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Comparative Differential Thermal Analysis of Epoxy Resin blends with Amic Acid-Copper Complexes

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Abstract:

This work deals with the thermal behaviour of epoxy resin blended with eleven mono-and dibasic maleamic acids and their copper complexes. DTA thermograms of all blands show two distinct exotherms (T_2 and T_4) at high temperatures if compared with those of epoxy alone. Values of T_1 and T_4 in copper containing blends are higher than their isomers in mono amic acids, while the inverse was observed in copper-diamic acid blends. The presence of copper in the blend shifts the position of the oxidation exotherm (T_4) to relatively higher temperatures.

Key words: Epoxy resin; Maleamic acid complexes.

Introduction:

The use of metal salts in the production and formulation of epoxy resins for use in composite materials has been widely studied. A large body of work involving the use of metal complexes to enhance (e.g. electrical, thermal and chemical, etc.) epoxy properties were described [1]. Many types of ligands were used as a complexing agents with the metals. Ligands like acetylacetone [2,3], acrylates [4], imadizole [5], phthalocyanine [6] and Schiffs bases [7] are widely used in this field. Recently, thermal stability of epoxy resin blended with polyurea-metal complexes were discussed [8]. The present work deals with the preparation and investigation of epoxy blends with maleamic acids and their copper complexes. This metal was choosed as a complexing agent due to the high stability of its complexes with amic acid if compared with other metals [9].

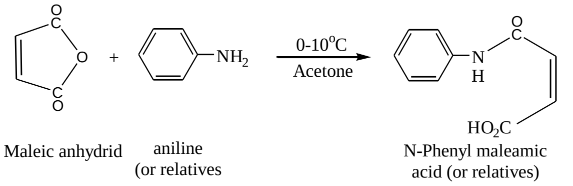
Experimental:

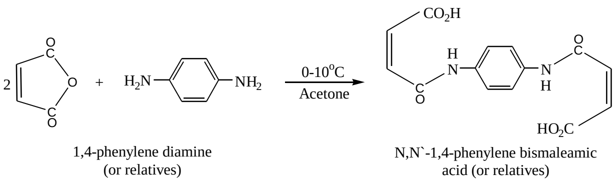
Chemicals:

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 (BDH), copper acetate (Fluka). All chemicals were reagent grade. Common organic solvents commercially available were used without further purification.

Preparation of precursors:

Monobasic maleamic acids are prepared by the reaction of 1mole of aniline (or its relatives) with 1mole of maleic anhydride. While dibasic maleamic acids are synthesized by the reaction of 1 mole of diamine with 2moles of maleic anhydride [10].





Copper complexes of amic acids are sunthesized by the reaction of the ligand (amic acid) with hydrated copper acetate $(CH_3CO_2)_2.Cu.H_2O$ in methanol. The complex is treated and isolated as mentioned elsewhere [9].

Preparation of epoxy blends:

Epoxy blends with amic acids and their copper complexes are prepared by mixing liquid epoxy (Lyco-Pox 103, Lycochem. Ger.) with the second component (1:1 by weight). After homogenization, epoxy hardener was added. The mixture is left for 72 hrs to complete crosslinking.

Instrumentation:

Differential thermal analysis (DTA) thermograms were recorded using a home-made apparatus designed according to reference [11] and calibrated by standard PVC sample. IR spectra were recorded on Pye-Unicam SP-2000 spectrometer with KBr pellets.

Results and Discussion:

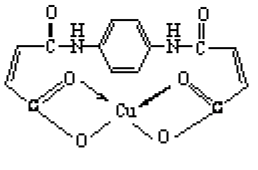
Table 1 shows the melting points and the important IR spectral bands of amic acids (ligands) and their copper complexes. Amic acids show characteristic bands around 3321-3250 cm^{-1} (acidic –OH) and 1610-1640 cm^{-1} (olifinic group) and 1710-1720 cm^{-1} (carbonyl group).

Table 1: Important IR absorptions (cm^{-1}) and melting points of amic acid and their copper complexes.

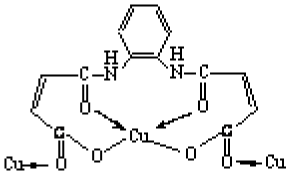
Maleamic acid	**m.p. (^{o}C)**	**-OH**	**-NH**	**-COO**	**C=C olefinic**	**aromatic**
PMA(*)	198	3314	3325	1705	1610	1432
2CMA	123	3321	3278	1713	1610	1439
3CMA	195	3316	3270	1708	1615	1420
2,6DCMA	157	3250	3260	1710	1623	1414
2BMA	112	3305	3268	1715	1626	1475
4NMA	216	3300	3265	1716	1618	1428
2HMA	185	3318	3260	1717	1621	1421
2MMA	216	3311	3267	1714	1620	1430
1,2PBMA	193	3277	3271	1718	1636	1452
1,4PBMA	227	3280	3205	1718	1635	1450
2,5TBMA	203	3287	3210	1720	1637	1451
Copper complexes	**m.p. (^{o}C)**	**-NH**	**-COO**	**C=O amide**	**C=C**	**aromatic**
PMCu(*)	155	3225	1690	1440	1624	1450
2CMCu	175	3235	1629	1436	1640	1456
3CMCu	173	3230	1685	1400	1644	1468
2,6DCMCu	188	3140	1671	1422	1644	1465
2BMCu	178	3150	1650	1425	1643	1480
4NMCu	243	3197	1666	1369	1647	1479
2HMCu	370	3200	1657	1375	1629	1479
2MMCu	234	3190	1685	1442	1648	1480
1,2PBMCu	302	3215	1680	1490	1650	1470
1,4PBMCu	325	3210	1642	1450	1640	1476
2,5TBMCu	272	3220	1675	1488	1645	1487

(*) Abbreviations: PMA=N-phenyl maleamic acid, PMCu= Cu complex of PMA, and so for the other compounds.

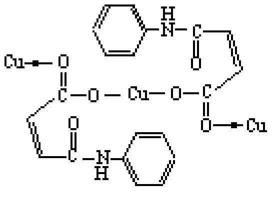
Complexation of amic acids with copper through the carbonyl groups makes the –OH absorption to disappear and shifts the other absorption bands to a near positions. Previous work shows that bisamic acids behave as tetradentate ligands leading to square planer complexes, while monobasic acids behave as a bidentate ligands [9] as shown below:



Cu(1,4-PBMA)



Cu(1,2-PBMA)



Cu(PMA)

Curing behaviour of epoxy resins:

Figure 1 shows a representative DTA thermogram of epoxy resin alone (a), epoxy-PMA (b) and epoxy-PMCu (c) blends. Analysis of these thermograms reveals that polymers in general transverse through different thermal phases [12]. T1, T2, from the figure, represent the first energy release and the maximum degree of orientation or cyclodehydration. The termination of arrangement or crosslinking are represented by T3. T4 is the temperature of phase changes like oxidation, degradation etc. which appeared at high temperatures [12, 13]. These representative temperatures for epoxy and its blends with eleven amic acids and their copper complexes are obtained from similar DTA thermograms and listed in tables 2 and 3.

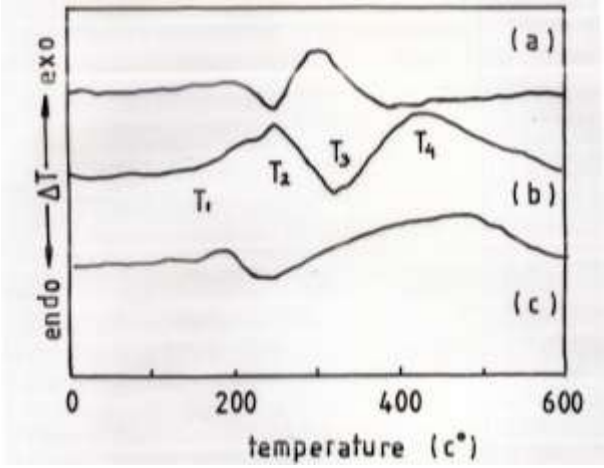


Fig. 1: DTA thermograms of:
(a) Epoxy resin (E) (**b**): E-PMA blend (**c**):E-PMCu blend

Table 2: Representative DTA temperatures for Epoxy-Amic acid blends

Blend	T_1 (°C)	T_2 (exo)	T_1	T_4 (exo)
Epoxy (E)	120	220	250	310
E-PMA	115	260	320	450
E-2CMA	140	300	325	450
E-3CMA	120	190	330	450
E-2,6DCMA	120	350	375	450
E-2BMA	120	180	330	420
E-4NMA	105	180	250	420
E-2HMA	100	125	300	430
E-2MMA	100	150	200	450
E-1,2PBMA	110	200	270	475
E-1,4PBMA	110	180	350	510
E-2,5TBMA	100	130	315	440

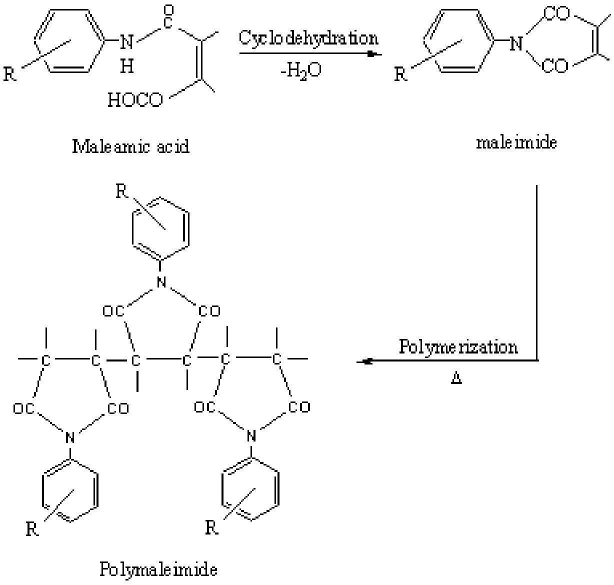
Table 3: Representative DTA temperatures for Epoxy-Copper/Amic acid complex blends

Blend	T_1 (°C)	T_2 (exo)	T_3	T_4 (exo)
E-PMCu	135	180	260	480
E-2CMCu	170	310	320	480
E-3CMCu	140	250	320	450
E-2,6DCMCu	130	230	360	460
E-2BMCu	130	150	250	420
E-4NMCu	110	170	380	420
E-2HMCu	130	160	390	490
E-2MMCu	110	140	200	490
E-1,2PBMCu	110	150	245	400
E-1,4PBMCu	110	155	270	420
E-2,5TBMCu	115	150	300	400

DTA of Epoxy- Maleamic acid blends:

Analysis of DTA thermogram of epoxy resin alone (fig 1a) reveals 2 exotherms at 220 and 310°C. the first belongs to partial orientation of molecules, the second to polymer oxidation [12]. The comparison of Epoxy-amic acid values with that of epoxy alone (Table 2) reveals the following conclusions:

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 belnds. The reason may be due to the interference of three effects (cyclodegydration of amic acids, polymerization through the olinific bond and orientation of the formed molecules:



2. The lower values of oxidation peak (T_4) noticed in the blends containing Br, NO_2 and OH. On the contrary, the maximum values of T_4 is obsereed in bisamic acid-epoxy blends as follows:

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

DTA of Epoxy-Cu/amic acid blends

The comparison of DTA values of copper containing blends (Table 3) with their isomers without copper (Table 2) shows the following notes:

1. Advancing of T_1 to higher values in the blends containing monobasic acids while those containing dibasic acids are not affected.
2. T_2 and T_3 show small intensities and shifted, in general, to lower values.
3. Creep of T_4 to higher values for most monoacid copper blends and to lower positions for diacid once as shown:

2MMCu ~ 2HMCu > PMCu ~ 2,6DCMCu > 3CMCu ~ 2BMCu ~ 4NMCu ~ 1,4PBMCu > 1,2PBMCu ~ 2,5TBMCu

To investigate the prementioned results, we have to note that all blends composed of two polymers. The first is the fixed epoxy resin while the second is a changeable polymer (11 maleamic acids and their copper complexes). Such blends are synthesised by interpentrating of the second component through the epoxy network. The new structure changes the thermal properties of epoxy resin and causes its (T) values to change their positions. The exotherm (T_4) has a special importance because it represents the beginning of oxidation and degradation of the resin. Higher values of T_4 reflect high thermal stability of this polymer. The minimum T_4 values are observed in the blends containing Br and NO_2. Such result may be related to electron-withdrawing nature of these substituents. On the contrary, the presence of OH and Me substituents enhances T_4 to high values. As well as, the presence of metal (Cu) in the blend show the same effect especially when complexed with monobasic acids. While lower T_4 values observed in bisamic acid/Cu complexes may be due to the bulky complex which causes a depression in network density. The decrease in polymer density lower its packing and affects its thermal and mechanical properties negatively [14].

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التحليل الحراري التفاضلي المقارن لسبائك راتنج الايبوكسي مع حوامض الاميك ومعقداتها النحاسية

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الملخص:

يشتمل البحث على دراسة حرارية تفاضلية مقارنة لمجموعة من سبائك راتنج الايبوكسي مع أحد عشر نوعاً من حوامض الاميك الأحادية والثنائية المجموعة الكاربوكسيلية وكذلك مع معقداتها مع النحاس. أشارت الدراسة أن معظم السبائك أعطت انبعاثين حراريين كبيرين T_2 و T_4 في درجات حرارية أعلى مما هي في حالة راتنج الايبوكسي منفرداً. كما لوحظ أن قيم T_1 و T_4 في السبائك الحاوية على فلز النحاس مع حامض أحادي أعلى من نظائرها المحتوية على الفلز مع حامض ثنائي المجموعة. كما أشارت الدراسة أن وجود النحاس في السبائك يحرف قيم T_4، والتي تمثل انبعاث الأكسدة، إلى درجات حرارية عالية نسبياً.