

Polyamic Acids: Thermal and Microwave Imidization and Film Properties

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SYNOPSIS

Polyamic acids were synthesized from benzophenonetetracarboxylic dianhydride and diamines, viz., 4,4'-diaminodiphenyl methane and 4,4'-diaminodiphenyl ether. The course of imidization of the polyamic acids both by thermal and microwave treatments was tracked by infrared spectroscopy. The mechanical properties, namely the tensile strength and toughness of the films of polyimides with varying degree of imidization obtained by the two treatments were compared. The effect of degree of imidization of polyimide coatings on adhesion to copper substrate was also studied. Nearly 100% imidization was achieved by the thermal process, whereas the maximum imidization that could be achieved by the microwave process was about 50%. In thermal imidization, the adhesion values of the coatings slowly increased, attaining a maximum value at 80% imidization, after which there was a decrease in adhesion. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Microwave technology has developed very rapidly in the last decade with the advances in techniques for achieving uniform heating,¹ temperature monitoring² and use of microprocessors in programming cooking time, defrost, etc.³ The frequency bands at 915 and 2450 MHz are the most developed microwave bands for power applications. Almost all microwave ovens work at 2450 MHz and many of the heating devices at 915 MHz. A great deal of information is now available on the use of microwave energy in analytical, chemical, and industrial applications.⁴

Microwave energy has of late been successfully exploited in curing of polymers, composites, laminates, coatings, etc. Mijovic and Wijaya⁵ have discussed in their review article the fundamental concepts of microwaves and their use in cross-linking polymers and composites, highlighting the advantages and disadvantages of curing by microwaves. The curing of epoxy resins by microwave energy has been extensively studied by a number of work-

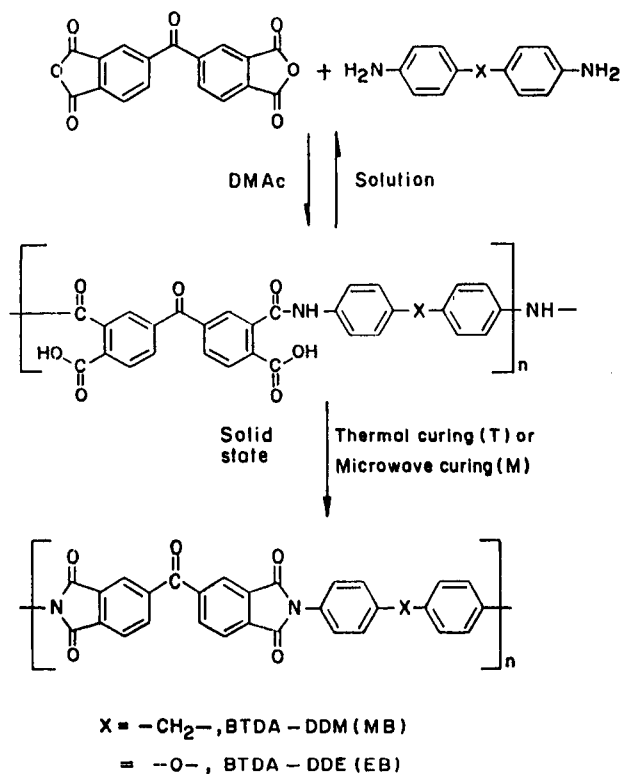


Figure 1 Simplified two-step reaction scheme for polyimide synthesis.

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ers.⁶⁻¹⁷ It was reported that pulsed microwave treatment was better than continuous treatment in inducing overall energy transfer,⁸ for activation of step growth polymerization,¹⁴ and eliminating overheating of the samples.¹⁷

The use of microwaves has been reported in curing composites,¹⁸⁻²³ plastic molding,^{24,25} laminates,²⁶

coatings,²⁷⁻³¹ foamed products,³²⁻³⁸ and bonding of various substrates.³⁹⁻⁴³

The imidization of polyamic acids that are the precursors of polyimides can be conveniently achieved by heat treatment. Recently, Lewis et al.⁴⁴ carried out studies on cure kinetics of polyamic acids by electromagnetic radiation and reported that the

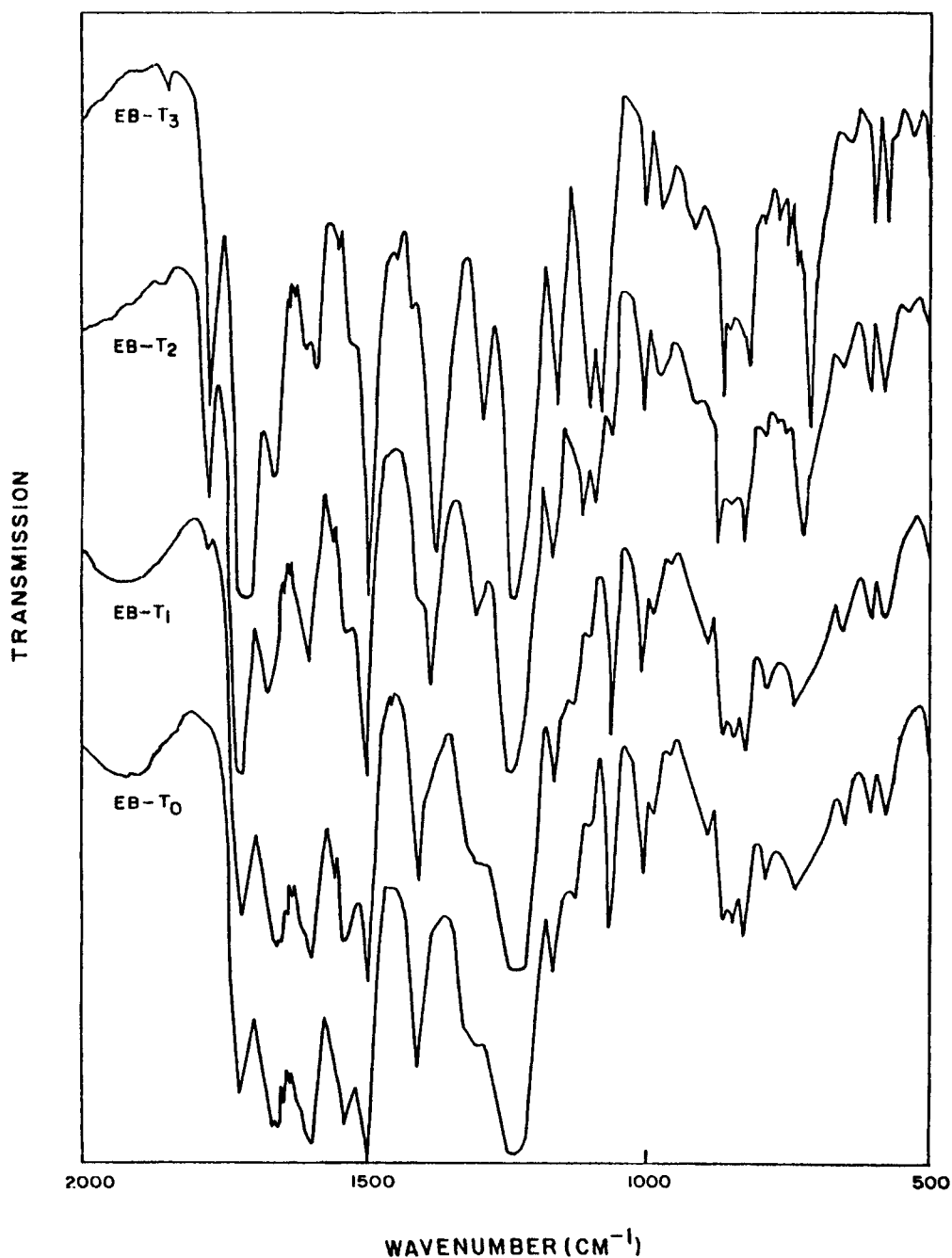


Figure 2 Infrared spectra of thermally cured polyimides at different stages of imidization: T_0 = uncured sample; T_1 = 100°C; T_2 = 150°C; T_3 = 175°C.

activation energy of electromagnetic imidization was lower than that of thermal imidization. A few reports^{32,33,37,38} are available on the production of foamed polyimides by microwave treatment of polyamic-based compositions.

In the present study, we describe the use of a domestic microwave oven in the imidization of polyamic acids to polyimides of varying degree of imidization and compare their mechanical properties with those of the similar products obtained by thermal imidization. Also, the effect of degree of imidization of polyimide coatings on adhesion to copper substrate is discussed.

EXPERIMENTAL

Materials

Reagents

Benzophenonetetracarboxylic dianhydride (BTDA) (Fluka) was recrystallised from acetic anhydride.

4,4'-Diaminodiphenyl methane (DDM) (Aldrich) was recrystallized from ethanol and toluene.

4,4'-Diaminodiphenyl ether (DDE) (Fluka) was purified by vacuum drying.

Solvents

N,N'-Dimethylacetamide was dried over P_2O_5 , distilled at low pressure, and stored over 4 Å molecular sieves.

Synthesis

Synthesis of Polyamic Acids

Polyamic acids were prepared using the stoichiometric proportions of dianhydride and diamines.

In a 250-mL conical flask were placed a Teflon-coated magnet, 5.94 g (0.03 mol) of DDM, and 156 mL of dimethyl acetamide. The flask was flushed with dry nitrogen and the contents stirred with a magnetic stirrer in a nitrogen atmosphere at room temperature until a clear solution of diamine was obtained. Then 9.67 g (0.03 mol) of BTDA were added in five aliquots, allowing each aliquot to dissolve in the solvent before the next aliquot was added. After complete addition of dianhydride, the reaction mixture was stirred under nitrogen for 4 h when there was no further increase in the viscosity of the solution. The polyamic acid solution (about 10%) was transferred to an air-tight bottle and stored in a refrigerator until it was used. The product was designated as "MB" polyamic acid. Similarly

the polyamic acid was prepared from BTDA and DDE and designated as "EB" polyamic acid.

Preparation of Polyamic Acid Films

The solutions of MB and EB polyamic acids were spread uniformly using a doctor blade on glass substrates to give approximately 28–30 μm dry film thickness. They were dried for about 16 h at ambient conditions and then peeled off. In order to remove the solvent entrapped by the films, a few samples of the EB films, air-dried for 16 h, were further vacuum-dried until they attained constant weights.

Imidization of Polyamic Acid Films

Thermal Imidization. The imidization of polyamic acid films was carried out in a circulating air oven by subjecting them to different temperatures programmed from 100 to 250°C with 25°C intervals for 30 min at each temperature. The thermally imidized polyimide films are designated as "MB-T" and "EB-T" films.

Microwave Imidization. The imidization of the MB and EB polyamic acid films was carried out in a domestic microwave oven, Microwin Mx 1100, manufactured by Microwin Electronic Ltd, India.

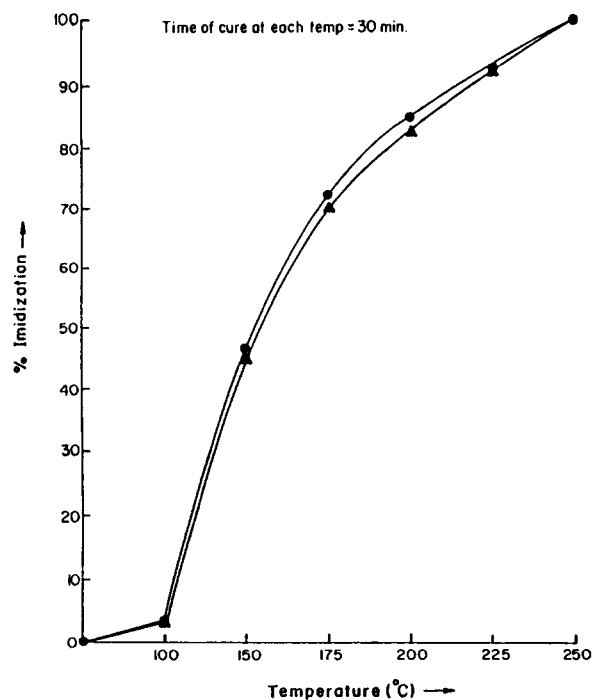


Figure 3 Programmed thermal curing of polyamic acids: (▲ — ▲) EB-T (air-dried for 16 h at ambient conditions); (● — ●) MB-T (air-dried for 16 h at ambient conditions).

The oven operated at a frequency of 2450 MHz has a full power level of 650 W with nine adjustable power settings. The microwave-imidized polyimide films are designated as "MB-M" and "EB-M" films.

The microwave oven was set for a full power level (power level setting nine) and the polyamic acid

films were placed in the oven and exposed to microwaves for different periods of time, programmed from 30 to 180 min, not exceeding 30 min at each operation.

The simplified two-step reaction scheme for polyimide synthesis is shown in Figure 1.

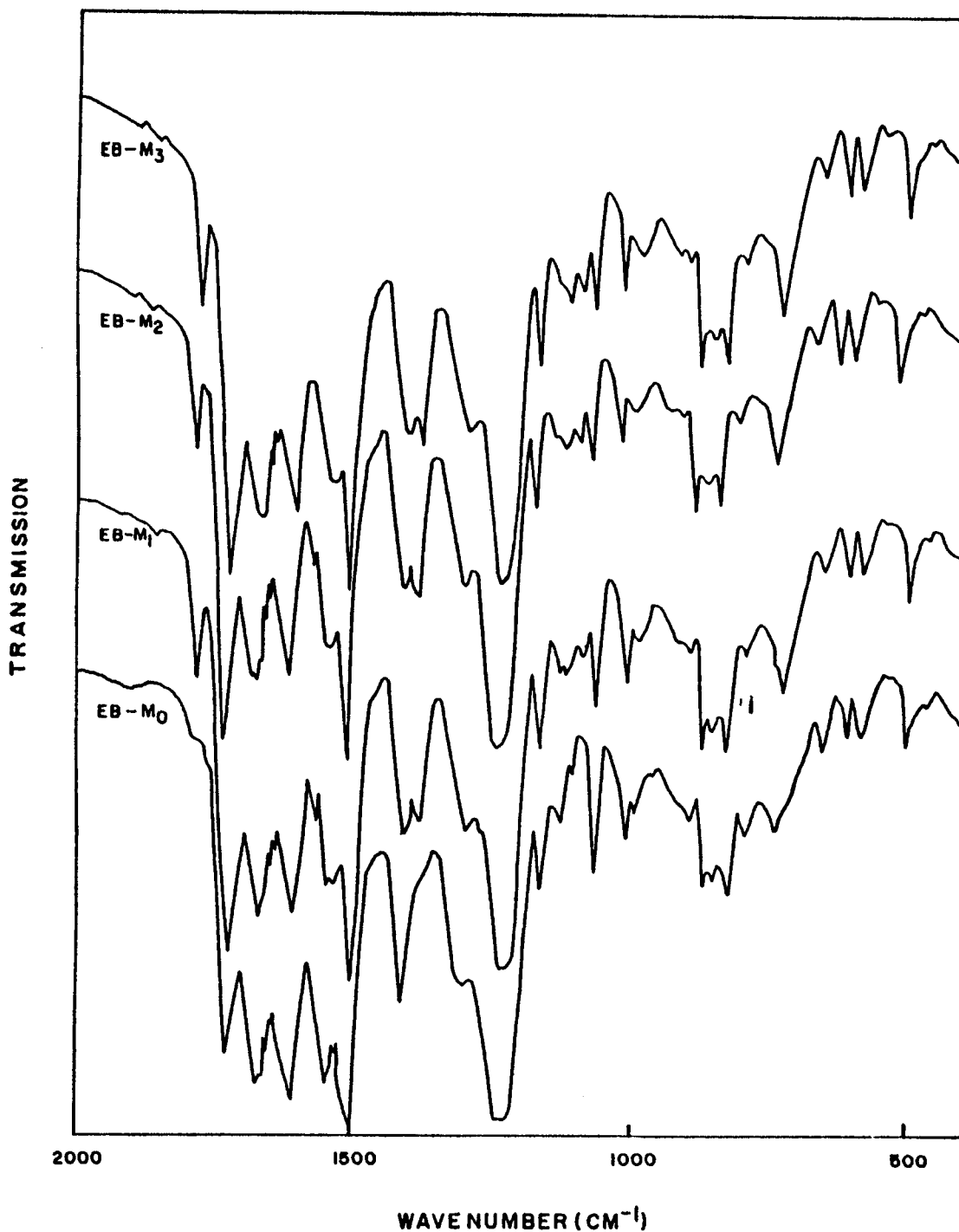


Figure 4 Infrared spectra of microwave cured polyimides at different stages of imidization: M_0 = uncured sample; M_1 = 30 min; M_2 = 60 min; M_3 = 90 min.

Characterization

Viscosity of Polyamic Acids

Inherent viscosity of the polyamic acid was determined with an Ubbelohde viscometer using 0.5% (g/mL) solution in dimethylacetamide.

Measurement of Imidization by Infrared Spectroscopy

The degree of imidization was determined by infrared spectroscopy using the Perkin Elmer Model 882 infrared spectrophotometer.

The spectra of polyamic acid/polyimide films were analyzed by a Band ratio method.^{45,46}

The area of the band due to the symmetric imide carbonyl stretching vibration at 1777 cm^{-1} was monitored during thermal imidization and ratioed with that of the reference aromatic absorption peak at 1500 cm^{-1} . The percent imidization of the specimen exposed to different schedules of curing was calculated by normalizing specimen band ratio with that of fully cured polyimide film.⁴⁵

percent imidization

$$= \frac{[A(1)/A(2)]_{Sx} - [A(1)/A(2)]_{So}}{[A(1)/A(2)]_{S\alpha} - [A(1)/A(2)]_{So}}$$

where, $A(1)$ = absorbance of imide peak at 1777 cm^{-1} ; $A(2)$ = absorbance of standard reference peak at 1500 cm^{-1} ; So = initial sample of polyamic acid; Sx = sample at a particular stage of imidization; $S\alpha$ = sample cured at 250°C , which showed near 100% imidization.

Percent imidization for different specimens obtained by microwave curing was calculated by normalizing the specimen band ratio with that of a fully cured sample obtained by thermal curing.

Tensile Strength, Elongation, and Toughness of the Films

The tensile strength, elongation, and toughness of the polyamic acid films, imidized at different schedules both by thermal and microwave treatments, were determined by the procedure described in ASTM-D-2370-73 using the stress-strain curve.⁴⁷

Adhesion

Copper discs (32-mm diameter and 0.8-mm thickness) were cleaned with methyl ethyl ketone and subjected to the various pretreatments in the following sequences:

1. The discs were first immersed for 10 min in a solution prepared by dissolving 5.46 g ferric sulphate and 4.1 g sulphuric acid (sp. gr. 1.84) in 100 mL of distilled water and then rinsed with cold water.
2. They were then immersed in a solution of 4.96 g sodium dichromate and 5.46 g sulphuric acid (sp. gr. 1.84) in 100 mL distilled water until the copper surface was clean and bright and then rinsed with cold water.
3. Finally, they were immersed for 10 s in concentrated ammonium hydroxide solution (28%) and rinsed with water.

The copper discs, thus treated, were immediately coated with polyamic acid solutions using an ICI spin coater and allowed to dry overnight at ambient conditions. The discs were then subjected to thermal curing schedules as described earlier. The sample discs obtained at each stage of curing were then tested for practical adhesion by the Sandwich Pull-off technique as described by Bullet and Prosser.⁴⁸ The values of tensile strength, toughness, and adhesion of the polyimide films cured at different stages are the mean of at least 10 different samples (Figs. 6–10).

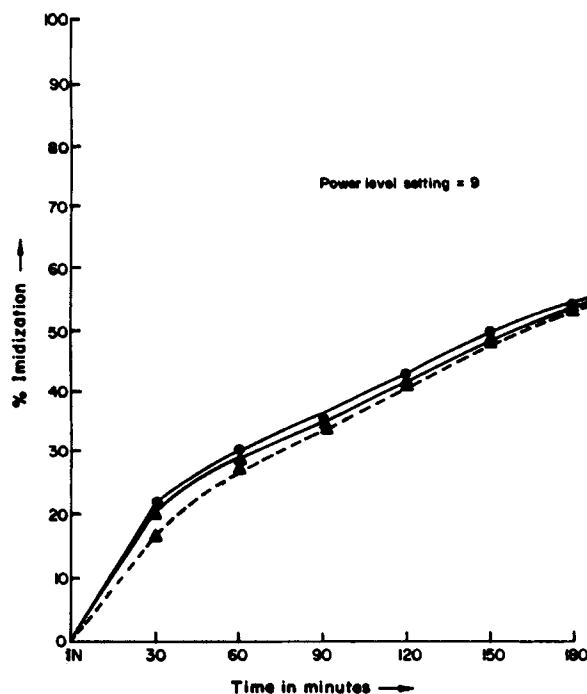


Figure 5 Programmed microwave curing of polyimides: (\blacktriangle — \blacktriangle) EB-M film (air-dried for 16 h at ambient conditions); (\blacktriangle - - - \blacktriangle) EB-M (air-dried for 16 h and vacuum dried at 60°C); (\bullet — \bullet) MB-M (air-dried for 16 h at ambient conditions).

RESULTS AND DISCUSSION

Inherent Viscosity

The inherent viscosities of the polyamic acids, obtained from the reaction of BTDA with DDM and DDE were 0.912 and 0.898, respectively, indicating the formation of high molecular weight polyamic acid.

Infrared Analysis

Thermal Imidization. The IR spectra showing the changes that occurred during programmed thermal curing of polyamic acid derived from BTDA and

DDE (EB-T) are presented for samples cured up to 175°C in Figure 2. The spectra include the regions used for measurement of imidization.

It can be noticed in Figure 2 that in the spectrum of polyamic acid (T_0) there is almost a zero level of imidization as indicated by the absence of the imide carbonyl symmetric stretching band at 1777 cm^{-1} . The band at 1777 cm^{-1} begins to appear in the spectrum T_1 of polyamic acid film-cured for 30 min at 100°C. The intensity of this band increases at a faster rate at 150°C and then slows down at curing beyond 150°C. The maximum imidization (about 77%) took place at the temperatures between 150 and 225°C (Fig. 3).

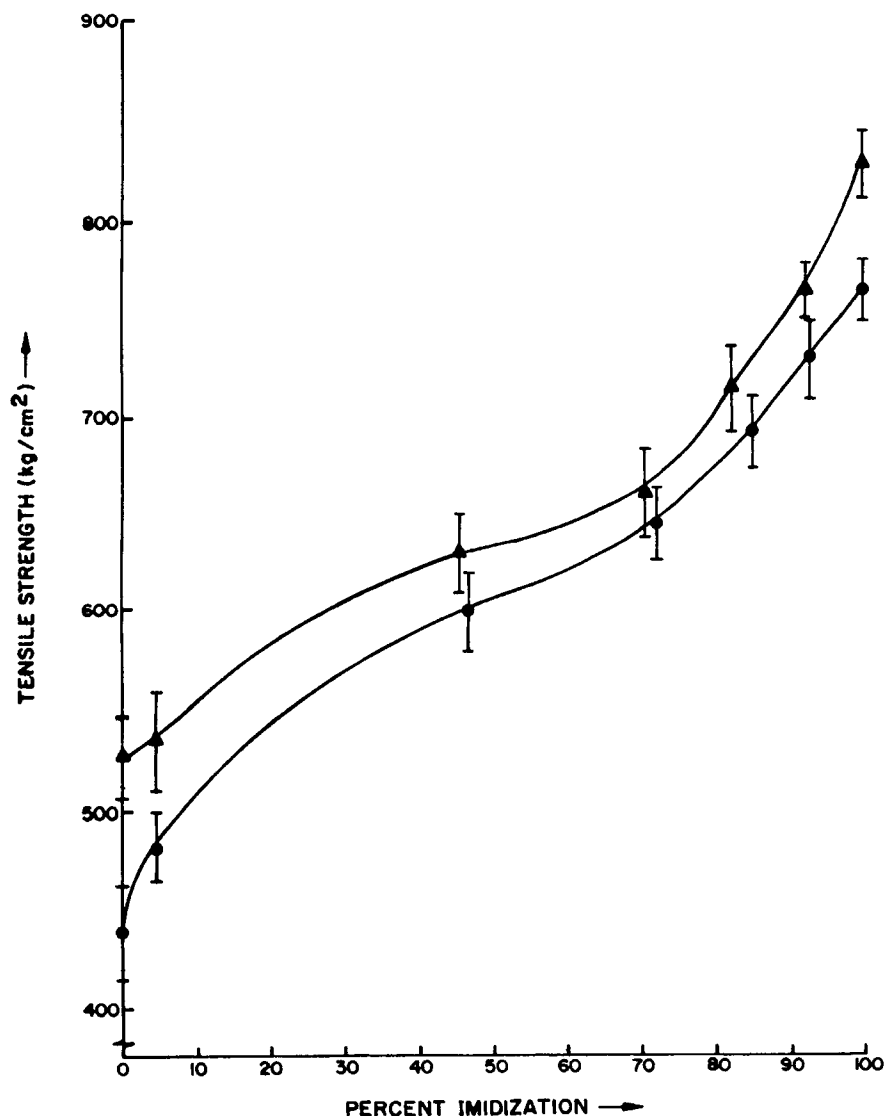


Figure 6 Tensile strength of polyimide films with different percent imidization obtained by thermal imidization: (▲) EB-T; (●) MB-T.

It is also interesting to note in the spectra of polyimides obtained by thermal cyclodehydration (Fig. 2) the appearance of a new band at 1860 cm^{-1} , particularly in the spectra of the samples cured at temperatures of 150°C and above. However, the rate of growth in intensity of this peak was found to be very slow as compared with that of imide formation. This band has been noticed in the imide spectra also by other workers.^{49,50} Kudryavtsev et al.⁴⁹ assigned this band to the isoimide structure that can thermally convert to imide. St. Clair and Progar⁵¹ attributed this band to residual anhydride.

Microwave Imidization. The infrared spectra showing the changes in imidization in the specimens obtained by the microwave curing for the period of 90 min, at different intervals of time are given in Figure 4. The microwave imidization of polyamic acid films was found to be fast at the initial stage of curing (Fig. 5). Both the EB-M and MB-M films air-dried for 16 h at ambient underwent about 22% imidization during the first 30 min of exposure to the microwaves. The solvent-free film subjected to both the air-drying and vacuum-drying before the exposure to the microwaves showed the lower percentage

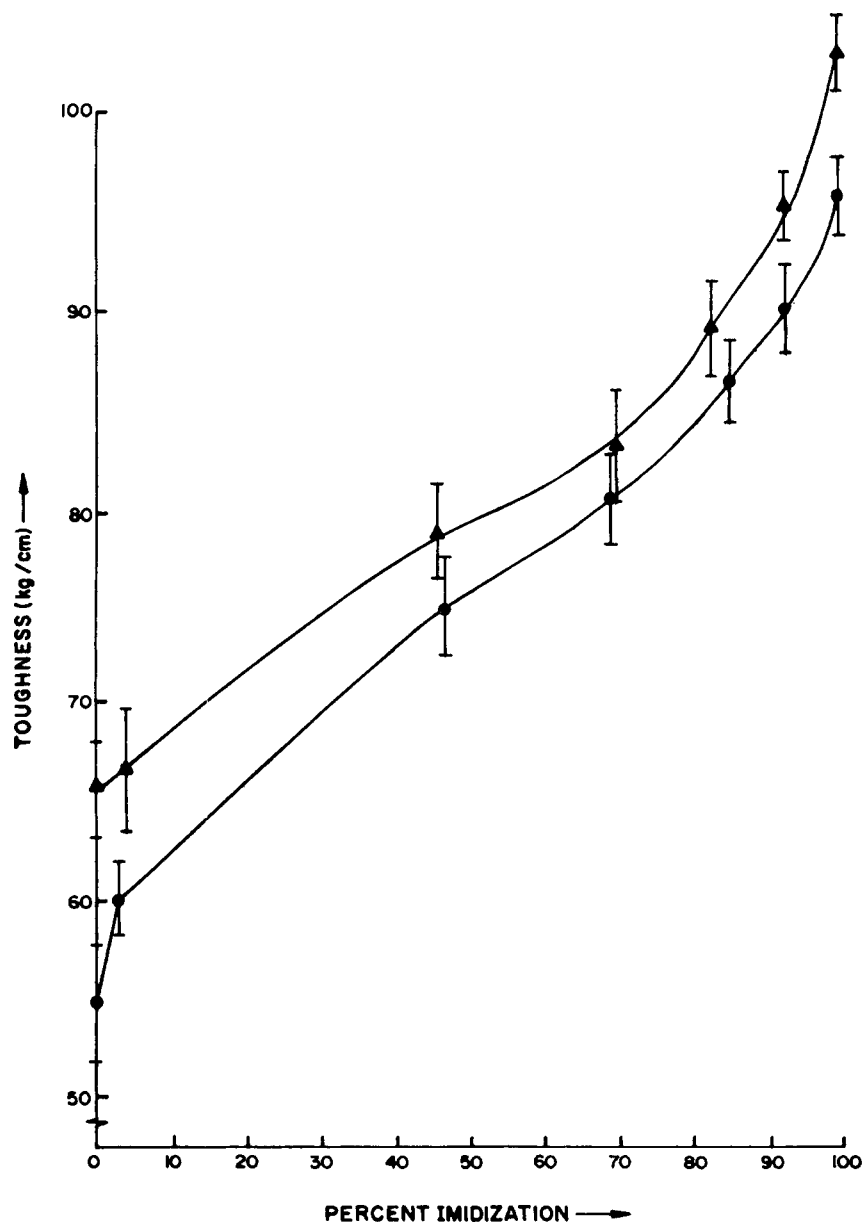


Figure 7 Toughness of polyimide films with different percent imidization obtained by thermal imidization: (▲) EB-T; (●) MB-T.

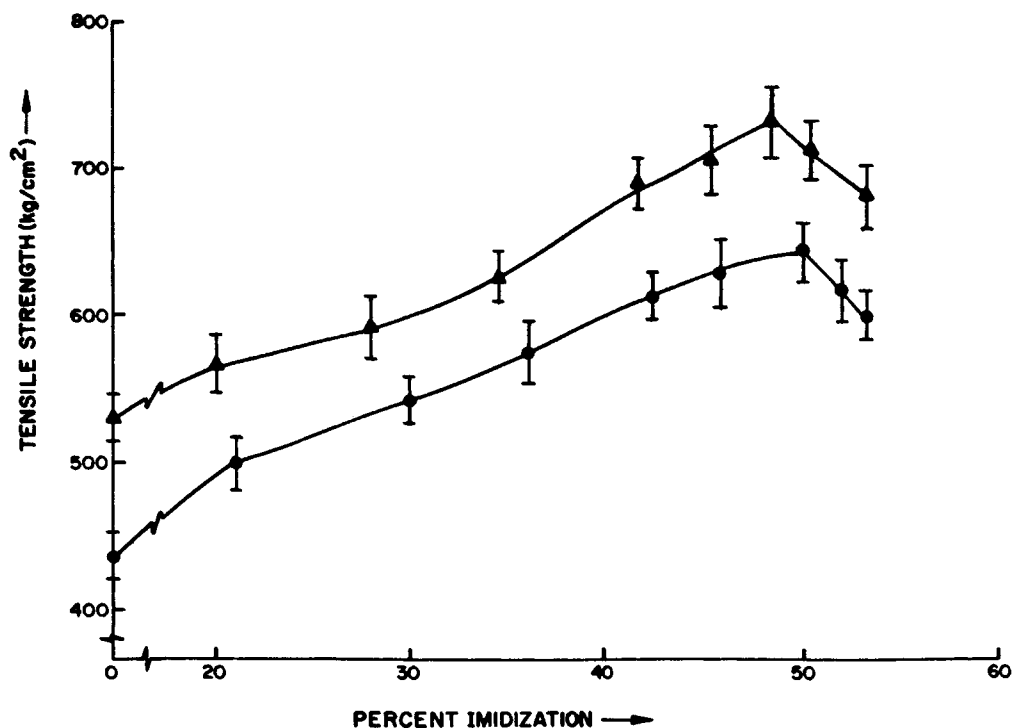


Figure 8 Tensile strength of polyimide films with different percent imidization obtained by microwave curing: (▲) EB-M; (●) MB-M.

of imidization (about 17%) in the first 30 min of curing. These results are indicative of the positive influence of the solvent on imidization reaction of polyamic acid. The solvent entrapped in the poly-

amic acid films appears to cause increases not only in the mobility of the functional groups by plasticizing the films, but also in the body temperature of the film due to its polar nature, thus enhancing the

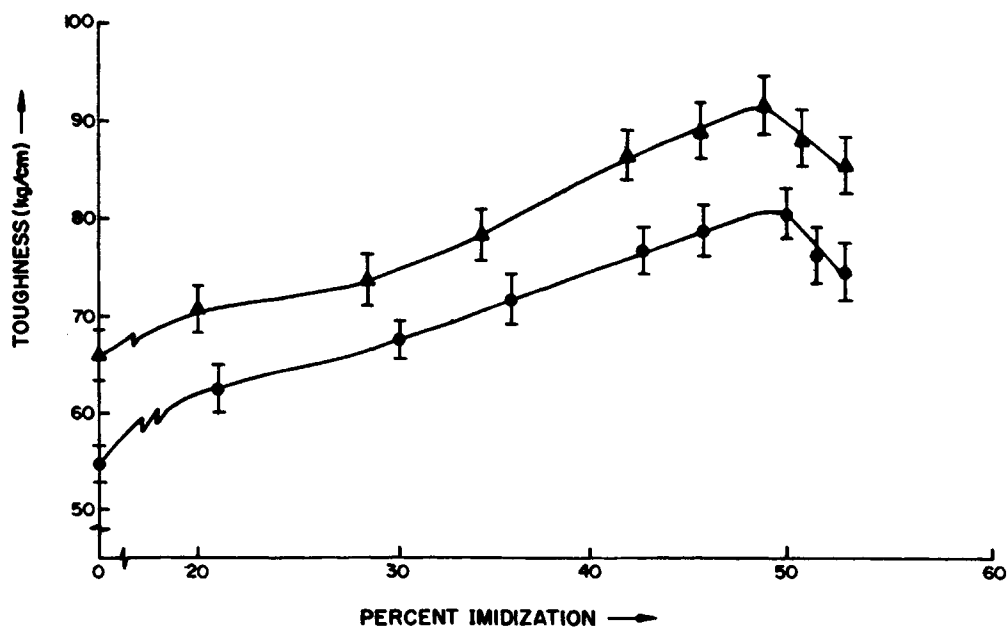


Figure 9 Toughness of polyimide films with different percent imidization obtained by microwave curing: (▲) EB-M; (●) MB-M.

rate of imidization. The curing became sluggish after the initial half-hour exposure in both the cases, and nearly stopped after reaching maximum imidization of 51–53% at the end of the 3-h exposure. The comparatively steep rise at the initial stage in the imidization time curve of the solvent-free EB-M film (Fig. 5) may be due to the initial faster imidization caused by the higher degree of molecular mobility of the softer polyamic acid films. The rigidity of the molecular chain increases with the degree of imidization. This may cause not only a decrease in the molecular mobility of the chain but also result in chain conformation unfavourable for the reaction and hence retardation in the curing rate.

Both the polyamic acids, EB-M and MB-M, have shown almost similar trends in the imidization reaction effected both by thermal and microwave treatments.

Tensile Strength and Toughness of Polyimide Films

Thermally Imidized Films. The tensile strength and toughness values of the polyimide films exposed to the thermal imidization are plotted against the percent imidization (Figs. 6 and 7).

The tensile strength of polyimide films of both of the polymer systems increases slowly with the increase in imidization until it reaches the value of about 70% imidization and then becomes slightly faster with a further increase in imidization. However, the polyimide EB-T containing ether linkages in the backbone exhibits slightly higher tensile

strength at each stage of imidization. The tensile strength of the specimen, which was taken as 100% imidized product, is about 825 kg/cm² for EB-T polymer, whereas for MB-T polymer the value is 760 kg/cm². At 50% imidization, the tensile strength values for these products are about 625 and 600 kg/cm², respectively.

Similar trends can be noticed in the toughness values of these polymers, shown in Figure 7.

Microwave Imidized Films. Figure 8 shows the plots of tensile strength versus percent imidization of polyimides, EB-M, and MB-M, obtained by microwave imidization.

It is interesting to note that the tensile strength increases with percent imidization, reaching a maximum value at about 50% level of imidization and then drops slowly when exposed for a longer period for further imidization. The higher input of power for a longer time may lead to oxidation and degradation, resulting in lowering of the tensile strength. However, this problem needs further study to understand it clearly.

The EB-M polymers exhibit higher strengths than MB-M polymers of equal percentage of imidization. The toughness values of these polymers (Fig. 9) follow a similar pattern to the tensile strength values.

Adhesion to Copper Substrates

This study was carried out for the coatings of polyimides cured by thermal treatment only. Due to use

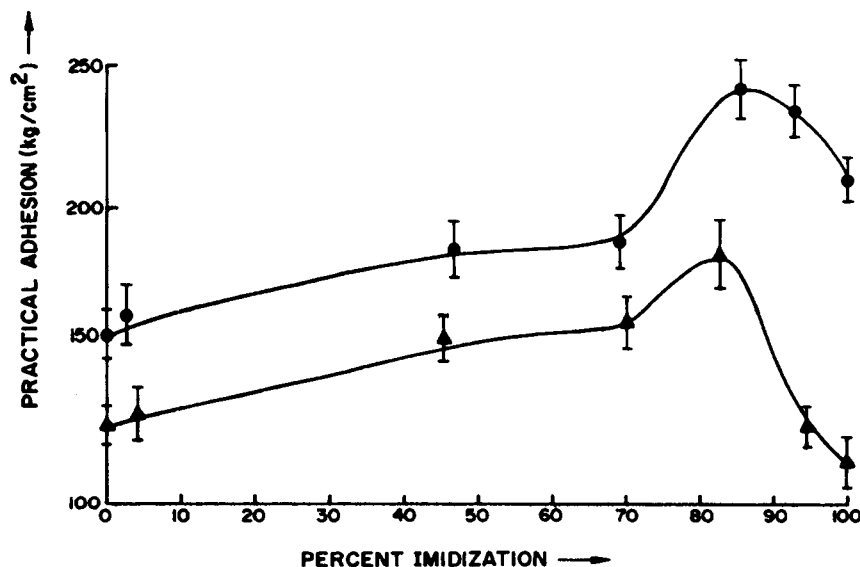


Figure 10 Adhesion of thermally cured polyimide coatings with different percent imidization to copper substrates: (▲) EB-T; (●) MB-T.

of a copper substrate, this study could not be carried out by microwave curing.

The plot representing adhesion versus percent imidization are shown in Figure 10. The results are found to be very interesting. It can be observed that the MB-T polymer films exhibit superior adhesion to copper substrates than the EB-T polymers with nearly equal degrees of imidization, though the latter possess higher tensile strength and toughness than the former.

The methylene bridges in the polymer might favour the orientation of the active groups in the polymers at the interface between copper substrate and polyimide film, thus increasing the adhesion of the film to the substrate.

There is a slow increase in adhesion values of the coatings of both polymers up to the level of 70% of imidization and maximum values are attained at 80% imidization. The polyimides possessing a higher content of imide ring than 80% show a decreasing trend in adhesion with further increase in imidization. This clearly indicates that the presence of free amic acid at an appropriate level in polyimide favours maximum adhesion of the films. The higher level of amic acid groups reduces the body strength of the film and the lower level reduces the adhesion strength.

CONCLUSIONS

The following conclusions can be drawn from the results of the present study:

1. Thermal curing is a more effective method as compared to microwave curing of polyamic acids. Near-completion can be reached in cyclodehydration of polyamic acid by thermal curing, whereas the maximum imidization achieved by microwave curing was only about 50% at the full power level.
2. Tensile strength of the thermally cured polyimide film increases with degree of imidization until it reaches nearly 100%. Microwave cured films also show similar behaviour, but only up to a certain level of imidization. Further exposure of the film to the microwave after this level of imidization shows a decline in the tensile strength.
3. The structural bridges in the polyimides are found to have some effect on tensile strength and adhesion. The ether containing polyimides are found to be slightly superior to the methylene-containing polyimides of equal

degree of imidization in tensile strength but are slightly inferior in adhesion strength.

4. The completely cured polyimide coatings obtained by thermal curing of polyamic acids exhibit lower adhesion strength than the product possessing about 80% imide content in the polymer. Thus, the presence of an optimum content of free amic acid is desired to have better adhesion to the metal substrate.

This paper is IICT Communication No. 2952.

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Received January 9, 1992

Accepted February 8, 1993