Thermal Comparative Study on Epoxy Resin Networks with Amic Acid and their Corresponding Imides

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Abstract

This work deals with the preparation and thermal investigation of eleven Epoxy-amic acid or Imide networks. The following monobasic amic acids were used: PMA, 2CMA, 3CMA, 2,6DCMA, 2BMA, 4NMA, 2HMA and 2MMA. Also the following dibasic amic acids were prepared: 1,2PBMA, 1,4PBMA and 2,5TBMA. After characterization with IR spectroscopy, thermal behaviour of the networks were investigated by using differential thermal analysis (DTA). The comparison of T_1 and T_4 values of amic acids alone with those in the networks shows that T_1 values are lower and T_4 values are higher in networks. As well as, the similarity of T_1 and T_4 values of amic acid networks with those of imide networks. The derivation of T_2 and T_3 values reveals that cyclo-dehydration process affects T_2 and T_3 positions but not the initial or final positions.

الخلاصة

يشتمل البحث على تحضير ودراسة مجموعة من شبكات راتنج الايبوكسي مع مجموعة من حوامض الاميك الأحادية: PMA, 2CMA, 3CMA, 2,6DCMA, 2BMA, 4MMA, 2HMA, 2MMA والحوامض الثنائية الآتية: 1,2PBMA, 1,4PBMA و 2,5-TBMA. بعد تشخيص هذه الحوامض ومشتقاتها باستخدام طيف IR حضرت منها شبكات متداخلة مع راتنج الايبوكسي بنسبة (1:1 وزناً) ودرست صفاتها الحرارية المقارنة باستخدام تقنية التحليل الحراري التفاضلي (DTA). وجد عند مقارنة قيم T_1 و T_4 لحوامض الاميك منفردة مع مثيلاتها في الشبكات البوليمرية أن قيم T_1 أعلى في الحوامض المنفردة وقيم T_4 أقل مما هي عليه الشبكات المتداخلة. كما وجد تشابه كبير بين قيم T_1 و T_4 لشبكات حوامض الأميك وشبكات الايمايدات واختلاف في قيم T_2 و T_3 لهما مما يدل على أن عملية تحلّق حامض الاميك يؤثر على واقع T_2 و T_3 ولا يؤثر على درجات البداية T_1 والنهاية T_4.

Introduction

Epoxy resins are reactive monomers, which are commonly cured with amine to form thermosetting polymers. If the epoxy is cured with an aromatic amine of sufficient functionality, the result is a high cross-linked network with relative high stiffness, glass transition temperature (Tg) and chemical resistance [1]. They are widely used for protective coatings due to the strong adhension and corrosion protection of metals [2,3]. Unfortunately, the temperature resistance of the cross-linked polymer is relatively low. It is therefore desirable to enhance toughness without adversly affecting the other useful properties of the polymer [4]. Moreover, polyimides which are known as high-temperature-resistant polymers may be used together with epoxy to improve its heat resistance. Many types of polyimides including flame-retradent [5], heat-resistant [6] were prepared and investigated [7,8].

The objective of this work is to examine the thermal behaviour of different epoxy-polyimide networks. Differential thermal analysis was used to assess the phase changes occurred through the heating process and to compare the polymeric networks behaviour with the Epoxy resin alone.

Experimental

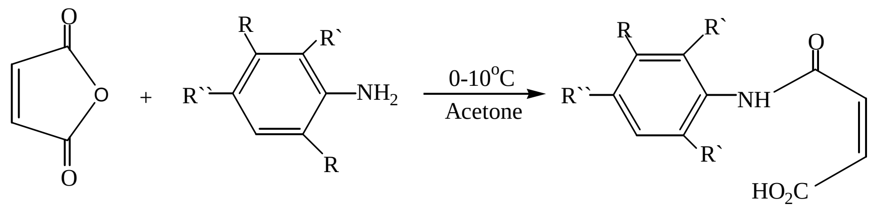
Chemicals

Aniline, 2-chloroaniline, 3-chloroaniline, 2,6-dichloroaniline, 2-bromoaniline, *o*-hydroxy aniline, *p*-nitroaniline, *o*-toluidene, 1,2-phenylene diamine, 1,4-phenylene diamine, 2,5-tolylene diamine, malic anhydride all supplied by (BDH), pool, England.

All chemicals were reagent grade. Common organic solvents commercially available were used without further purification.

Preparation of the starting materials:

Monobasic amic acids are prepared by the reaction of 1 mole of aniline (or its relatives) with 1 mole of maleic anhydride [9].

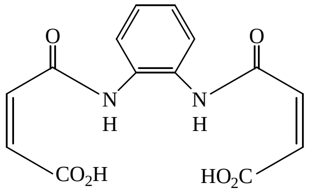


Maleic anhydride **aniline** **N-Phenyl maleamic acid**

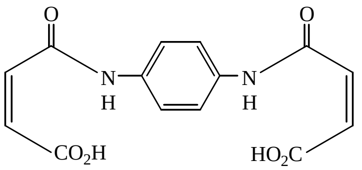
(or its relatives) (or its relatives)

R = H, Cl
R` = H, Cl, Br, OH, CH_3
R``= H, NO_2

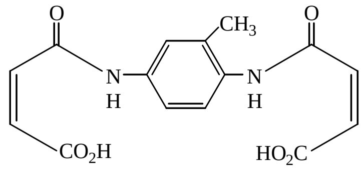
While dibasic amic acids are synthesised by the reaction of 1 mole of diamine with 2 moles of maleic anhydride. Three bismaleamic acids are prepared using the same procedure from their corresponding diamines:



N,N`-1,2-Phenylene bismaleamic acid

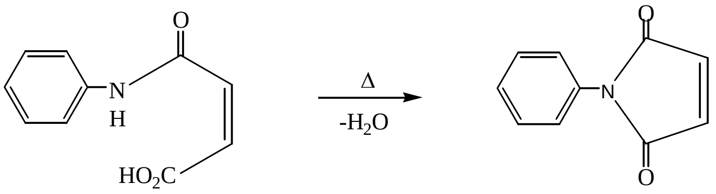


N,N`-1,4-Phenylene bismaleamic acid



N,N`-2,5-Tolylene bismaleamic acid

The (mono and bis) maleimides are obtained from their amic acids using thermal *cyclo*-dehydration reaction [7]:



N-Phenyl maleamic acid (PMA) N-Phenyl ,a;eimide (PMI)

The abbreviations of the synthesied maleamic acids and their melting points are listed in table 1. While the main IR absorption band are shown in table 2.

Table 1. Abbreviations and melting points of amic acids

Amic acid	Abbreviation	m.p. (^oC)
N-phenyl maleamic acid	PMA	198
2-chloro-N-phenyl maleamic acid	2CMA	123
3-chloro-N-phenyl maleamic acid	3CMA	195
2,6-dicholro-N-phenyl maleamic acid	2,6DCMA	157
2-bromo-N-phenyl maleamic acid	2BMA	112
4-nitro-N-phenyl maleamic acid	4NMA	216
2-hydroxy-N-phenyl maleamic acid	2HMA	185
2-methoxy-N-phenyl maleamic acid	2MMA	216
N,N`-1,2-phenylene bis maleamic acid	1,2PBMA	193
N,N`-1,4-phenylene bis maleamic acid	1,4PBMA	227
N,N`-2,5-tolylene bis maleamic acid	2,5TBMA	203

Preparation of networks:

Epoxy networks with maleamic acids and maleimides are synthesised by mixing equal weights of liquid epoxy (lyco-Pox 103, lycochem, Germany) with the other component. After homogenization, the epoxy curing agent is added. The mixture was left for 72 hrs. to attain complete crosslinking of epoxy network containing the second component.

Table 2: Important IR absorption bands (cm^{-1}) of amic acid and maleimides

Amic acid	**OH**	**NH**	**C=O**	**C=C**	**C=C arom.**	**others**
PMA	3314	3225	1705	1610	1432	-
2CMA	3321	3278	1713	1610	1439	726 (C-Cl)
3CMA	3316	3270	1708	1615	1420	710 (C-Cl)
2,6DCMA	3250	3260	1710	1623	1414	740 (C-Cl)
2BMA	3305	3268	1715	1626	1475	576 (C-Br)
4NMA	3300	3265	1716	1618	1428	597 (C-NO_2)
2HMA	3318	3260	1717	1621	1421	579 (C-CH_3)
2MMA	3311	3267	1714	1620	1430	575 (C-OH)
1,2PBMA	3277	3271	1718	1636	1452	-
1,4PBMA	3280	3205	1719	1635	1450	-
2,5TBMA	3287	3210	1720	1637	1451	582 (C-CH_3)
Imide	**Imide structure**				**C=C arom.**	**C=C arom.**
PMI	1780	1727	1406	733	1466	-
2CMI	1740	1700	1400	800	1486	693 (C-Cl)
3CMI	1760	1699	1380	820	1416	690 (C-Cl)
2,6DCMI	1760	1706	1367	813	1456	700 (C-Cl)
2BMI	1763	1700	1400	814	1485	550 (C-Br)
4NMI	1760	1701	1400	816	1467	691 (C-NO_2)
2HMI	1751	1700	1395	811	1480	693 (C-CH_3)
2MMI	1760	1701	1390	810	1484	692 (C-OH)
1,2PBMI	1766	1666	1381	786	1480	-
1,4PBMI	1765	1668	1323	788	1479	-
2,5TBMI	1761	1668	1324	789	1480	700 (C-CH_3)

Instrumentation

IR spectra were recorded on Pye-Unicam SP-2000 spectrophotometer with KBr pellets. DTA thermograms were recorded by using home-made apparatus designed according to reference [10] and calibrated by standard PVC sample.

Results and Discussion

Characterization of amic acids and maleimides:

The important IR band assignment for the prepared materials are listed in table 2. Amic acids show characteristic bands located in the range 3321-3250 cm^{-1} (acidic-OH) and 1610-1640 cm^{-1} (olifinic group). *Cyclo*-dehydration and polymerization of amic acids leads to complete disappearance of the acidic hydroxy and olifinic groups. Instead new strong absorption bands at 1760-1780 cm^{-1} belong to imide carbonyl are observed.

Curing behaviour of epoxy networks:

Thermal behaviour of epoxy networks with maleamic acids and maleimides are investigated by DTA. Figure 1 shows a representative DTA thermograms of epoxy-amic acid networks. To analyse these thermograms we have to mention that polymers, in general transverse through different thermal phases [11]. T_1 is the temperature of the first energy release (fig. 1). T_2 belongs to the maximum degree of orientation or cyclodehydration process. The termination of arrangement or crosslinking are represented by T_3. T_4 is the temperature of phase changes like oxidation, degradation etc, which appeared at high temperatures [11, 12].

DTA of Epoxy-Amic acid networks

Examination of DTA thermogram for epoxy resin alone (fig. 1) reveals 2 exotherms appeared at 220 and 310^{o}C. The first exotherm belongs to partial orientation of molecules, and the second belong to polymer oxidation [11]. Comparison of epoxy-amic acid thermograms with that of Epoxy alone shows the following features:

1- Expansion of the distance between T_1 and T_3 which appeared as a wide band as shown in PMA, 2MMA, 2CMA, 3CMA and 2BMA networks. The reason may be due to the interference of three exothermic effects (*cyclo*-dehydration) of amic acid, polymerization of olifinic group and orientation of the formed molecules.

2- The appearance of three exotherms, the second is stronger than the first one as shown in the 4NMA, 2MMA and 1,2PMA networks. Interference of the second and the third exotherms as in 1,4PBMA and 2,5TBMA networks. This behaviour may be explained by that the oxidation process pass through two steps. The presence of two amide groups (as in bismaleimides) causes separate energy emission.

3- Lower value of T_4 (oxidation peak) in the networks containing Br, NO_2, OH groups. The maximum values observed in bisamic acids; while T_4 of other networks is ranged between 430-450°C. These values are in the following trend:

1,4PBMA > 1,2PBNA > PMA ~ 2MMA ~ 2CMA ~ 3CMA > 2,6DCMA ~ 2,5TBMA > 2HMA > 4NMA > 2BMA

DTA of Epoxy-Imide networks

The comparison of DTA traces of epoxy-imide networks (fig. 2) with their isomers of epoxy-amic acid networks (fig. 1) shows that:

1. The general features of DTA thermograms in fig. 2 are similar to that observed in fig. 1, where two exotherms for some and three for others. The values of T_1 and T_4 are still in similar positions.
2. Lowering in T_2 and T_3 values in most networks which indicates that energy liberation due to imide polymerization (one step) is released before energy emission of amic acid polymerization (two steps: cyclodehydration and polymerization).
3. The appearance of 3 exotherms (in imide networks) exactly as shown in amic acid networks. The only difference is that they are bound in amic acid exotherms and separated in imide once.
4. The values of T_4 are decreased in the following trend:

2MMI ~ 1,4PBMI > 1,2PBMI > 3CMI > PMI > 2CMI > 2,5TBMI > 2,6DCMI ~ 4NMI = 2HMI > 2BMI

Mohamed and Al-Halim [7] show that the presence of halo-substituents in aromatic maleimides shifts the first exotherm to lower values if compared with their positions in nonsubstituted maleimides. At the mean time, the first exotherm of the bismaleimides (e.g. 1,4PBNI) appears before the mono (unsubstituted) maleimide (e.g. PMI). This observation indicates that the presence of more than one olifinic group increases the released energy which causes the polymerization to start at lower temperatures. This explanation fitts our results where T_1 of the bismaleimide networks show relatively lower values if it is compared with T_1 of mono-maleimide networks. The effect of halogen substituents on T_1 is minor if compared with their effect on T_4 values.

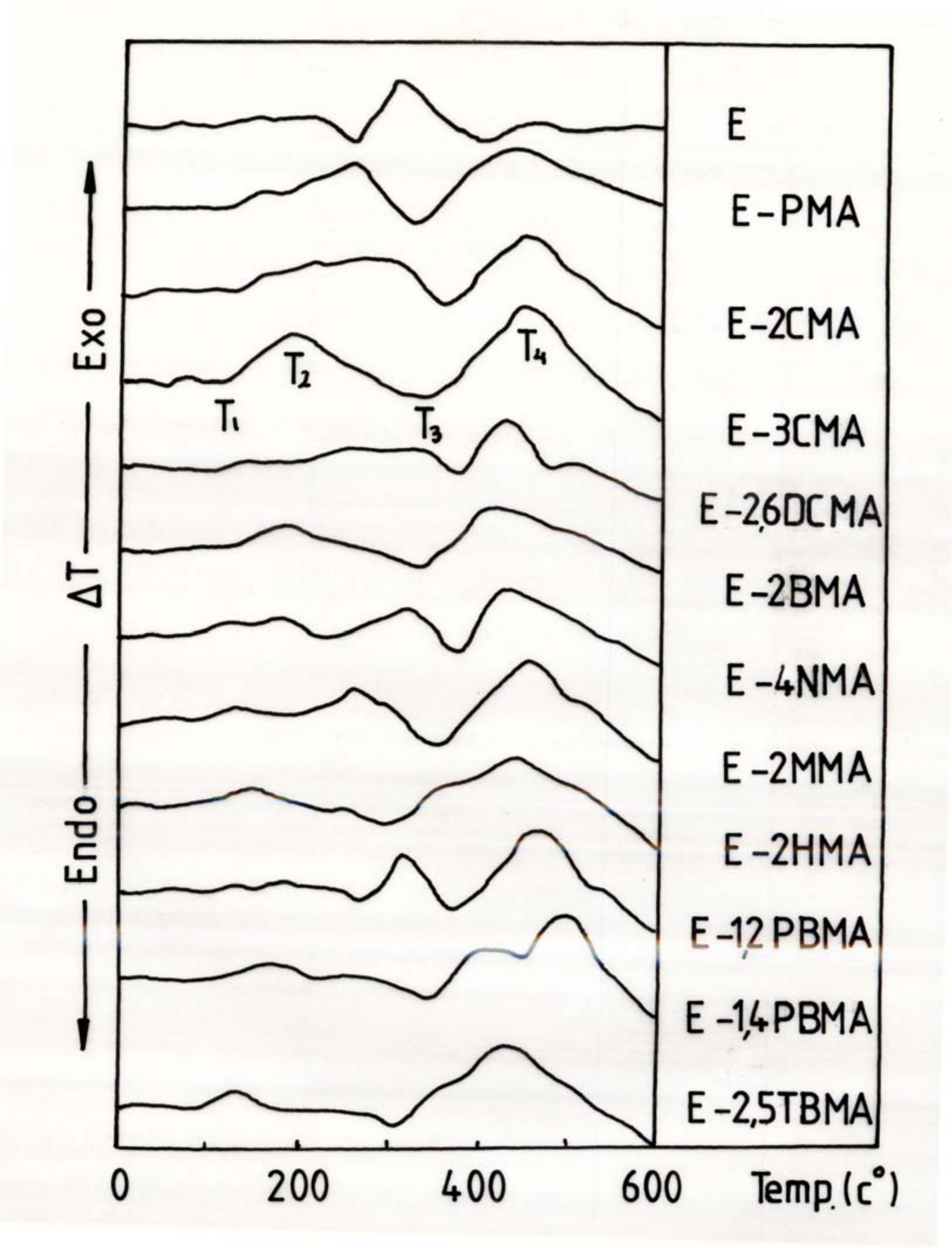
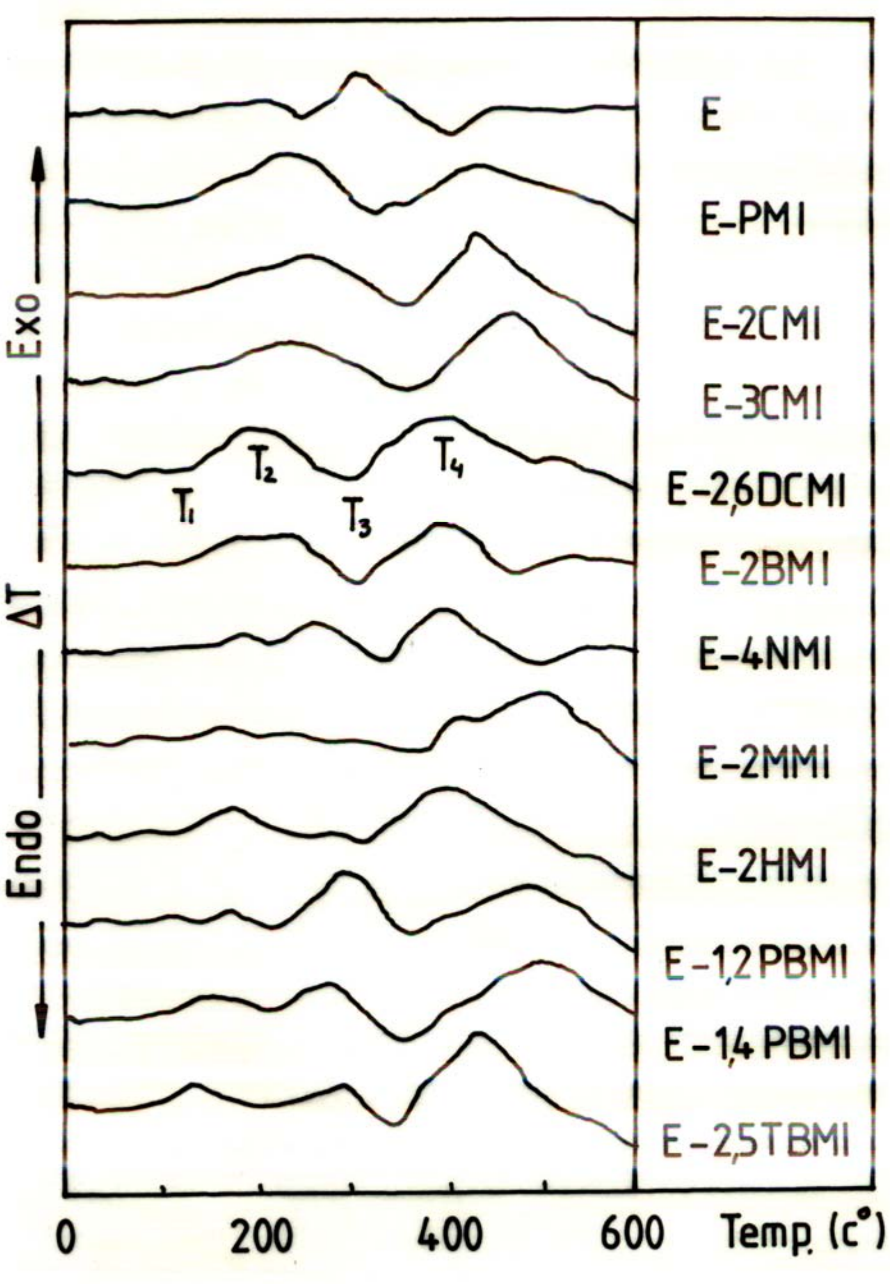


Fig. 1: DTA thermograms of Epoxy-amic acid networks

Fig. 2: DTA thermograms of Epoxy-maleimide networks



Comparison of DTA values of pure amic acids and Epoxy-amic acid networks:

T_1 and T_4 values of epoxy-amic acid networks are compared with the same values of pure six amic acids obtained from reference [7] and listed in table 3. The comparison shows that the networks have the lower T_1 and the higher T_4 values. This behaviour may explained by two factors; the first is the dilution of amic acid with epoxy molecules leads to low T_1 values if compared with the pure amic acid. The second effect is the crosslinking of epoxy network throughout amic acid molecules causes the energy release of the second exotherm (T_4) to appear at higher temperatures

Table 3: T_1 and T_4 values of pure amic acid [7] and its networks with epoxy resin

Amic acid	Epoxy / amic acid		Amic acid alone	
	T_1 (°C)	**T_4 (°C)**	**T_1 (°C)**	**T_4 (°C)**
PMA	115	440	273	430
2CMA	140	430	190	340
3CMA	120	460	255	340
2,6DCMA	120	400	185	300
2BMA	120	390	170	280
1,2PBMA	110	475	228	450

Conclusion

The comparison of T_1, T_2, T_3 and T_4 of epoxy-amic acid (fig. 1) with E-Imide networks (fig. 2) shows, in general, similarity in most values. This means that cyclodehydration process, that converts amic acid to imide, has no significant effect on the general features of DTA thermogram at the beginning (T_1) and the end (T_4) but affects the positions of T_2 and T_3. The lower values are observed in the networks containing Br and NO_2; and this may due to their electron-withdrawing nature which has a negative effects on the T values negatively. In contrast, the networks containing electron-donating groups like Me as well as, those containing bis-amic acids show the highest T_4 values.

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