Diels–Alder Adducts as Epoxy Resin Hardeners

TADEUSZ MATYNIA, *Institute of Chemistry, Maria Curie-Skłodowska University, 20-031 Lublin, Poland*

Synopsis

The influence of hydroxyl modifiers on the properties of Diels–Alder adducts—terpene hydrocarbons with maleic anhydride—was studied. The mechanical, thermal, and dielectric properties of the composition of Epidian 5 epoxy resin hardened with an adduct modified by ethylene glycol, propylene glycol, dipropylene glycol, glycerin, or hexanetriol are described.

INTRODUCTION

Diels–Alder products, among others, are the products of the reaction of maleic anhydride with various dienes.[1,2] They belong to the acid anhydride group of hardeners of epoxy resins. The above products are comprised of methylendomethylenetetrahydrophthalic anhydride (the so-called methyl nadic anhydride),[3] chlorotetrahydrophthalic anhydride,[4] maleic anhydride adducts with colophony,[5] hexachlorocyclopentadiene adduct with tetrahydrophthalic anhydride,[6] and maleic anhydride adducts with terpene hydrocarbons.[7]

Some adducts serve as liquid condensation products at room temperature, for example, the maleic anhydride adduct with terpene hydrocarbons modified with glycerin.[8,9] This paper reports the influence of hydroxyl modifiers on the properties of the maleic anhydride adduct with terpene hydrocarbons and on the properties of epoxy compositions hardened with the modified adducts.

EXPERIMENTAL

Materials

The materials used in these studies were Diels–Alder adducts of terpene hydrocarbons with maleic anhydride (BTM),[8] epoxy resin with epoxy number LE_p = 0.5 gram-equivalent of epoxy groups (100 g type Epidian 5, Chemical Plant Sarzyna), DMP-30 accelerator (Rohm and Haas), ethylene glycol (Veb Jenapharm Laborchemie Apolda), dipropylene glycol, and hexanetriol (Merck).

Modification of Diels–Alder Adduct

The modification of the Diels–Alder adduct of terpene hydrocarbons with maleic anhydride consisted of heating the adduct at 130°C for 3 hr with the glycols and hexanetriol.[8,9] A 0.163 gram-equivalent of the compound containing hydroxyl groups was used per 100 g adduct. Some physical properties of the modified adducts are presented in Table I and illustrated graphically in Figure 1.

Journal of Applied Polymer Science, Vol. 25, 1–13 (1980)

0021-8995/80/0025-0001$01.00

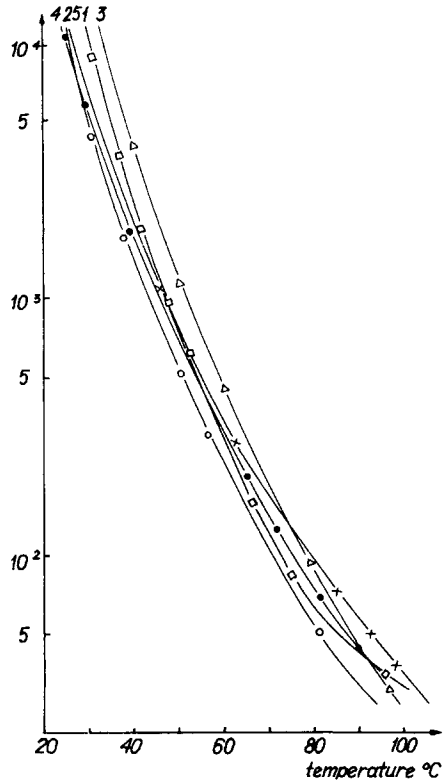

Fig. 1. Viscosity of modified terpene–maleic anhydride adducts in relation to temperature, composition, and designations according to Table I.

TABLE I
Chemical Composition (in Parts by Weight) and Physical and Chemical Properties of Modified Adducts-Hardeners

Chemical compositions (parts by weight) and physical and chemical properties	BTMG-1 (1)	BTMG-2 (2)	BTMG-3 (3)	BTMG (4)	BTMG-4 (5)
Adducts of terpene with					
Maleic anhydride (BTM)	100	100	100	100	100
Ethylene glycol	5.0	—	—	—	—
Propylene glycol	—	6.1	—	—	—
Dipropylene glycol	—	—	10	—	—
Glycerin	—	—	—	5.0	—
Hexanetriol	—	—	—	—	7.3
Density at 20°C, g/cm³	1.15	1.15	1.14	1.14	1.15
Viscosity, cP					
at 25°C	19,200	9,000	33,630	33,000	11,538
at 50°C	660	493	1,185	1,000	700
at 100°C	24	21	19	30	34
Breakdown coefficient n_p^{20}	1.512	1.510	1.509	1.513	1.513
Color in iodic scale	35	76	16–21	35	76

TABLE II
Composition (in Parts by Weight), Hardening Conditions, and Properties of Hardened Compositions

Composition	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Hardener BTMG-1	100	100	100	—	—	—	—	—	—	—	—	—	—	—
Hardener BTMG-2	—	—	—	100	100	100	—	—	—	—	—	—	—	—
Hardener BTMG-3	—	—	—	—	—	—	100	100	100	—	—	—	—	—
Hardener BTMG	—	—	—	—	—	—	—	—	—	100	100	—	—	—
Hardener BTMG-4	—	—	—	—	—	—	—	—	—	—	—	100	100	100
Epoxy resin Epidian 5	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Accelerator DMP-30	1.0	0.6	0.3	1.0	0.6	0.3	1.0	0.6	0.3	1.0	0.6	1.0	0.6	0.3
Hardening temp.°C/time, min	100/16	100/16	100/16	100/16	100/16	100/16	100/16	100/16	100/16	100/16	100/16	100/16	100/16	100/16
Improved hardening temp.,°C/time, min	130/24	130/24	130/24	130/24	130/24	130/24	130/24	130/24	130/24	130/24	130/24	130/24	130/24	130/24
Vicathermal resistance after Martens T_M,°C	108	104	—	96	90	—	105	96	—	118	97	115	103	—
Glass temp. T_g,°C	116	123	—	110	106	—	113	104	—	117	87	114	100	—
Softening temp. Vicat T_V,°C	153	115	—	140	117	—	120	118	—	124	115	139	152	—
Bending strength, kg/cm^2	1222	1135	—	1197	1127	—	1089	1162	—	959	1092	—	—	—
Charpy impact,[a] kg cm/cm^2	26.3	27.8	—	29.7	27.1	—	25.6	22.6	—	18.8	15.4	26.3	21.3	—

[a] See ref. 4.

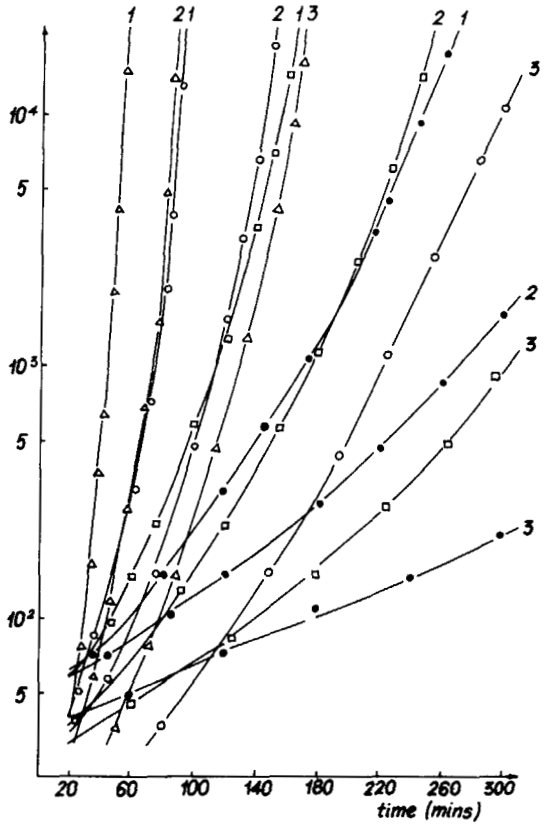

Fig. 2 Curves of viscosity variations during hardening of compositions 1, 2, and 3. Composition components and designations according to Table II: (△) 120°C; (○) 110°C; (□) 100°C; (●) 90°C.

Testing Procedures

Viscosity measurements, dependent upon temperature and time, were made with a rheoviscosimeter of type RV.

Bending temperature under a load according to Martens was determined in an apparatus of type FWM. Shaped pieces measuring 120 × 15 × 10 mm were used. Softening temperature after Vicat was measured in an apparatus of type FWV. The glass transition temperature T_g was determined by means of a modified Heppler consistometer, at a pressure of 9.81 10^5 N/m^2, using cylinders of diameter 11.3 × 8 mm.

Thermogravimetric analyses were made in atmospheric air by means of a MOM apparatus. A 50-mg sample was tested up to 500°C while programmed at 10°C/min.

The following measurements were also performed: coefficient of dielectric loss $t_g\delta$, dielectric permeability ξ_r, specific slant resistance ρ_r, and specific surface resistance ρ_s. Dielectric strength was measured in oil with an electric current of 50 Hz by using an electrode having a 25-mm upper diameter and a 75-mm lower diameter.

Endurance testing for static bending was performed by means of an apparatus

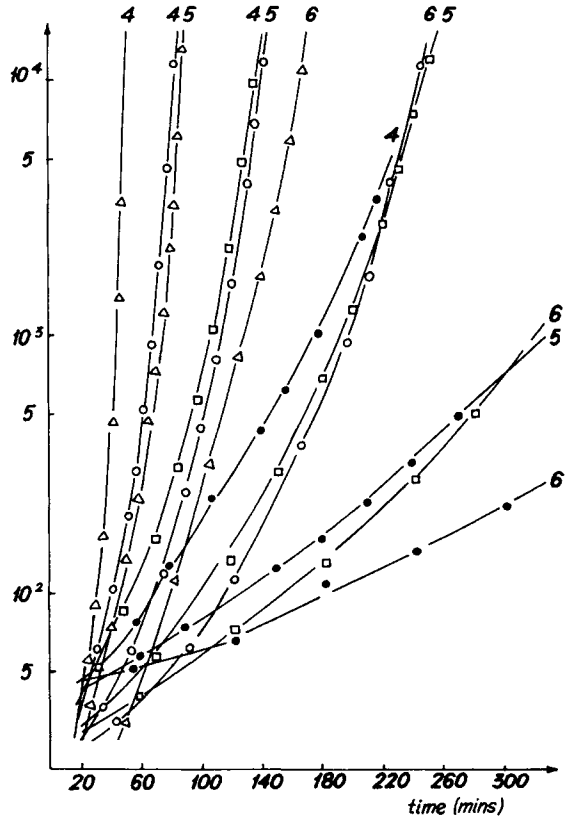

Fig. 3. Curves of the viscosity variations during hardening of compositions 4, 5, and 6. Composition components and designations according to Table II: (△) 120°C; (○) 110°C; (□) 100°C; (●) 90°C.

of type FU 1000e. Impact testing, according to Charpy's method, was accomplished by means of a drop hammer using shaped pieces measuring 120 × 15 × 10 mm.

RESULTS AND DISCUSSION

The viscosity was determined for the Diels–Alder adducts of terpene hydrocarbons with maleic anhydride modified with compounds containing hydroxyl groups such as ethylene, propylene, and dipropylene glycol, as well as glycerin and hexanetriol. The viscosity of the modified adducts depends largely upon the kind of the hydroxyl compound used for the modification (Fig. 1). The lowest viscosity at room temperature was found in the adduct modified with propylene glycol, while higher viscosities were observed for adducts with glycerin or with dipropylene glycol.

From the viscosity curves during hardening at 90, 100, 110, and 120°C for compositions consisting of Epidian 5 resin, amine accelerator DMP-30, and the above-mentioned modified adducts (Table I), it appears that the compositions (Table II) are characterized by suitable technological and processing properties in a wide temperature range. The time of viscosity increase up to 1000 cP at 100

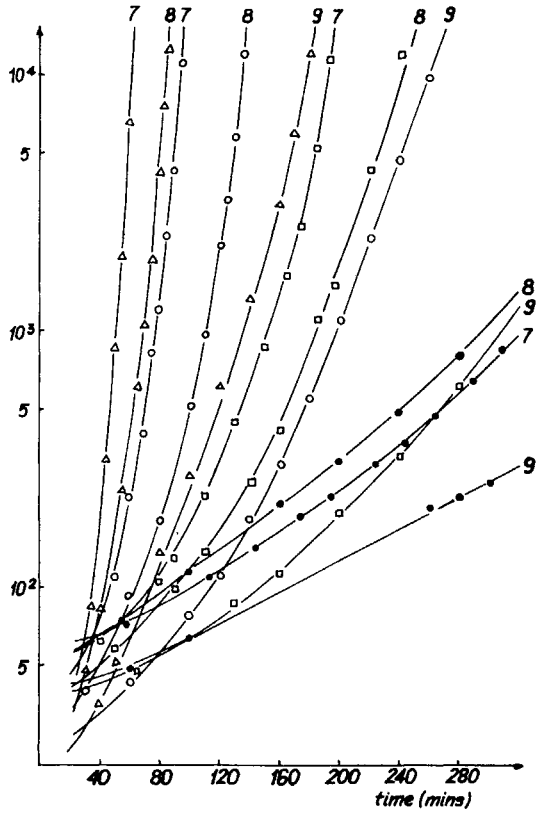

Fig. 4. Curves of the viscosity variations during hardening of compositions 7, 8, and 9. Composition components and designations according to Table II: (△) 120°C; (○) 110°C; (□) 100°C; (●) 90°C.

and 120°C of the curves of viscosity variations (Figs. 2–5) was determined as a function of the amine accelerator (Fig. 6).

The rate of polyaddition at 100°C depends to a large extent upon the amount of the accelerator. The rate of polyaddition of the composition depends on the nature of the hydroxyl modifier (Fig. 6).

The compositions containing 0.3 and 0.6 parts by weight of the amine accelerator yield the following series arranged according to reactivity: propylene glycol, ethylene glycol, dipropylene glycol, glycerin, and hexanetriol. With the use of 1.0 part by weight of the accelerator, the most reactive composition contains the adduct modified with dipropyl glycol. The mechanical properties of impact and bending strength show that maximum values are obtained for compositions containing the adduct modified with ethylene or propylene glycol (Table II).

The thermal properties of the glass transition temperature, determined from the thermomechanical curves (Fig. 7), and softening temperature after Vicat have been analyzed (Table II).

Thermogravimetric analyses demonstrate the good thermal stability of the compositions (Figs. 9–12). Rapid decomposition occurs at 270–280°C. Comparing the dielectric properties, such as breakdown strength, it appears that the highest values are attained with the compositions containing propylene glycol (Fig. 8).

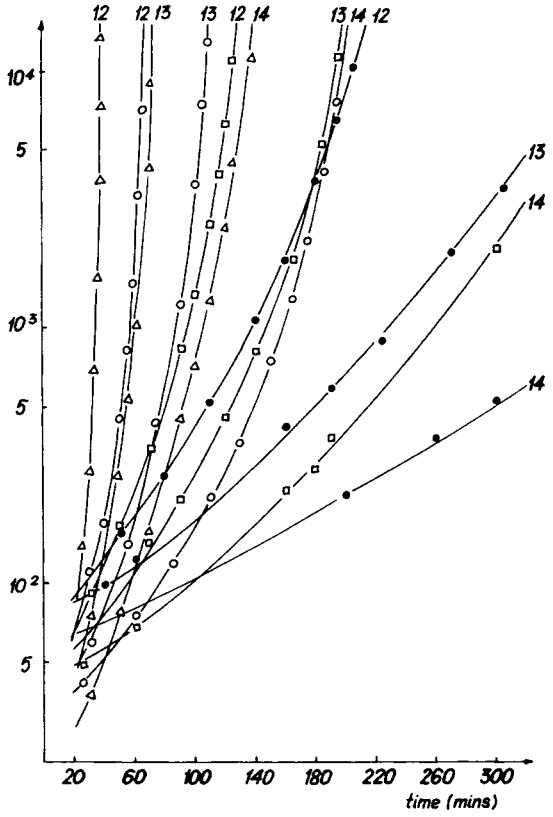

Fig. 5. Curves of the viscosity variations during hardening of compositions 12, 13, and 14. Composition components and designations according to Table II: (△) 120°C; (○) 110°C; (□) 100°C; (●) 90°C.

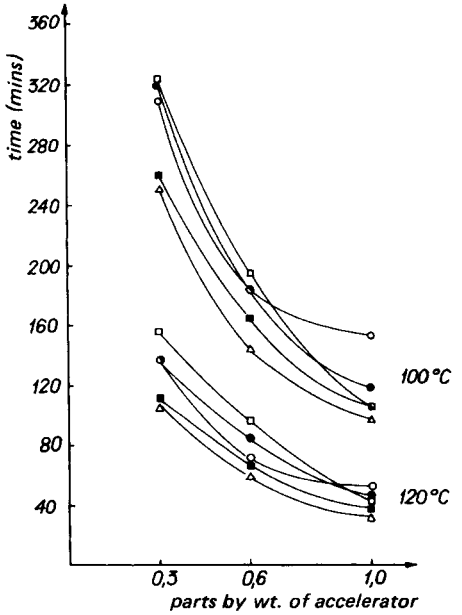

Fig. 6. Changes of viscosity increase with time dependent on accelerator amount. Parts by weight of the accelerator.

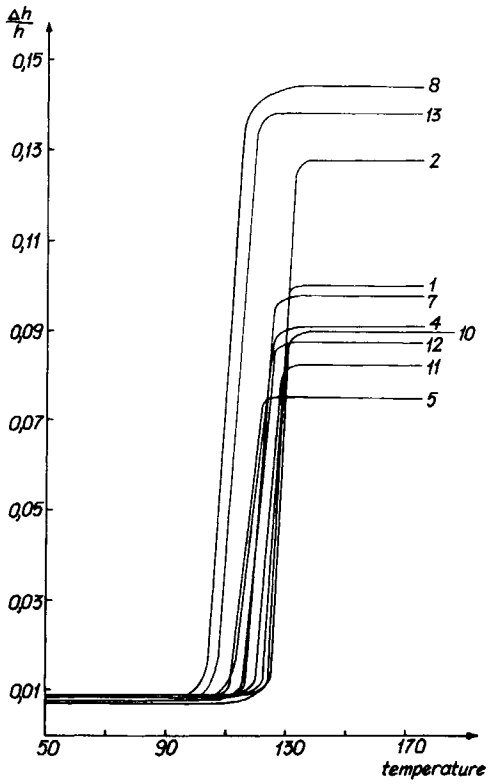

Fig. 7. Thermomechanical curves of the compositions studied. Composition components and designations according to Table II.

Measurements of specific slant and surface resistance (Table III) and dielectric loss coefficient (Table IV) were performed. It was found that dielectric loss $t_g\delta$ in the temperature function increased with increasing glass transition temperature.

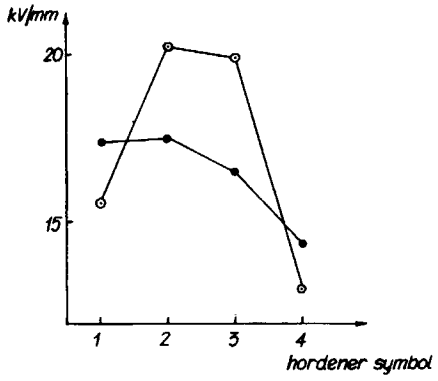

Fig. 8. Dielectric strength of the composition dependent upon the hardener used and the content of the amine accelerator. Composition components according to Tables I and II: ⊙, 0.6; ●, 1.0; parts by weight of accelerator.

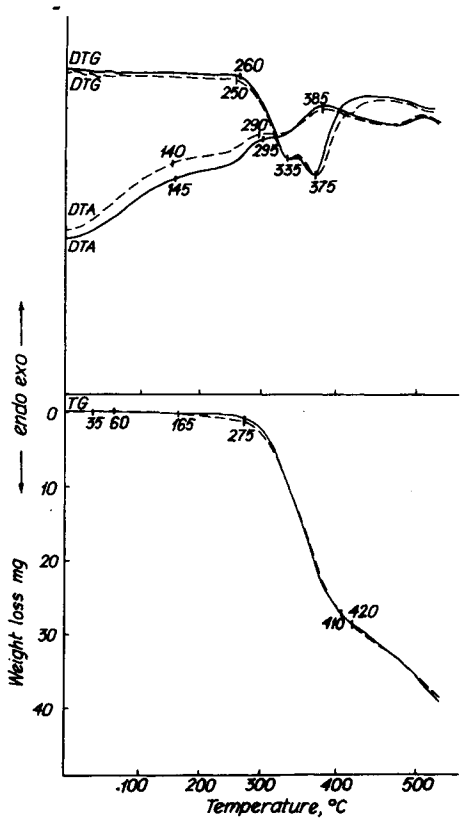

Fig. 9. Derivatogram of composition 1 (—). Derivatogram of composition 2 (---). Composition components and designations according to Table II.

CONCLUSIONS

The hydroxyl compounds studied can be used for modification of Diels–Alder adducts of terpene hydrocarbons with maleic anhydride. The compositions hardened with modified adducts are characterized by good mechanical, thermal, and dielectric properties. The best results are obtained for compositions

TABLE III
Specific Slant Resistance ρ_r and Specific Surface Resistance ρ_s[a]

Composition no.	ρ_r, Ω cm				ρ_s, Ω cm/cm
	1′	2′	5′	10′	1′
1	1.2×10^{17}	2.2×10^{17}	3.5×10^{17}	5.8×10^{17}	3.0×10^{17}
2	1.0×10^{17}	1.9×10^{17}	2.1×10^{17}	3.5×10^{17}	7.3×10^{17}
3	5.3×10^{16}	8.9×10^{16}	2.7×10^{17}	5.3×10^{17}	7.3×10^{17}
4	1.2×10^{17}	2.0×10^{17}	4.6×10^{17}	9.3×10^{17}	4.5×10^{17}
7	9.8×10^{16}	1.8×10^{17}	3.5×10^{17}	5.9×10^{17}	8.2×10^{17}
8	6.7×10^{16}	6.7×10^{16}	1.4×10^{17}	2.4×10^{17}	7.1×10^{17}
10	8.6×10^{16}	1.1×10^{17}	1.5×10^{17}	1.5×10^{17}	1.7×10^{17}
11	7.6×10^{16}	1.1×10^{17}	2.7×10^{17}	3.5×10^{17}	4.3×10^{17}

[a] From ref. 4.

TABLE IV
Coefficient of Dielectric Loss $t_g\delta$ and Dielectric Permeability ϵ Depending Upon Frequency and Temperature

Comp. no.	Temp., °C	$t_g\delta \times 10^4$			ϵ_r		
		0.06 kHz	0.1 kHz	300 kHz	0.06 kHz	0.1 kHz	300 kHz
1	20	17	19	165	3.4	3.4	3.3
	60	14	15	111	3.4	3.4	3.4
	100	156	135	78	3.4	3.4	3.3
	120	750	820	165	4.6	4.3	3.4
	180	6069	3830	480	6.6	5.3	4.2
2	20	15	16	141	3.5	3.4	3.3
	60	15	15	90	3.5	3.4	3.4
	100	246	230	78	3.5	3.5	3.4
	120	552	630	189	5.0	4.9	3.5
	180	3087	1860	420	5.0	4.7	4.4
3	20	16	17	135	3.4	3.4	3.3
	60	15	15	90	3.4	3.4	3.4
	100	420	350	60	3.4	3.4	3.3
	120	624	680	240	4.8	4.7	3.4
	180	2628	1590	207	5.0	4.7	5.8
4	20	17	19	156	3.5	3.5	3.3
	60	14	14	90	3.5	3.5	3.3
	100	210	200	72	3.5	3.5	3.3

	120	910	750	129	4.3	4.2	3.5
	180	2214	1340	216	5.0	4.9	5.9
7	20	20	22	204	3.5	3.5	3.3
	60	15	17	111	3.5	3.5	3.5
	100	468	230	48	3.6	3.6	3.5
	120	564	500	135	4.0	3.8	3.5
	180	9186	5800	750	9.5	6.7	4.3
8	20	17	19	186	3.5	3.5	3.4
	60	26	26	135	3.6	3.5	3.5
	100	87	88	33	3.5	3.5	3.4
	120	276	320	600	5.5	5.4	4.0
	180	8868	5800	600	9.3	6.7	4.6
10	20	21	23	141	3.1	3.1	3.1
	60	20	18	90	3.1	3.1	3.1
	100	23	23	59	3.1	3.1	3.1
	120	108	95	63	3.1	3.1	3.1
	180	194	200	555	4.4	4.4	3.5
11	20	16	17	138	3.1	3.1	3.1
	60	21	21	156	3.3	3.3	3.1
	100	200	180	81	3.5	3.5	3.1
	120	780	760	159	4.1	4.1	3.3
	180	882	830	675	4.5	4.5	3.9

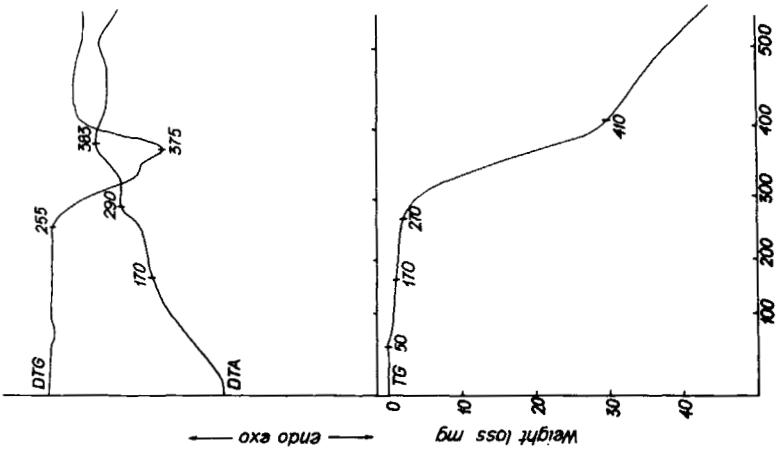

Fig. 11. Derivatogram of composition 7. Composition components and designations according to Table II.

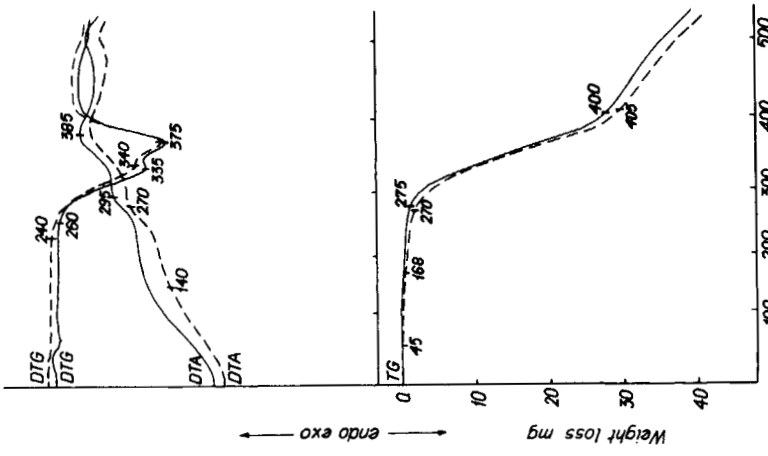

Fig. 10. Derivatogram of composition 4 (—). Derivatogram of composition 5 (- - -). Composition components and designations according to Table II.

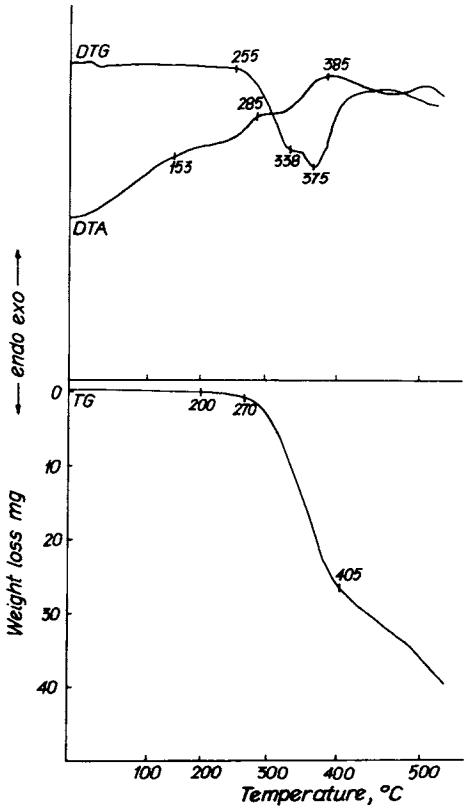

Fig. 12. Derivatogram of composition 12. Composition components and designations according to Table II.

hardened with Diels–Alder adducts modified with propylene or ethylene glycol.

Because of their physical properties, compositions composed of Epidian 5 resin Diels–Alder adducts modified with ethylene, propylene, or dipropylene glycol, as well as glycerin and hexanetriol, can be used for electro-insulating materials.

References

1. T. W. Bieleckaja, P. J. Morzuńskji, and M. F. Stecjuk, *Plast. Massy*, **6**, 23 (1973).
2. M. C. Sałachow, M. M. Gusejnob, E. M. Trejbys, and G. M. Gasanob, *Plast. Massy*, **6**, 26 (1973).
3. H. K. Weiss, *Ind. Eng. Chem.*, **49**, 1089 (1957)
4. I. Smrčka, *Plast. Hmoty Kauc.* **4**, 241 (1967).
5. H. G. Cook and I. E. Masters, US Pat. 2947711 (1960).
6. M. Dunkel, US Pat. 3417063 (1963); *Chem. Abstr.*, **70**, 38495 (1969).
7. A. M. Paquin, *Epoxydverbindungen und Epoxydharze*, Berlin, 1958, p. 315.
8. T. Matynia, *Polimery*, **9**, 404 (1976).
9. T. Matynia, PRL Pat. 93044 (1977).

Received June 30, 1978
Revised May 17, 1979