Solid-State ^{13}C-NMR Study on Bismaleimide/Diamine Polymerization: Structure, Control of Particle Size, and Mechanical Properties

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ABSTRACT: Bismaleimide polymers (BMI) are known for their good thermal stability and are used in a temperature range of 200–250°C, but they are brittle. New generations of BMIs with added comonomers or elastomers are less fragile. During the polymerization, the main reactions involved are the Michael's reaction (addition of a BMI with an aromatic diamine) and the ene reaction. Because the chemical structure of the network is dependent on the temperature, the reaction kinetics as a function of the thermal cycles of processing are compared using solid-phase ^{13}C-NMR. The morphology of the two-phase structure and the mechanical properties (K_{IC}) are also studied. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 2379–2388, 2000

Key words: ^{13}C-NMR; bismaleimide; polymerization kinetics; morphology; mechanical properties

INTRODUCTION

Thermostable polymers are widely used in aeronautics. For such applications, some components are expected to maintain their properties in high temperature environments up to 250°C for short periods of time. The requirements of space technology and other industrial applications like equipment thermal protection stimulated the development of several classes of polymers that withstand high temperatures or even fire.[1,2]

The commercial success of bismaleimide polymers (BMIs) is due to the fact that the basic products (maleic anhydride and aromatic diamines) are inexpensive and easily chemically synthesized. Moreover, these resins, which exhibit excellent physical properties at high temperatures and in wet environments, have dielectrical properties over a broad temperature range and have good fire resistance.[3,4] They do not show good impact resistance, but this can be optimized by adding an elastomer without reducing the thermal stability of the system.

Considerable effort has gone into improving the processing of these composites, for example, with hot melt preimpregnation, filament winding, and resin transfer molding.[5,6] The choice of processing depends on the molecular weight of the resin and the chemical structure of the polymerizable reactive end-capped functions. BMI resins are chemical species with low molecular weight, including monomers and difunctional prepolymers. Reactive terminal functions may undergo a homo- or/and copolymerization by a thermal, catalytic, or irradiative mode.
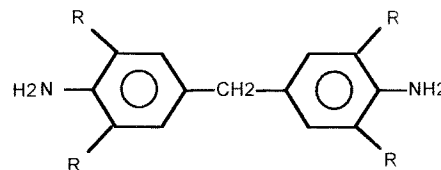
In homopolymerization the obtained material offers excellent thermal stability but poor toughness due to a high crosslinking density. To increase the network flexibility, a comonomer, generally of the aromatic diamine type, is added and it reacts on the reactive functions of the BMI, according to Michael's addition reaction.[7]
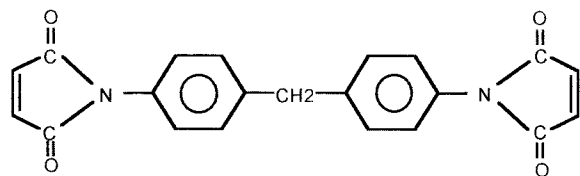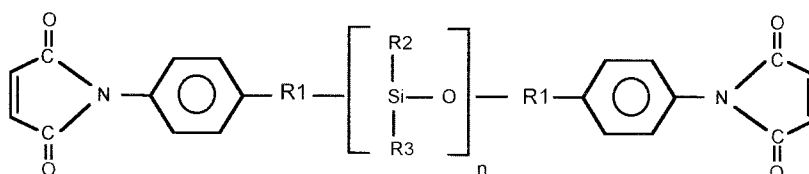
BISMALEIMIDE

TETRASUBSTITUTED AROMATIC DIAMINE

MALEIMIDE TERMINATED SILOXANE ELASTOMER

Scheme 1   The structures of the main monomers of K736.

The homo- and copolymerization of the BMI/aromatic diamine systems are in competition and depend on the reactivity of the diamine, the stoichiometry of the mixture, and the reaction temperature.

For aeronautical applications, SNECMA Corporation manufactures structural components made with reinforced carbon or glass BMI prepregs. During the cure cycle, autoclave processing leads to the formation of temperature heterogeneities because of the large size and fitness of the components.

In this work we studied the temperature effect on the chemical structure, the thermal and mechanical properties, and the morphology of the crosslinked material. We know that the crosslinking density of the polymer is a function of the thermal conditions during the polymerization.

EXPERIMENTAL

Materials

The BMI resin used in this study was Kerimid 736 (K736) furnished by Cemota Co. This resin includes a BMI monomer modified with a tetrasubstituted aromatic diamine and combined with a maleimide terminated siloxane elastomer.

The chemical structures of the three monomers are shown in Scheme 1.

Monomer Polymerization

Six polymerization thermal cycles were studied. For cycles I–IV the temperature of the first stage was varied, while for cycles V and VI (based on cycle I) the temperature scanning rates were varied from 0.5 to 1°C/min. These cycles are described schematically in Figure 1.

Instrumentation

The ^{13}C solid-state [cross polarization magic angle spinning (CP/MAS)] NMR spectra were recorded on a Bruker MSL-200 spectrometer at 50.32 MHz resonance for ^{13}C.

CP/MAS ^{13}C-NMR spectra were obtained at room temperature by using hydrogen–carbon contact times of 3 ms with the hydrogen 90° pulse length equaling 4.1 μs. The cured samples were crushed into a powder under liquid nitrogen before being introduced into the spectrometer. The high power decoupling during acquisition was a 0.015 s acquisition time, and the recycle delay was 5 s.

The toughness of the samples was evaluated on an Instron 1121 tensile testing machine. The values (K_{IC}) were obtained by a test on a compact tension specimen as described by the Afnor A03 180 specification. The crossbeam rate of displacement setting was 0.1 mm/min. Thermomechanical analyses (TMA) were performed on a Perkin–Elmer TGS2 type apparatus with an expansion probe and a high temperature furnace. The temperature scanning rate was 10°C/min.

RESULTS AND DISCUSSION

Generally, the BMIs modified by aromatic amines react mainly according to two processes,[8-11]

Cycle I

Cycle II

Cycle III

Cycle IV
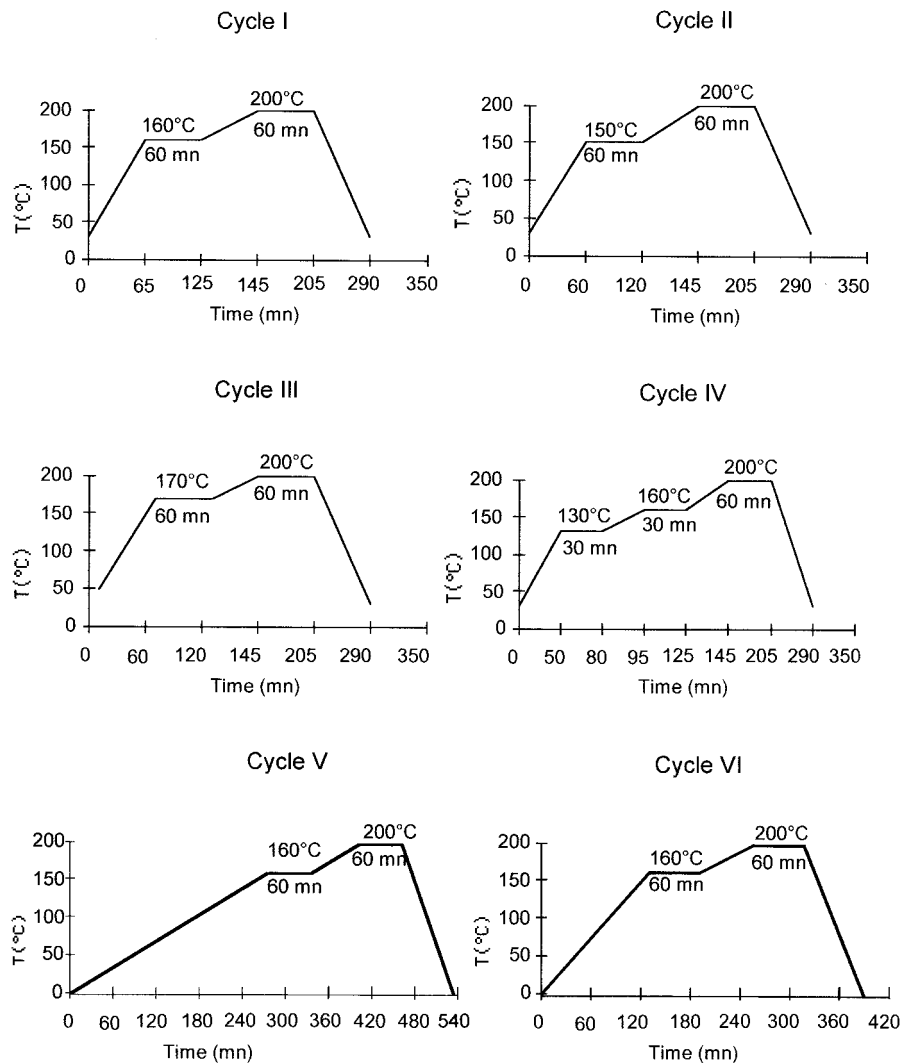
Cycle V

Cycle VI

Figure 1 The K736 polymerization cycles.

which are shown in Figure 2: chain extension, as described by Michael's reaction, and network formation by homopolymerization. The chemical changes during the curing process were studied by ^{13}C solid-state NMR analysis (Fig. 3).

Quantitative determination of the progress of the cure reactions was obtained by measuring the relative areas between the reactant and product resonance in the carbonyl area. The different types of carbonyl detected are shown in Figure 4. The chemical shifts of the different carbonyls were 174 and 177 ppm for Michael's reaction, 175 ppm for the crosslinking reaction, and 169 ppm for the residual BMI double bonds. For the BMI/aromatic diamine system it was possible to detect on the deconvoluted ^{13}C-NMR spectra at 166 ppm a third reaction that was determined as an aminolysis chemical reaction.[12]

During crosslinking, the evolutions of the Michael's reaction and ene reaction were monitored. The ratio between these reactions and the ratio of unreacted maleimide double bonds are plotted in Figure 5.[13,14]

During the beginning of the cure cycle, we noted that the chain extension caused by diamine addition on the maleimide double bond was greater than the homopolymerization reaction. At the end of the first stage the Michael's reaction rate stabilized while the ene reaction increased quickly, except for cycle VI.

Michael's Reaction

In order to observe the temperature effect on the network structure, we compared the rates corre-
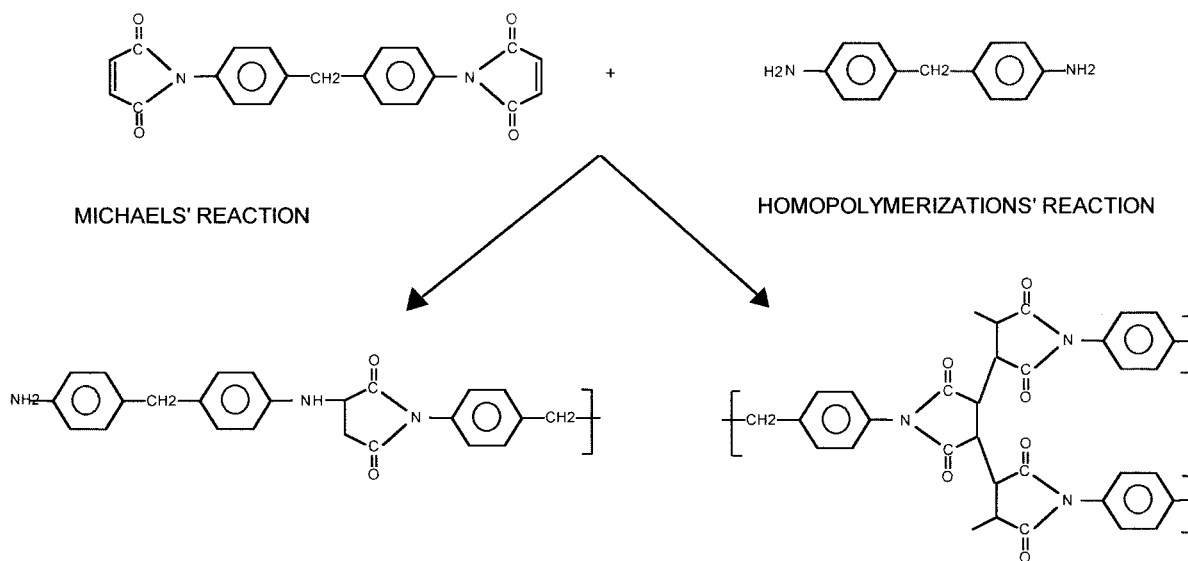
Figure 2 Michael's reaction and homopolymerization.

sponding to the Michael's reaction between each cycle (Fig. 6).

We note that cycle III (with a 170°C first stage) exhibited a maximum Michael's reaction rate of about 41% while that of cycle II (stage at 150°C) was 28%. The difference between these two process cycles reached 13%. As for cycle IV, which contained an additional stage at 130°C, this led to a material with a chain extension of 32%.

The values observed in cycle V (0.5°C/min) showed a Michael's reaction rate close to that of cycle I. As soon as the first temperature stage was reached (160°C), the rate progression stabilized until the end of the polymerization cycle. For cycle VI it seemed that the thermal gradient (1°C/min) affected the chain extension rate: a difference of 15% was found between the end of the first temperature stage and the end of the second.

According to this data, it is important to emphasize the difference in the chain extension reaction rate between the temperature stage at 150°C and the one at 170°C. In other words, depending on the stage temperature, more or less "free" aromatic diamine will remain in the network. It may be thought that 10% of the unreacted diamine may affect some characteristics of the material, especially the mechanical properties, the hydrophilic properties, or the thermal stability of the crosslinked material.

Homopolymerization Reaction

As shown in Figure 7, which is the evolution of the ene reaction for each cycle, there is a little

variation of the homopolymerization reaction of the maleimide functions in the first part of the cure cycles (from 0 to 125 min).

Cycle II (150°C stage) exhibited the highest homopolymerization rate of 55%. This was in agreement with the low Michael's reaction rate that gave a larger amount of free potentially polymerizable maleimide function. Cycle III (170°C stage), which was characterized by a higher Michael's reaction rate, led to a material with a lower homopolymerization proportion (38%). The results of cycle IV fit between cycles II and III and showed an ene reaction rate of 47% at the end of polymerization. The ene reaction ratio of cycle V was rather low (35%), which can be explained by the high Michael's reaction rate. Cycle VI exhibited an intermediate variation with 45% homopolymerization at the end of the cycle.

If we now consider the amount of maleimide function that had not reacted at the end of each cycle, we see that the results were not widely spread and the ratio varied between 8 and 11%.

In examining the aminolysis we saw that it was relatively unimportant (about 10%) and remained roughly constant all through the cycle, whatever the cycle considered.

Resin Morphology

The reaction kinetics analysis by ^{13}C-NMR showed the temperature influence on the chemical structure of the network. Thus, the next step of this work was to know if the K736 two-phase
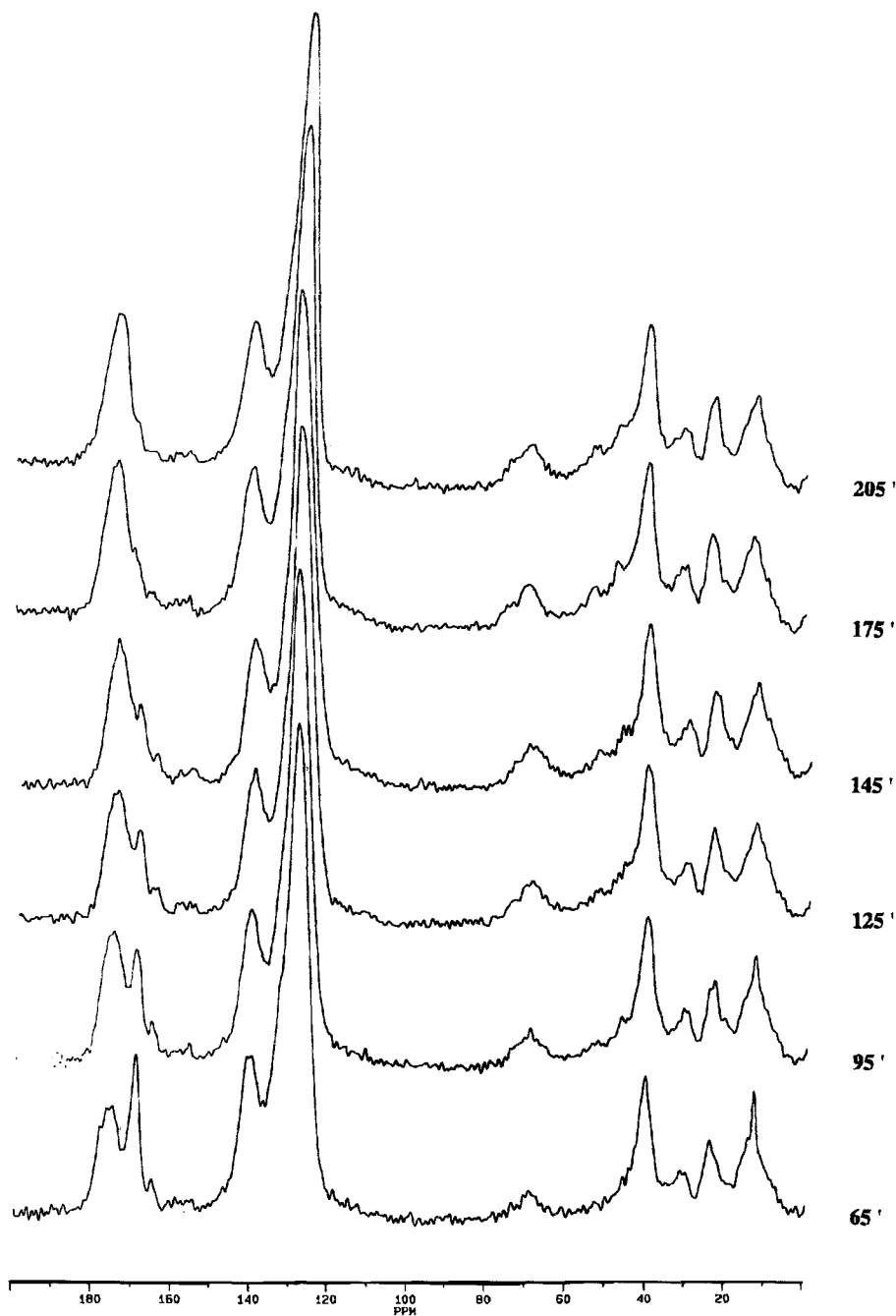
Figure 3 The polymerization evolution of K736 cured during cycle I by ^{13}C solid-state NMR.

morphology (i.e., the nodule size and distribution) was modified by the temperature of the processing cycle.[15,16]

Figure 8 gives scanning electron microscopy (SEM) photographs of a sample that was polymerized according to cycles I and IV.

The two-phase structure of the crosslinked material IV was not very different from that obtained from cycle I. The nodule distribution was homogeneous, and their sizes were similar. For the other cycles the SEM showed no evidence of important changes in the morphology.

We studied the nodule formation between 130 and 160°C. The nodule formation observed by SEM started at 140°C and their size ranged between 1 and 2 μm (Table I).
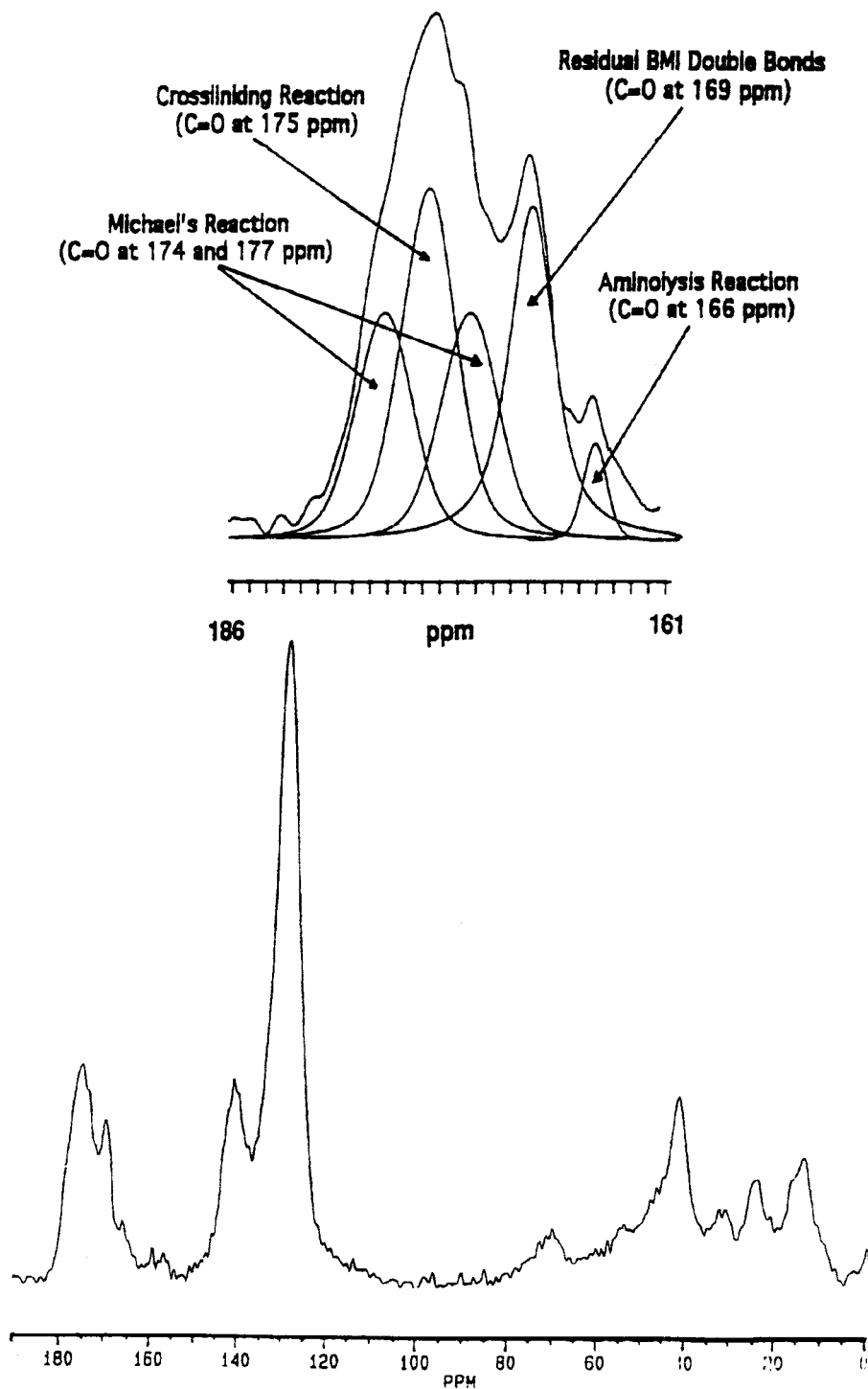
Figure 4 Typical solid-state ^{13}C-NMR spectra of the K736 resin during the cure cycle. The upper section shows the extension of the deconvoluated carbonyl zone.

Once 150°C was reached, the nodules became larger and the size was more homogeneous. The dispersion occurred in a narrower window of 2–2.5 μm. At 160°C the two-phase structure ex-

amined by SEM showed little difference from the structure observed at 150°C.

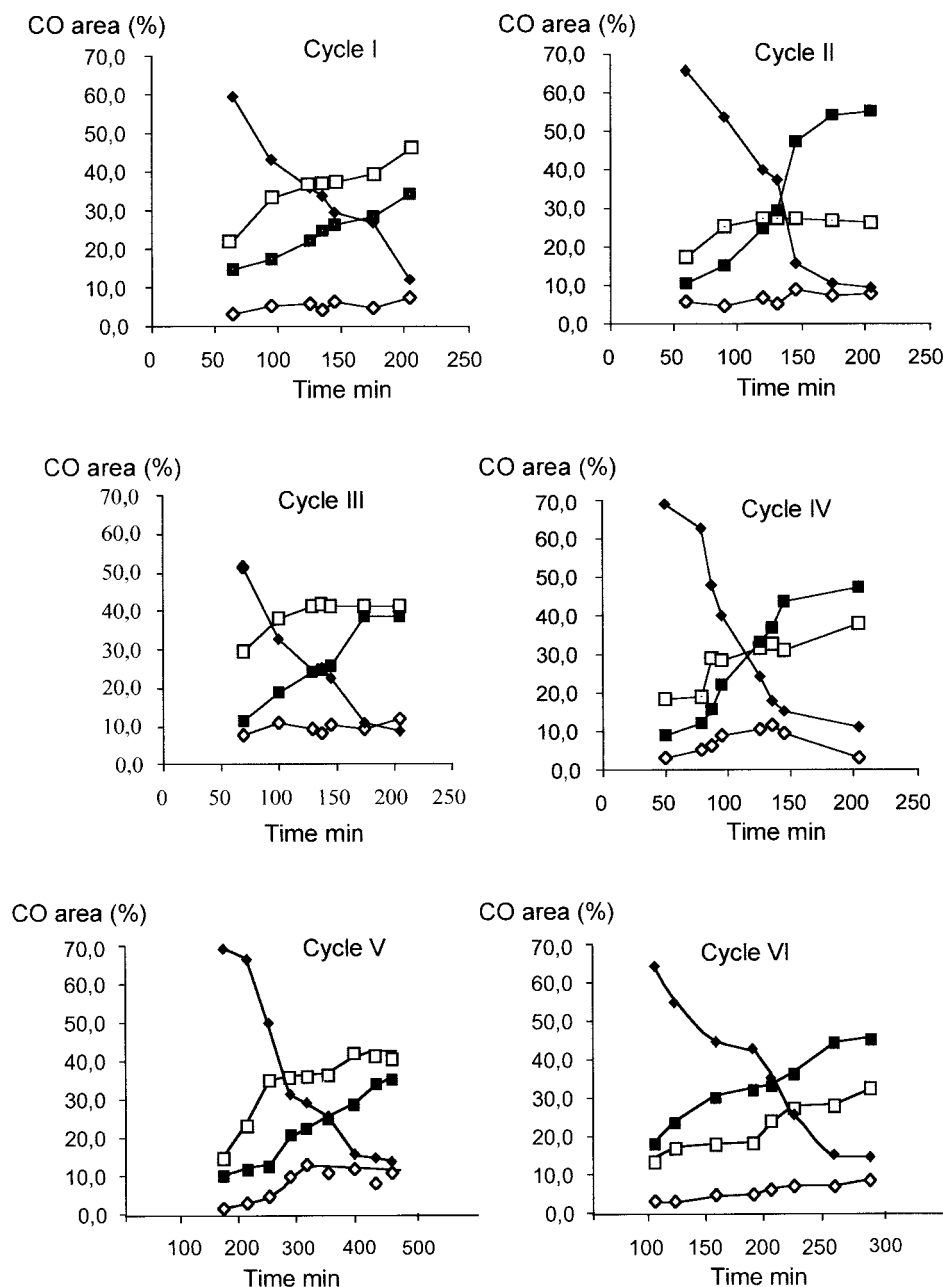This explains why there was no modification between the morphologies of the crosslinked ma-

Figure 5 The variation of (□) Michael's reaction rate, (■) the homopolymerization content, the (◆) the residual maleimide function content, and (◇) the aminolysis reaction content.

terials studied. One can suppose that the development of the nodules occurred before the hardening of the BMI phase.

Seris et al.[17] demonstrated the difficulty of interpreting the results. So, it seemed to be important to make the most exhaustively parametric analysis possible to get a clear view of the phenomena.

Too hasty a conclusion would nonetheless lead us to mistakes. The polymerization process of such a system is still very complex, and many parameters have to be taken into account.[18]

Mechanical Properties

Because the SEM characterization did not enable us to develop a relationship between the structure
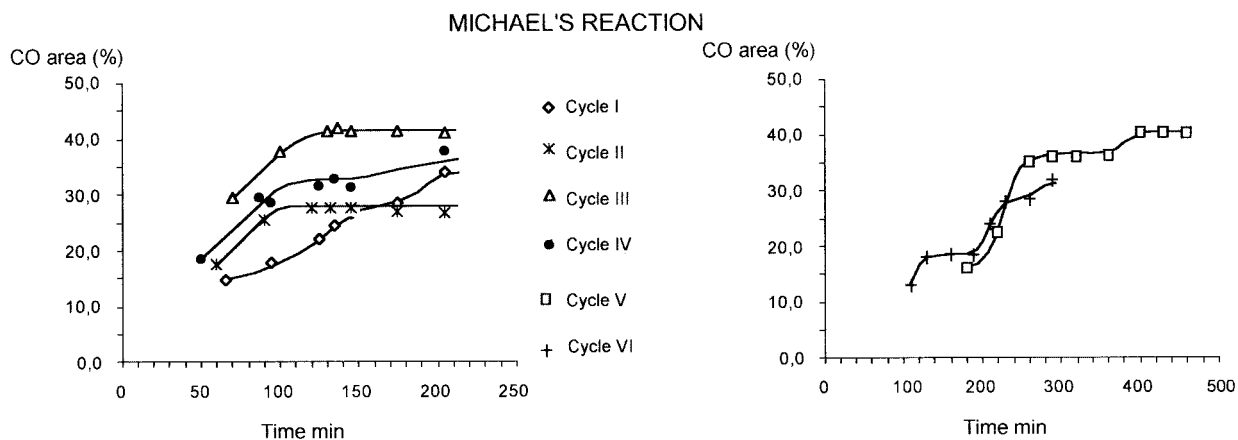
MICHAEL'S REACTION

Figure 6 The solid-phase ^{13}C-NMR variation of the Michael's reaction as a of the polymerization cycles for K736.

and morphology, we decided to study the material toughness.

The toughness values (K_{IC}) are given in Table II. They were obtained for the samples manufactured according to the different thermal cycles.

It can be seen that the mean value is between 4.1 and 4.9 MPa $\sqrt{m}$. Neither the temperature variations of the stage nor the heating rate of 0.5 or 1°C/min seemed to have any effect on the toughness of the material obtained.

Viot et al.[18] found K_{IC} values of the order of 0.55 MPa $\sqrt{m}$ for BMI resins without inclusions of elastomer. It can be seen that adding an elastomer phase improved the toughness by a factor of 10.

Glass Transition and Density

Donnellan et al.[19] associated the increase in the glass-transition temperature (T_g) determined by

dynamic mechanical analysis with the increase in the BMI content for a BMI/aromatic diamine system. The development of the crosslinking density associated with the reduction in the molecular mobility were in perfect agreement with the results obtained on the thermosetting systems.[20,21] They showed that thermal stages held at low temperature give rise preferentially to chain extension compared with homopolymerization for a given resin composition.

In our study the T_g of the materials subjected to industrial postcrosslinking conditions (5 h at 200°C + 10 h at 250°C) was determined by TMA. The results are reported in Table III.

The T_g of the crosslinked resin whose thermal gradient was the same (cycles I–IV = 2°C/min) exhibited a mean value that was not very different from the other two cycles (V and VI = 0.5 or 1°C/min). The temperature effect on the chemical
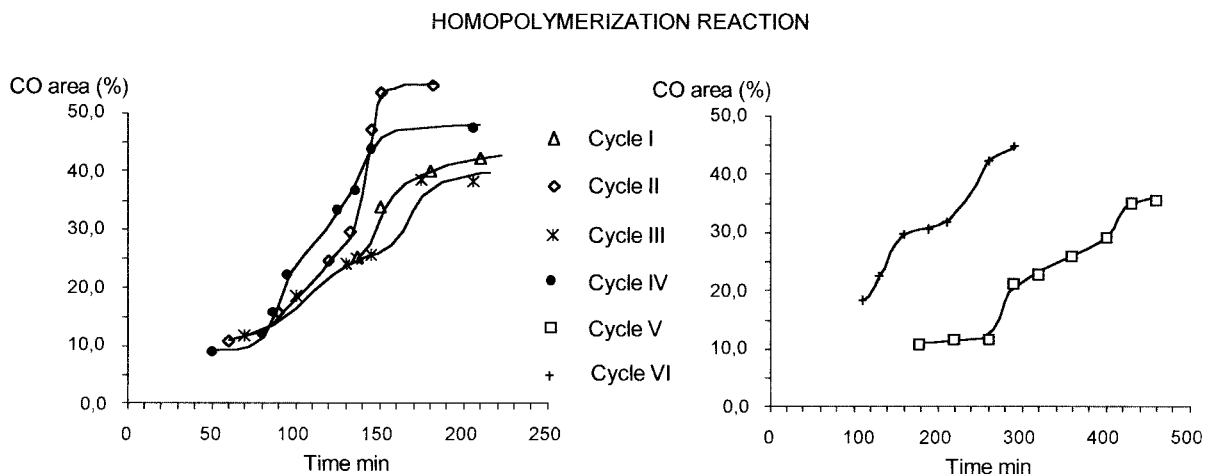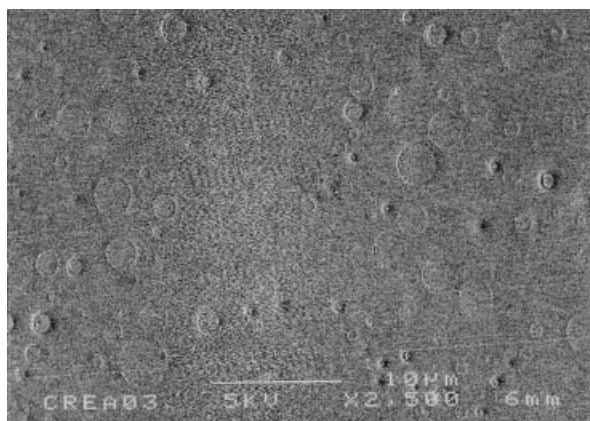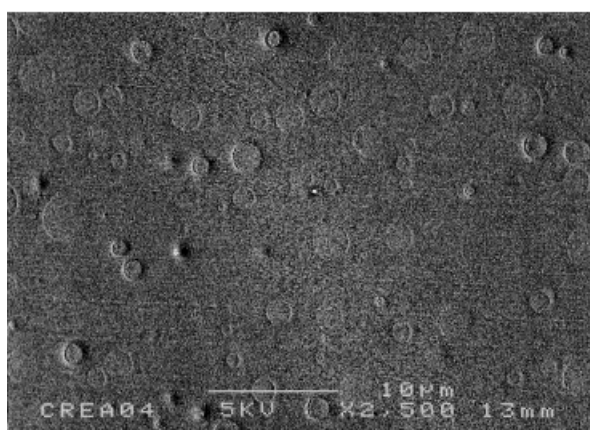
HOMOPOLYMERIZATION REACTION

Figure 7 The solid-phase ^{13}C-NMR variation of the homopolymerization reaction of K736 as a function of the various thermal cycles.

(a)

(b)

Figure 8 SEM photos of K736 polymerized by cycles I and IV. Original magnification ×2500.

structure observed by spectroscopy could not be revealed by TMA. However, the error in the measurement by this technique was quite important, considering that this was a thermosetting material whose thermal degradation begins at 380°C.

Density measurements were performed for various crosslinked materials. The values ob-

Table I Nodule Formation and Size Between 130 and 160°C

Temperature (°C)	Nodule Formation	Size
130	No	—
140	Yes	1–2 μm
150	Yes	2–2.5 μm
160	Yes	2.5 μm

Table II K736 Toughness Test Results for Different Thermal Cycles

Cycle No.	Description of Cure Cycle	K_{IC} (MPa $\sqrt{\mathrm{m}}$)
I	160 + 200°C $V = 2$°C/min	4.1 ± 0.6
II	150 + 200°C $V = 2$°C/min	4.9 ± 0.4
III	170 + 200°C $V = 2$°C/min	4.9 ± 0.3
IV	130 + 160 + 200°C $V = 2$°C/min	4.9 ± 0.1
V	160 + 200°C, $V = 0.5$°C/min	4.5 ± 0.3
VI	160 + 200°C $V = 1$°C/min	4.1 ± 0.6

tained show good homogeneity among all the cycles studied (Table III).

CONCLUSION

The purpose of this study was to get a better understanding of the BMI network architecture. Structural analysis of the BMI resin confirmed that two main chemical reactions, Michael's reaction and ene reaction, occurred in the crosslinking process of the K736 material.

The effects of various temperature cycles on the chemical structure of the crosslinked material were studied. Solid-phase NMR spectroscopic analysis showed the quantitative variation of the main chemical reactions involved in the polymerization. In one case we observed an increase in the chain extension at low temperature; in the other crosslinking density rose for higher temperatures.

The K736 resin was combined with an elastomer, which improved the material impact resistance. During polymerization, the BMI resin led to a two-phase material that was characterized by SEM. The morphology was not modified by the thermal parameters of the cure cycle.

Table III Glass-Transition Temperature (T_g) and Density of Different Crosslinked Materials of K736 Resin

Cycle No.	T_g (°C)	Density
I	346	1.252
II	342	1.248
III	346	1.25
IV	334	1.25
V	342	1.249
VI	348	1.249

The K_{IC}, T_g, and density of the crosslinked material were not much affected by the thermal cycles studied in this work. The relation between the T_g and the molecular mobility will be complemented by TM tests using a torsion pendulum. All the data concerning the organic matrix will then be applied to the composite materials.

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