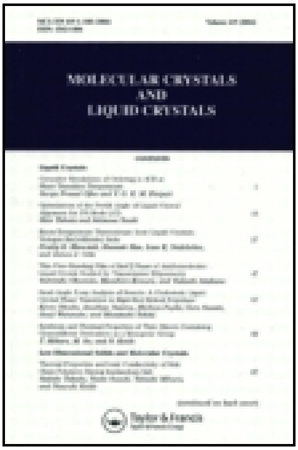

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Thermal Aging Tests Of the Composites Based On Epoxy Modified Poly-(Amine-Dimaleimides)

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THERMAL AGING TESTS OF THE COMPOSITES BASED ON EPOXY MODIFIED POLY-(AMINE-DIMALEIMIDES)

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The paper presents some accelerated thermal aging tests of the electrical insulating composites based on glass fabrics and cross-linked polymers obtained by the nucleophilic polyaddition between 4,4-dimaleimide-di-phenyl-methane (DMI), 4,4′-di-amine-di-phenyl-methane (DDM), 4,4′-di-amine-di-phenyl-sulphone (DDS) and epoxy resins.

The cross-linked polymers themselves, like disks specimens or powders, were tested too.

The results of the accelerated thermal aging test of these composites materials and those of the rigid laminated sheets STRATITEX S680 composites, based on DMI and DDM, qualified for the insulating class H (180°C), accordingly to IEC 216 standard test method, were compared.

It was observed that the polymer obtained from DMI and DDS shows the highest thermal stability, while some polymers obtained from DMI, DDS and epoxy novolac resin (Novox), show a better thermal stability as the polymer based on DMI and DDM.

Keywords: composites materials; epoxy modified poly-(amine-dimaleinimides); thermal aging tests; mechanical properties

INTRODUCTION

The main researches in Romania, in the field of poly-maleimides, in Institute of Macromolecular Chemistry–Petru Poni Iassy have been developed [1,2,4,6]. The best known materials obtained from dimaleimides were the rigid laminated sheets STRATITEX S680 and MOLDIMID type moulding compounds.

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STRATITEX S680 based on glass cloths and poly-(amine-dimaleimides) for class H (180°C) were qualified according to IEC 216 standard test method. Since the technological problems (the toxicity of the polar solvents, low storage life of prepreg) and small composites quantities required on the market, the production was stopped.

The research resumed in ICPE in the field of the electrical insulating prepregs for electrical traction engines, revealed some results regarding the use of usual solvents with low toxicity and the achievement of the impregnating varnishes and prepregs with a long storage life. Also the thermal stability of the poly-amine-dimaleimides was analysed.

Surprisingly, the composite based on, poly-(amine-dimaleimides) low temperature indexes (IT 20 kh) presented (last test of prepregs dated in 1987).

Thus, STRATITEX S680 had the followings IT 20 kh: 177°C (for 10% weight loss), 180°C (for 50% of initial flexural modulus, 182°C (for 50% of initial flexural modulus).

The prepregs for STRATITEX S680 had IT 20 kh: 145°C (for 10% weight loss) and 144°C (for 50% initial dielectric strength).

EXPERIMENTAL

The following materials were used:

- glass fabric E 020 Z 6040 (FIROS Company, Bucharest), with thickness of 0,18 ± 10% mm, specific weight 205 ± 10 g/sq.m and 0,5–0,6% γ-aminesilane as finishing agent (Z6040);
- dimaleimide (DMI) with the melting point (mp) of about 155°C (Institute P. Poni Iassy);
- epoxy novolac type resin (Novox, Policolor Company, Bucharest) with epoxy equivalent of 208 g;
- bisphenol A glycidyl ether type epoxy resin (DINOX 010 S, Policolor Company) with epoxy equivalent of 202 g;
- diaminodiphenyl methane with mp 89–91°C (Araldite HT 972, Ciba-Geigy);
- Diaminodiphenyl sulphone, with mp 167–170°C (Araldite HT 976, Ciba Geigy).

From these materials, prepregs, laminated sheets, polymer disks specimens and powders were prepared.

The prepregs, by the glass fabric impregnation were obtained. The drying cycles were established by the resin gel point, volatile contents and flow test. The prepreg storage at the room temperature in polyethylene bags was made.

The rigid laminated sheets were obtained by hot pressing between the two metallic plates or by hot pressing in special mould.

The pressing cycle was: 1 h/160°C + 1 h/180°C + 1 h/200°C, pressure of 2 MPa. Some of the plates and testing specimens 48 h/200 ± 2°C, in electrical ovens were post cured.

Besides the composites, the polymer specimens, by hot mixing of the monomers at about 150°C, casting in a hot glass tubes and hot curing were obtained.

The polymeric specimens for the thermal aging as small disk (diameter of 13–14 mm, thickness of about 3 mm) or powders (file dust) were prepared.

Accelerated aging tests in isothermal conditions in special ovens with and without air reciclation were carried out.

RESULTS AND DISCUSSIONS

The Tables 1, 2 and 3 present some properties of the prepregs and laminated sheets in initial state.

In the Table 2 and 3, the properties of the rigid laminated sheets with those of STRATITEX S680, IEC 60893 values of PIGC 301, epoxy laminate for class H, Isoval 11/200 (Isovolta) and the laminated specimens obtained by hot pressing of the tape Isola 251.70, were compared [3,5,7].

The four types of epoxy modified poly-(aminedimaleimides) composites are: P(L)-50-D based on 50% DMI, DDM, and Dinox 010S, and P(L)-60-S based on 60% DMI, DDS and Novox.

The high flexural strengths of the L-60-S at 180°C and 250°C, after postcuring, reveal the low reactivity and sterical hindrance in the thermoset cross-linking.

TABLE 1 The Properties of Prepregs

No	Property	Units	Prepreg type	
			P-50-D	P-60-S
1	Thickness	Mm	0.250	0.225
2	Specific weight	g/sq.m	292	273
3	Thickness of glass cloths	Mm	0.19	0.185
4	Specific weight of glass cloths	g/sq.m	204	199
5	Resin content by weighting	%	31.6	28.1
6	Resin content by burning (1 h/600°C)	%	30.8	27.2
7	Volatile content (15 min./160 ± 2°C)	%	1.6	0.37
8	Flow test (10 min./160 ± 2°C, 2 Mpa)	%	15	12

TABLE 2 The Properties of Laminates

			Laminate tipes		
No	Property	Units	STRATITEX S680 (STAS)	L-50-D	L-60-S
1	Density	g/cm^3	1.8–2.0	1.92	1.96
2	Tensile strength	MPa	220	317	305
3	Flexural strength at:				
	23°C	Mpa	350	415	385
	180°C		120	250	–
	200°C			200	–
4	Flexural strength after postcuring ($48\,h/200 \pm 2$°C) at				
	180°C	Mpa	–	305	360
	200°C		–	216	345
5	Insulating resistance 24 h/23°C/water	Ohm	5×10^{10}	9×10^{11}	$3{,}5 \times 10^{12}$
6	Dielectric strength	kV/mm	–	24	22
7	Water absorption (1 h/100°C)	mg	–	32	36
8	Resin content (1 h/600°C)	%	–	28	26
9	Thickness	mm	–	1.92	1,96

Since the low reactivity and high flow resin, the composites prepared from DMI and DDS only, were not representative for the polymer type.

Some thermal aging results of the composites in ovens with air reciclation in Table 4 were presented.

The good results of the prepreg P-60-S hot pressed at 0,35 mm thickness were revealed.

In the Table 5 the thermal aging results of the composites without air reciclation were presented.

Two other types of composites: L-30-D and L-40-D with a lower DMI content (30; 40%) were tested.

The thermal aging results of the polymer disks in the Table 6 and the results of the polymer powders in Table 7 were presented.

A general conclusion of the accelerated thermal aging tests was the lower thermal stability of the poly-(amine-dimaleimides) as the aromatic polyimides and some thermosets based on class H (180°C) epoxy resins.

The weak thermal points of poly-(amine-dimaleimides) are the followings: the tertiary carbon, the amine groups and the aliphatic cycles. The sterical hindrance in the cross linking reaction are important too.

TABLE 3 Flexural Strength of Some Laminated Sheets

		Imposed flexural strength (MPa)						
		Obtained after pressing			After postcuring			
No	Laminated type		23°C	180°C	200°C	23°C	180°C	200°C
1	STRATITEX	STAS	300	120	–	–	–	–
	S680	8144	>400	>300	–	–	–	–
2	Laminated sheet	IEC	400	–	300	–	–	–
	PIGC 301	60893	–	–	–	–	–	–
3	ISOVAL 11/200[1]	Prospect	400	150	–	–	–	–
			–	–	–	–	–	–
4	ISOLA 251.70[2]	–	–	–	–	–	–	–
			292	195	–	–	–	–
5	L-50-D	–	–	–	–	–	–	–
			416	215	200	395	305	216
6	L-60-S	–	–	–	–	–	–	–
			395	186	–	385	360	345

[1] Epoxy laminated sheets for class H (180°C) made by ISOVOLTA (Austria).
[2] Laminated specimens obtained by hot pressing in mould of the tape 251.70 (Von Roll Isola Group) used in Romania for the insulation of class F (155°C) traction motors.

TABLE 4 Thermal Aging of the Composites in Air Reciclation Ovens

		Thermal life (h)			Activation energy, E	
Type of the composite	Δm(%)	210°C	234°C	E/R	(kcal/mol)	IT 20 kh°C
Rigid laminate	3,5	1125	155	20,2	40,2	179
ISOLA 2,98 mm	5,0	1584	601	9,88	19,6	157
	10,0	3121	1433	7,94	15,8	161
Epoxy prepress 0,36 mm	3,5	249	130	6,63	13,2	93
	5,0	503	245	7,34	14,6	116
	10,0	1205	614	6,94	13,8	131
P-60-S 0,35 mm	3,5	594	240	9,06	18,0	134
	5,0	850	339	9,34	18,6	142
	10,0	2317	758	11,4	22,6	169
L-50-D 1,40 mm	3,5	1509	764	9,75	19,4	160
	5,0	2767	1304	7,52	14,9	155
	10,0	–	–	–	–	–
L-60-S 1,57 mm	3,5	893	349	9,54	19,0	144
	5,0	1317	516	9,56	19,0	152
	10,0	4125	1671	9,21	18,3	173

TABLE 5 Thermal Aging of the Composites in No Air Reciclation Ovens

		Thermal life (h)				Activation energy, E (Kcal/mol)			IT 20 kh (°C)		
Type of composites	Δm (%)	212°C	235°C	250°C	271°C	212–235°C	235–250°C	250–270°C	212–235°C	235–250°C	250–270°C
Rigid laminate	3,5	1617	243	119	33	40,3	25,1	34,5	185	158	180
ISOLA	5,0	2377	387	193	53	38,6	24,5	34,8	187	164	186
	10,0	–	989	584	184	–	18,5	31,1	–	163	193
L-30-D-S	3,5	1904	475	211	63	29,5	28,5	32,5	177	176	184
	5,0	2859	1075	483	137	20,8	28,1	33,9	172	187	196
L-40-D	3,5	1439	440	253	72	21,7	19,5	33,8	161	151	188
	5,0	2207	802	557	183	20,1	18,1	30,0	166	132	192
L-50-D	3,5	1543	484	363	179	28,5	–	–	173	–	–
	5,0	2267	706	823	304	24,8	–	–	174	–	–
L-60-D	3,5	1163	411	145	88	22,1	36,6	13,4	159	186	–
	5,0	1564	555	208	126	22,0	34,5	13,5	163	187	–

TABLE 6 Thermal Aging of the Polymer Disks in Air Reciclation Ovens

Polymer type	Δm %	Thermal life (h) 210°C	Thermal life (h) 232°C	Activation energy (kcal/mol)	IT 20 kh (°C)
T-78-D	5,0	554	–	–	–
	10,0	1160	–	–	–
	15,0	1840	–	–	–
T-30-D-S	5,0	751	134	38,0	173
	10,0	3869	875	32,7	187
	15,0	–	2480	–	–
T-40-D	5,0	845	140	39,6	176
	10,0	4039	1147	27,7	185
	15,0	–	2971	–	–
T-60-D	5,0	1617	513	22,5	163
	10,0	5683	2271	26,7	189
	15,0	–	–	–	–
T-60-S	5,0	1509	583	20,9	159
	10,0	3326	1693	14,9	167
	15,0	–	2293	–	–

The epoxy modified poly-(amine-dimaleimide) keep these thermal weakness.

The use of some epoxy resins for class H (180°C) can surely ameliorate these behaviour.

The thermal weakness of all poly-(amine-dimaleimides) unmodified or epoxy modified at high temperature are better revealed.

The thermal aging of the polymer powders (Table 7) in the range of not so high temperatures (190–210°C) reveal the better thermal stability of T-60-S as that of the T-78-D, unmodified with epoxy resins.

CONCLUSIONS

Some composites based on epoxy modified poly (amine-dimaleimides), as a result of their properties for electrical insulation can be used [8,9].

Thus, the prepreg P-50-D, very flexible, storage stable with a good hot resin flow, as insulation for class F (155°C) traction electrical motors are recommended.

The rigid laminated sheets L-60-S type based on BMI (60%), DDS and Novox epoxy resin has the flexural strength at 200°C, better than IEC requirements.

After the accelerated thermal aging tests of this laminate, a qualification for class H (180°C) after actual IEC 216, which requires four testing

TABLE 7 Thermal Aging of the Polymer Powders in Air Reciclation Ovens

		Thermal life (h) at			Activation energy (kcal/mol)			IT (20 kh)		
Polymer type	m %	190°C	210°C	232°C	190–210°C	210–232°C	190–232°C	190–210°C	210–232°C	190–232°C
T-78-D*	10,0	555	161	48	27	27	27	140	138	139
	15,0	807	294	92	22	26	24	136	144	140
	20,0	1486	489	173	25	23	24	140	145	142
	25,0	2158	863	275	21	25	23	148	158	153
T-30-D-S	10,0	1078	422	139	21	25	23	137	146	142
	15,0	1795	732	234	20	25	23	144	156	150
	20,0	2426	1016	350	19	24	21	148	157	152
	25,0	–	1360	488	–	23	–	–	160	–
T-40-D	10,0	–	–	–	31	–	–	141	–	–
	15,0	370	90	–	28	–	–	143	141	142
	20,0	608	170	–	24	–	–	139	143	141
	25,0	842	303	–	24	–	–	–	139	–
T-60-D	10,0	257	77	20	27	–	–	139	–	–
	15,0	467	134	38	25	28	25	140	138	139
	20,0	748	245	68	25	28	25	139	147	143
	25,0	1026	381	125	–	25	–	139	145	143
T-60-S	10,0	701	115	50	40	18	–	157	107	–
	15,0	1246	310	158	31	23	27	155	139	147
	20,0	157	612	230	25	22	23	155	145	150
	25,0	2486	956	320	21	24	23	152	158	155

*DMI percent in thermoset.

temperatures and a lot of standardised tesing specimens, can be surely obtained.

After the accelerated thermal aging tests the highest thermal stability of the DMI-DDS polymer, and the better thermal stability of the polymer DMI–DDS–Novox (60%DMI), as that of the DMI–DDM polymers (70–78% DMI) were observed.

REFERENCES

[1] Mandric, Gh. (1983). Romanian Patent, 78.081.
[2] Constantinescu, M. (1976). Romanian Patent, 59.672.
[3] Rhone–Poulenc's high performance plastics for 200°C and over (bismaleimide resin kerimide 601 and glass cloths.
[4] Mandric, Gh., Bruma, M., & Stoicescu, L. (1977). Progrese in domeniul polimerilor organici termostabili. *Materiale Plastice*, *14*(1), 5–11.
[5] Prospect CIBA–GEIGY – Resine pour stratifies a base de dimaleinimide et diallye bisphenol A.
[6] Pecincu, S., Taranu, V., & Sava, M. (1993). Lacuri de impregnare pe baza rasinilor amino-bismaleimidice utilizate la obtinerea de stratificate termostabile. *Materiale Plastice*, *30*(1), 23–27.
[7] IEC 893-3-7/1994 – Specification for industrial rigid laminated sheets based on thermo-setting resins for electrical purposes – Requirements for rigid laminated sheets based on polyimide resins.
[8] Stere, E. (1996). Prepreguri si stratificate electroizolante pe baza de poliaminobismale-imide, *Lucrarile ICPE*, *(3–4)*, 9–14.
[9] Cotescu, S. L., Stere, E., & Ionescu, A. (2001). The thermal properties of the poly-(amine-dimaleimides), The 2nd National Conference "New Research trends in material science" ARM–2, Constanta, Romania, 24–26 September.