study

Figure 8 shows the change in film thickness with cure duration. As reported previously, shrinkage was observed

Figure 5
FTIR Spectra obtained at normal incidence and at Brewster's angle



Source: Dow (1995)

Figure 6
FTIR spectra showing depletion of 985 cm^{-1} peak with curing

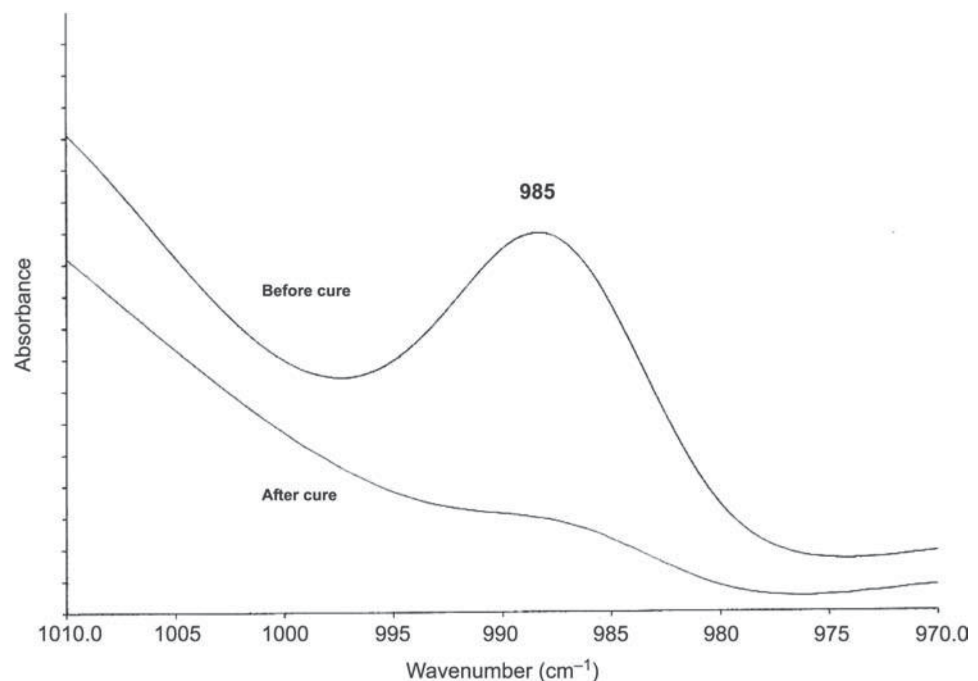


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Figure 7
Degree of cure as a function of curing condition

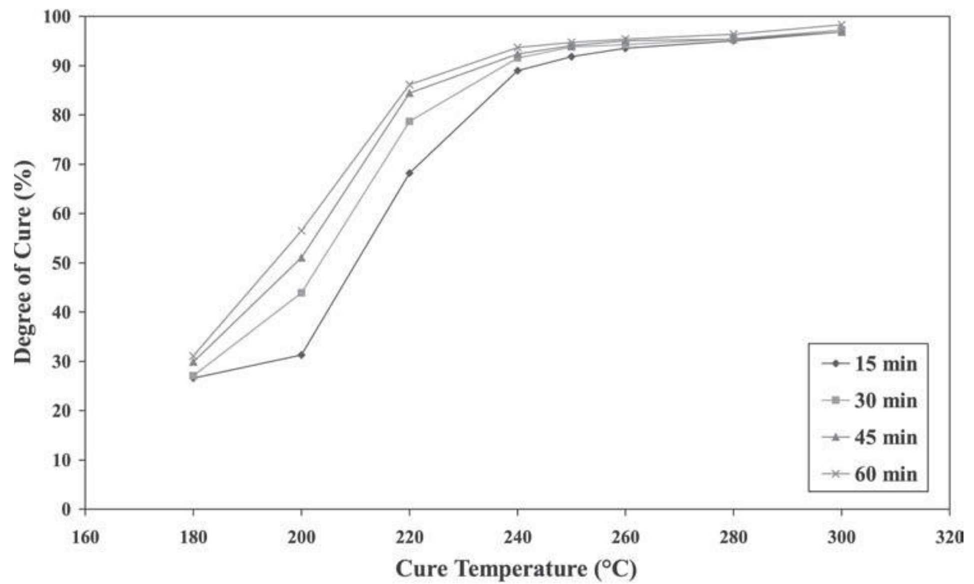
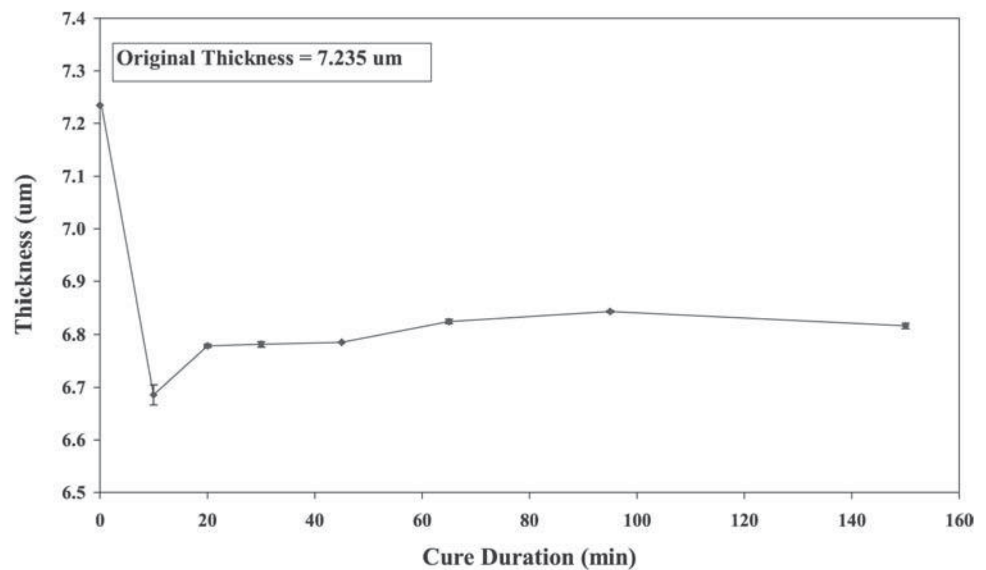


Figure 8
Film thickness for cumulative curing time study



regardless of curing conditions. However, an interesting trend observed here was that the BCB film actually expanded after the initial shrinkage until 95 min, where it started shrinking again.

Figure 9 shows percentage shrinkage with cure duration. After the initial shrinkage, an expansion of close to 2 per cent was detected. Minimum shrinkage of 5.4 per cent was observed at cure duration of 95 min. As expected from percentage shrinkage results, refractive index results also showed a minimum at 95 min, seen in Figure 10. This minimum refractive index suggests a minimum *k* value.

The degree of cure as a function of cure duration is shown in Figure 11. Degree of cure increased with cure duration, but the rate of increase started slowing down significantly close to 95 min. The degree of cure obtained at 95 min was 89.27 per cent, which coincides with the vitrification point as reported for BCB polymerization reaction (Stokich *et al.*, 1991). The gel point (30 per cent cure) was reached within the first 10 min, indicating that an extended network starts to exist.

Results obtained from cumulative curing time study showed that BCB film initially shrank upon curing. This is due to densification of the film with crosslinking. A minor part may be because of evaporation of residual solvent and other volatiles present in the film. Subsequently, an expansion of 2 per cent was detected, implying an increase in film volume and drop in film density. This could be due to the formation of the network structure as crosslinking proceeds.

With higher degree of cure at longer curing time, remaining dangling bonds in the structure tend to be separated further apart. For further crosslinking, a greater amount of bond rotation has to take place to align these dangling bonds. This creates more free volume in the film.

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Figure 9
Percentage shrinkage for cumulative curing time study

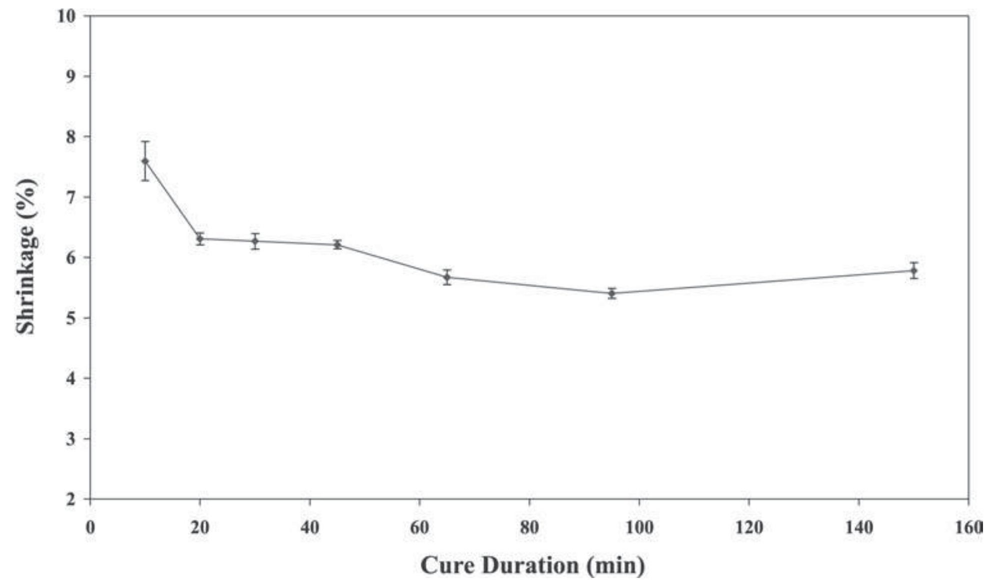
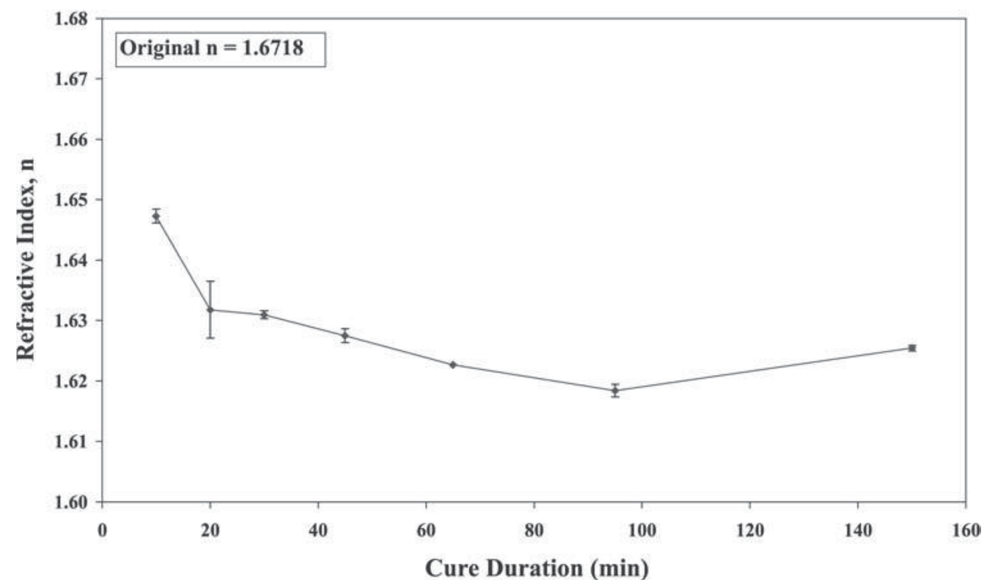


Figure 10
Refractive index for cumulative curing time study



Hence, shrinkage and refractive index dropped with curing time. However, at 95 min, or at the vitrification point (corresponding to 90 per cent degree of cure) (Stokich *et al.*, 1991), the material becomes glassy, and there is a physical collapse of the network structure, leading to decreased free volume. Therefore, both shrinkage and refractive index started to increase after this point.

These observations could be applied to previous thin film characterization done for different curing conditions. At cure temperatures above 240°C, 90 per cent degree of cure was attained within 15 min. Hence, all the samples cured above 240°C were vitrified. Before vitrification occurs, formation of the network structure causes increase in free volume. In addition to this, a higher cure temperature increases reaction rate, leading to the formation of a less dense network due to random crosslinking. Therefore, both shrinkage and refractive index dropped rapidly with temperature before 240°C. After vitrification, the physical collapse of the network due to the glass transition means a denser network structure formed. However, since there is free volume increase associated with higher cure temperatures, shrinkage and refractive index still fall with temperature, but occur to a smaller extent.

Therefore, determination of vitrification point is crucial for curing characterization of BCB film. To achieve lowest *k*, BCB film should be cured to just before vitrification. However, industrial applications usually require fully cured films for mechanical integrity and stability. Therefore, considering cure temperatures above 250°C where BCB films showed more than 95 per cent degree of cure, film properties investigated did not show significant change with curing conditions.

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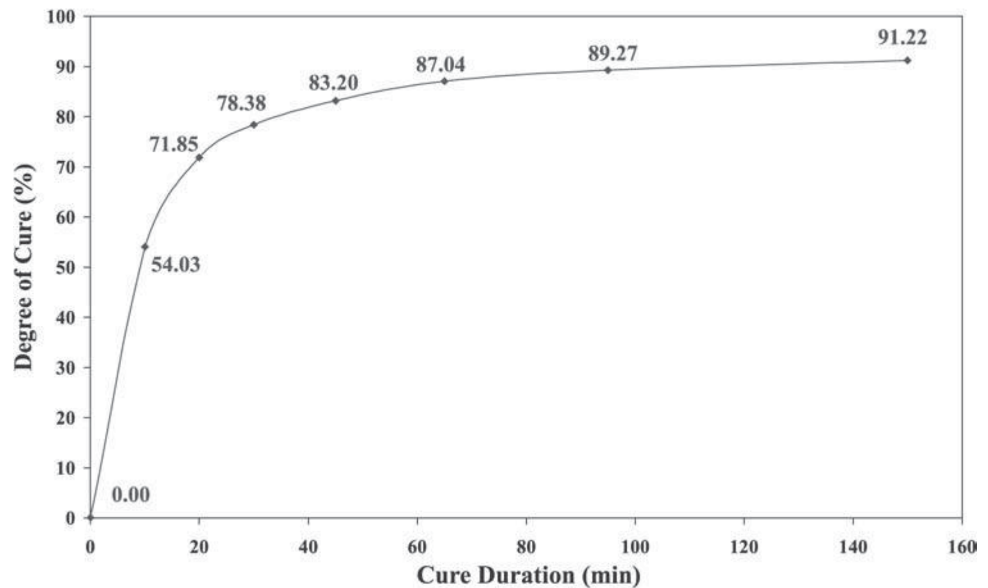
Figure 11
Degree of cure for cumulative curing time study



Thermal stability evaluation

Figure 12 shows the TGA spectrum obtained for soft baked BCB sample. Four peaks could be observed from the derivative weight loss plots. Table II summarizes the details of the peaks.

From TGA results, close to 6 per cent weight loss was detected up to 350°C. These include the decomposition of the light-sensitive component, 2,6-bis {(4-azidophenyl)methyl}-4-ethylcyclohexanone, which has been reported to start decomposing when heated above 60°C. Evaporation of residual solvent (mesitylene) was observed close to its boiling point of 162°C. The third peak could be due to decomposition of the antioxidant (polymerized 1,2-dihydro-2,2,4-trimethylquinoline) added in the formulation (Dow, 1998, 1999). The onset of degradation for BCB was found to be between 380 and 420°C. This is against what was reported in literature which states no weight loss occurring below 400°C (Johnson *et al.*, 1990). Therefore, the thermal stability of BCB may limit its implementation in IC processing where thermal stability greater than 400°C is required, especially for aluminium and tungsten metallization processes (Chiu *et al.*, 2001; Mills *et al.*, 1997).

Curing kinetics study

Dynamic approach

DSC scans obtained from the multiple heating rate runs were analysed to determine the peak temperatures. Figure 13

Figure 12
TGA spectrum obtained for soft baked BCB sample

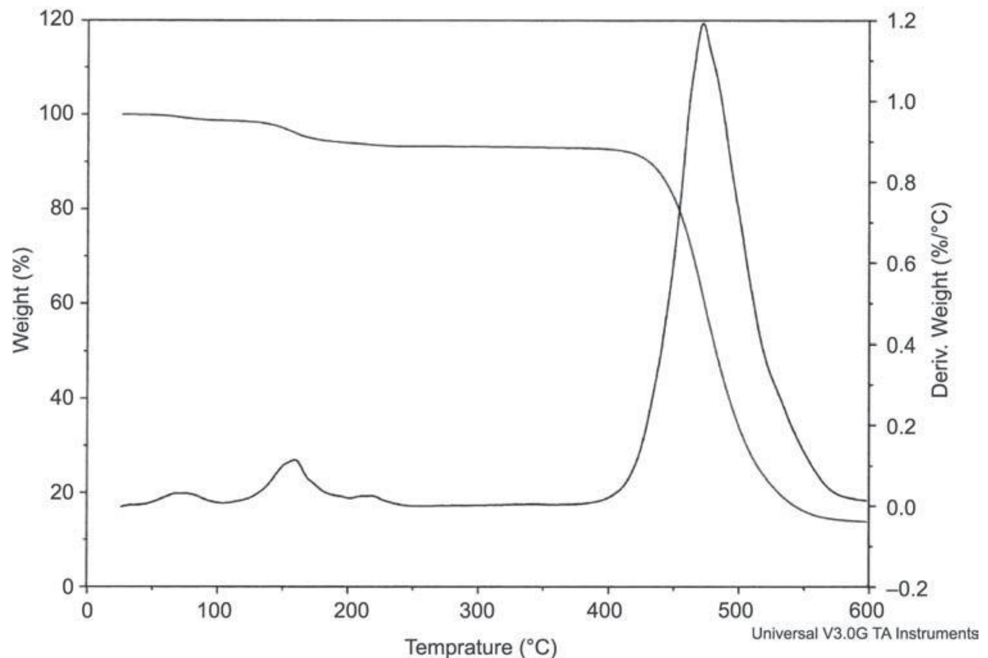


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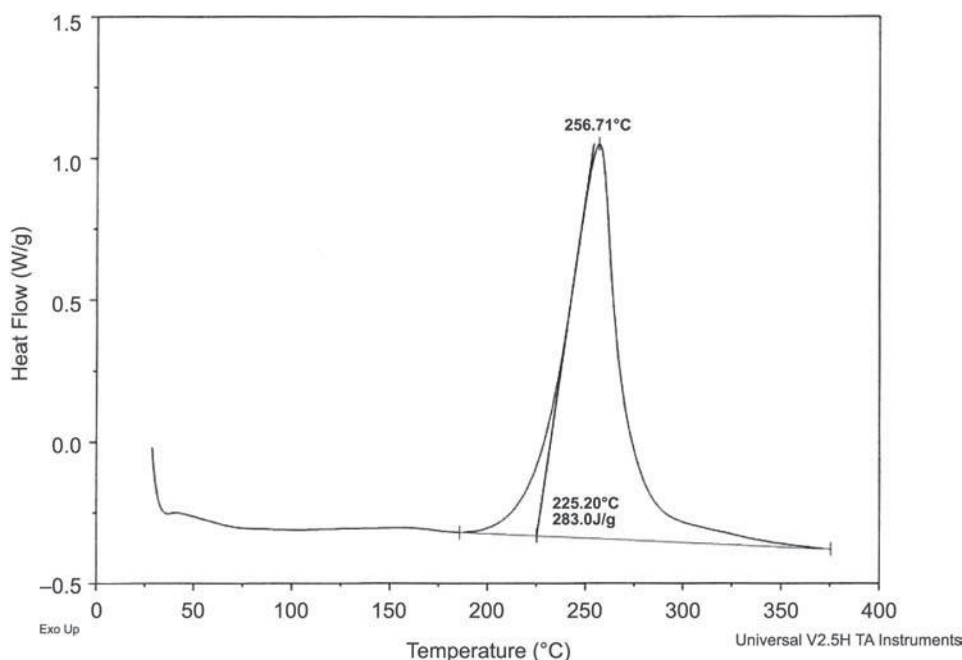
Table II
Details of weight loss from TGA spectrum

Peak	Event	Onset point (°C)	Peak temperature (°C)	End point (°C)	Per cent change
1	Decomposition of light-sensitive component	41.18	73.53	104.41	1.67
2	Solvent evaporation	104.54	160.29	197.06	3.71
3	Possibly decomposition of antioxidant	202.94	222.06	244.12	0.77
4	Decomposition of BCB	382.35	482.35	594.12	76.92

Figure 13
Typical plot from DSC dynamic scan



shows a typical plot from DSC dynamic scan. From the exotherm, both peak temperature (T_p) and heat of reaction (ΔH) can be obtained. Table III shows the results obtained from ASTM E698 method.

From these results, the natural logarithm of the heating rate (°C/min) was plotted against 1,000/T_p (K^{-1}) to obtain Figure 14. The plot shows that all the data points fit into a straight line. Hence, assumptions that the reaction is of first order and follows Arrhenius behaviour are valid. These had also been reported in literature (Stokich *et al.*, 1991).

The activation energy (E_a) can be calculated from the expression (Ozawa, 1970):

$$\frac{d \ln \phi}{d\left(\frac{1}{T}\right)} = -\frac{E_a}{R} \tag{2}$$

$$\text{Slope} = -17.566$$

$$\frac{E_a}{R} = 17.566$$

$$E_a = 17.566 \times 8.314\,\text{kJ/mol}$$

$$E_a = 146.0\,\text{kJ/mol}$$

where ϕ is the heating rate (°C/min), T is the absolute temperature, R is the gas constant and E_a is the activation energy.

The activation energy obtained in this study is quite close to the reported value of 36.0 ± 0.9 kcal/mol or 150.7 kJ/mol from real-time FTIR reaction kinetics study (Stokich *et al.*, 1991). Hence, degree of cure predicted by both FTIR and DSC methods should give close correlation. This also indicates that thin film characterization could be coupled with bulk sample thermal analysis techniques in thermal curing study of BCB.

Isothermal approach

DSC scans from the isothermal runs were analysed to determine the partial heats and hence the degree of cure (α) with different holding time was calculated from equation (3) below (Chen *et al.*, 1997):

$$\alpha = \left(\frac{\Delta H}{\Delta H_0}\right) \times 100 \text{ per cent} \tag{3}$$

Figure 15 shows a typical plot obtained from DSC isothermal scan. The partial heat of reaction at a particular time (ΔH) can be obtained from the integral of the exotherm. The total heat of reaction (ΔH_0) was determined from the average value taken from the multiple heating rate runs done previously, as shown in Table IV.

Figure 16 shows the time dependence of degree of cure at various cure temperatures. Cure degree of 90 per cent could be obtained in less than 15 min by isothermal curing at 240°C and higher temperatures. This tally with results obtained from FTIR analysis for film samples. Degree of cure attained after 60 min isothermal curing increased with higher cure temperature, with a maximum of 93.5 per cent obtained for 300°C.

From Figure 16, as cure temperature increases from 180 to 260°C, the point at which curing rate starts to slow down occurs at higher degree of cure and in a shorter time.

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Table III
Results obtained from ASTM E698 method

Heating rates (°C/min)	ln (heating rate in °C/min)	Peak temperature, T_p (°C)	T_p (K)	1,000/T_p (K^{-1})
2.5	0.916	235.44	508.44	1.967
5	1.609	246.81	519.81	1.924
7.5	2.015	252.30	525.3	1.904
10	2.303	256.71	529.71	1.888

Figure 14
Plot obtained from ASTM method

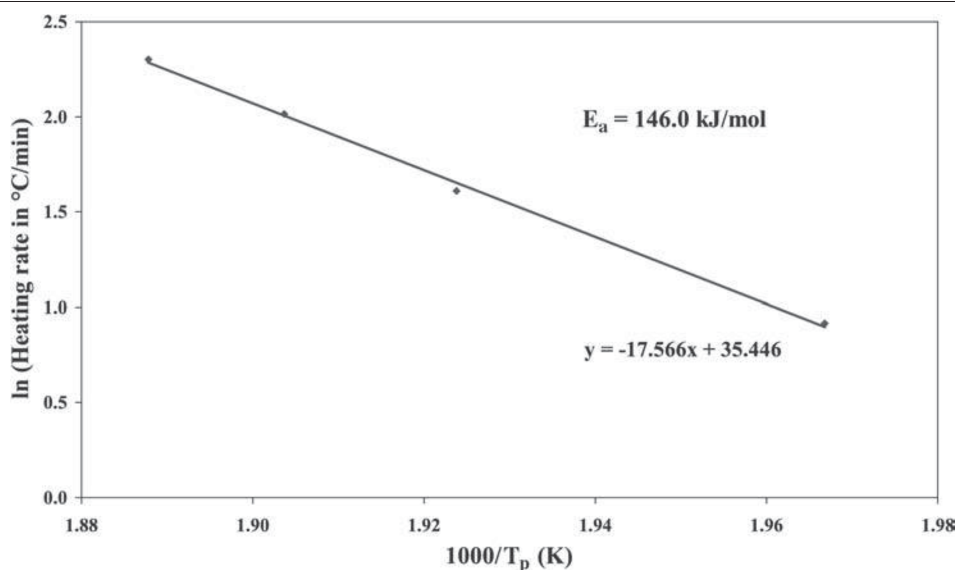
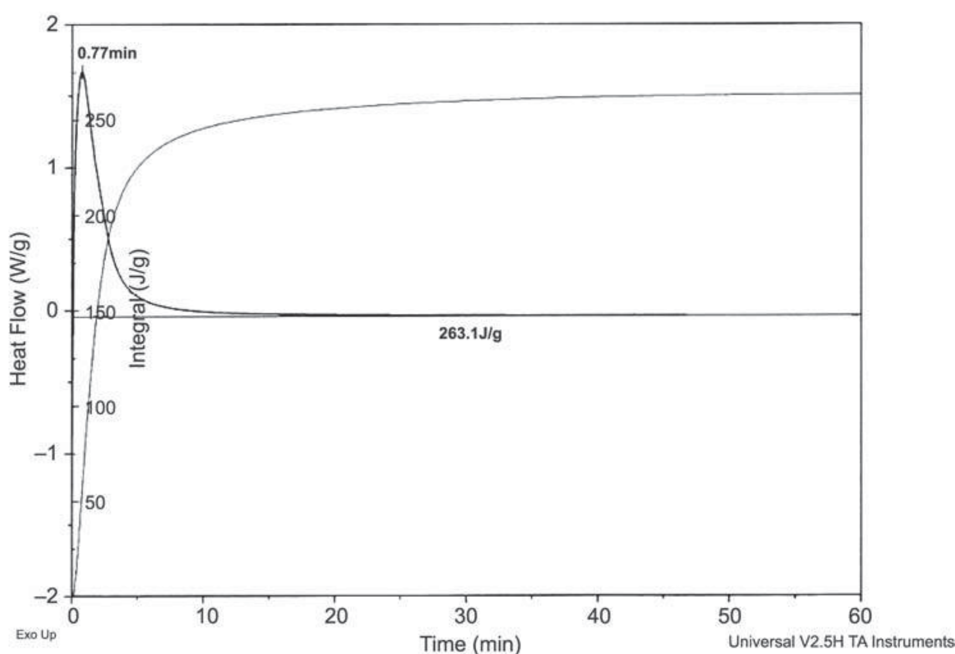


Figure 15
Typical plot from DSC isothermal scan



However, at 280 and 300°C, the rate starts to slow down at lower extent of cure. This could be due to clustering effects at very high temperatures, where initial reactions occur too rapidly. Many small clusters start to form in a very short time as a result of the non-selective, random crosslinking. Many dangling bonds were thus left in the structure. As mobility dropped due to the clustering effects, reaction rate starts to slow down at a lower extent of cure. Therefore, curing at 260°C may enable a reasonable high degree of cure to be achieved in the shortest time.

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Degree of cure predicted from thermal and FTIR approaches

Comparison was made between the degree of cure obtained from thermal approaches (isothermal after 1 h, and residual heat obtained after isothermal curing) and FTIR approach. Figure 17 shows the degree of cure obtained by these three methods.

Table IV
Determination of ΔH_0 for isothermal curing kinetics

Heating rates (°C/min)	ΔH (J/g)
2.5	305.3
5	292.1
7.5	284.9
10	283.0
ΔH_0 (J/g)	291.3

Results show good correlation for cure temperatures above 220°C. Overall, isothermal approach predicts lower degree of cure compared to the other two methods. This could be due to difficulty in collecting data from the initial stage of the reaction. Data collections for isothermal scans were initiated only when temperature was within 4°C of the desired holding temperature. Therefore, some amount of heat from initial reaction during ramp up to the desired temperature may be unrecorded, leading to a recorded value lower than the actual heat of reaction. This error is very much observed at 200°C, where isothermal approach predicted only 16 per cent degree of cure, but predictions from residual heat and FTIR approach are 41 and 56 per cent, respectively. This error could be due to delayed initiation of data collection for the isothermal scan at 200°C.

At 180°C, FTIR gave a much higher degree of cure prediction compared to both thermal methods. This could be

Figure 16
Time dependence of degree of cure from DSC curing kinetics

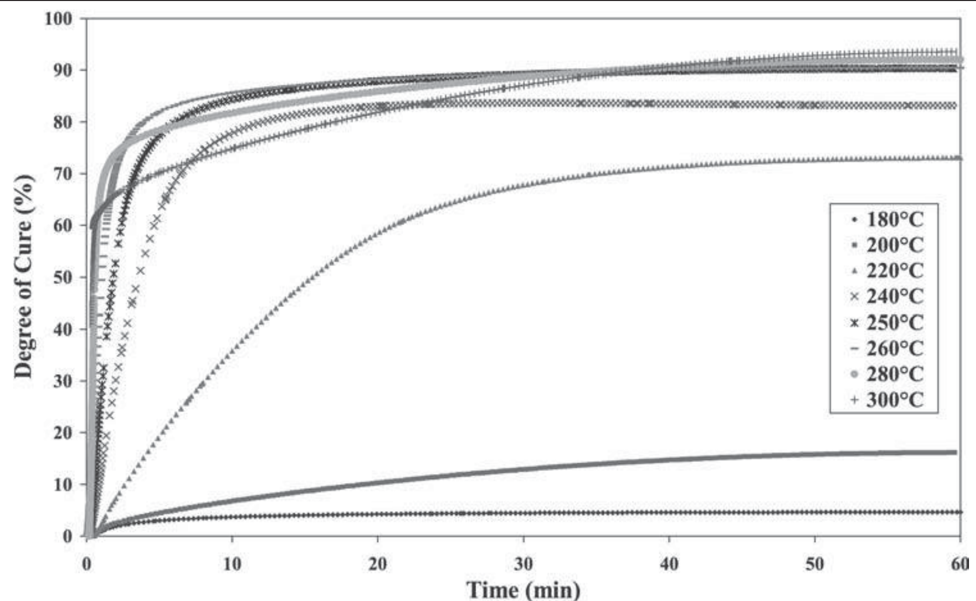
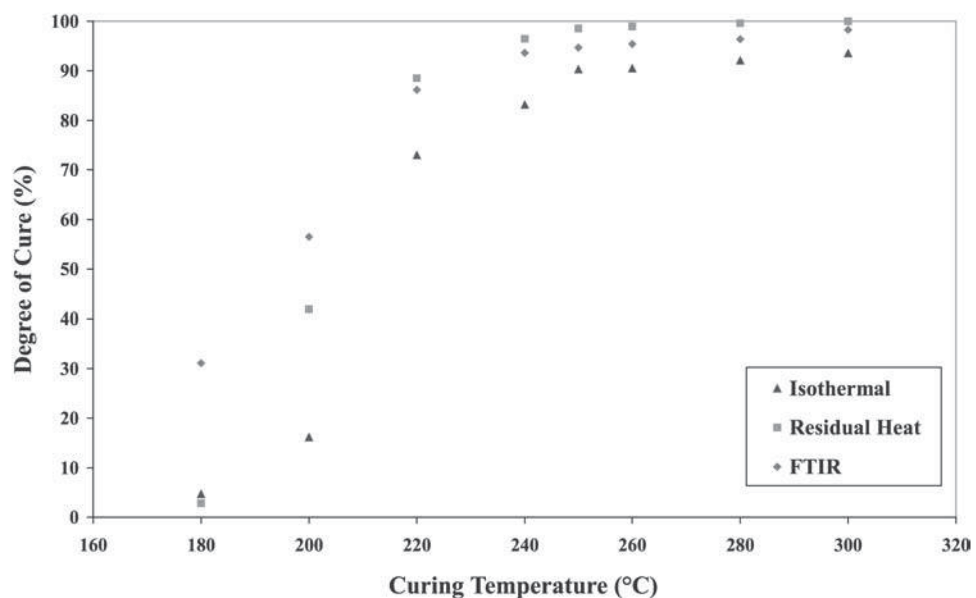


Figure 17
Comparison of results obtained from thermal and FTIR approaches



because heat of reaction at 180°C is too small to be fully detected by the DSC. Another reason could be some errors when calculating the peak areas in FTIR spectrum, due to interference fringes present.

Nevertheless, at high temperatures, all three methods gave rather close predictions. This again suggests that both thin film and bulk sample characterizations could be used in BCB thermal curing study.

Conclusions

The effects of curing conditions on film properties such as film thickness, refractive index and degree of cure were investigated. From results obtained, shrinkage was observed after all curing conditions. All three properties investigated showed a strong dependence on cure temperature. Both shrinkage and refractive index decreased with cure temperatures, but started to level off above 240°C. Degree of cure increased with both cure temperature and time, and also started to level off above 240°C. A cumulative curing time study was conducted on the same sample at 220°C for a total of 150 min. Results showed that the BCB film initially shrank upon curing. Subsequently, an expansion of 2 per cent was observed up to a degree of cure equal to the vitrification point (90 per cent cure). This increasing free volume also caused refractive index to drop with curing time. However, upon vitrification, the film started shrinking again, leading to increased refractive index.

Similarly, with increasing curing time, degree of cure and hence amount of crosslinking increases. However, upon vitrification (90 per cent degree of cure), the material undergoes a glass transition, which is accompanied with a physical collapse of the network structure. Therefore, free volume decreases, leading to increase in shrinkage and refractive index after vitrification point.

Determination of vitrification point during thermal curing of BCB is crucial to predict the final film properties. By curing to just before vitrification, lowest refractive index, hence dielectric constant could be obtained.

In the BCB thermal stability study, bulk sample was used for TGA run by ramping to 600°C in nitrogen atmosphere. From the derivative weight loss plot obtained, four peaks were observed, which included evaporation of residual solvent, and decomposition of the light-sensitive component, antioxidant, and BCB itself. Weight loss of 6 per cent was detected till 350°C, and the degradation onset of BCB was found to be between 380 and 420°C. This contradicts what was reported in literature, which claims no weight loss for BCB up to 400°C.

The last study was on curing kinetics using DSC. Both ASTM and isothermal methods were used. From ASTM dynamic approach, the activation energy was calculated to be 146.0 kJ/mol, close to reported value of 150.7 kJ/mol from real-time FTIR reaction kinetics study. Hence, degree of cure predicted by both FTIR and DSC methods should give close correlation.

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