Investigation on Curing and Destruction of Crosslinked Modified Phenolformaldehyde Polymers

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Synopsis

Curing and destruction of crosslinked phenolformaldehyde polymers modified with a varying quantity of polycaprolactam were studied by means of IR and ESR spectra and by derivatography. In the curing process of the polymers, hexamethylenetetramine was found degrading, with formation of dimethyleneimine, and other groups causing spatial crosslinking of the polymers. Incorporation of nitrogen in the polymer chains was proved by means of IR spectra and elemental analysis. The activation energy of destruction was determined by the thermogravimetric curves, and it varied in the range of 25 to 32 kcal/mol. On the ground of the investigations made, it was presumed that in hardening and destruction of the polymers under study a definite role was played also by free-radical processes. An evidence of this was the presence of free radicals in the products during hardening and destruction as well as the kinetic data—the low activation energy of destruction.

INTRODUCTION

Crosslinked phenolformaldehyde polymers are highly brittle and have low dielectric properties. This is a considerable limitation to their application in the various branches of industry. Therefore, phenolformaldehyde polymers are being modified at present with polyamides to improve their physical, mechanical, and dielectric properties.[1–9]

In producing polycaprolactam, waste polymer of lower physical and mechanical properties is obtained in considerable quantities, which has not yet found its rational application. The use of this waste polycaprolactam to modify phenolformaldehyde resins is of indisputable theoretical and practical interest.

In the present report, we are publishing only a few of the results obtained from the investigations on curing and destruction of phenolformaldehyde resins modified with waste polycaprolactam.

EXPERIMENTAL

For the purpose of the investigation, six types of Novolak phenolformaldehyde resins (PFR) modified with a varying quantity of waste polycaprolactam (PC) were synthesized using hydrochloric acid as catalyst. The waste PC as powder, fibers, etc., from different technological process steps has a relative viscosity of 1.74 in sulfuric acid as solvent and a monomer content up

to 5%. The modified resins thus obtained had a softening point from 86° to 138°C determined by the ring-ball method, and free phenol from 2.4% to 8.27%.[10] They were cured with varying quantities of hexamethylenetetramine (HMTA) for 2 hr at 150°C. The deepness of hardening was determined by a gravimetric method with acetone extraction in the Soxhlet apparatus.[10]

Thermal analysis was carried out by means of a derivatograph OD-102 Paulik-Erdey[11] with simultaneous measuring of weight with time (TG), the rate of change of weight (DTG) and the differential thermal analysis curve (DTA) characterizing the change of enthalpy, using one and the same specimen in pure nitrogen. The weight of the tested polymer was 450 mg, and the average rate of heating was 5°C/min. Annealed aluminum oxide was used as a reference material. The overall activation energy of destruction was calculated from the thermogravimetric curves using the Doyle's formula.[12]

IR spectra were obtained by means of a Unicam SP-200 spectrophotometer using samples in the form of potassium chloride tablets containing 2 mg of the tested specimen for each 200 mg of potassium chloride.[13]

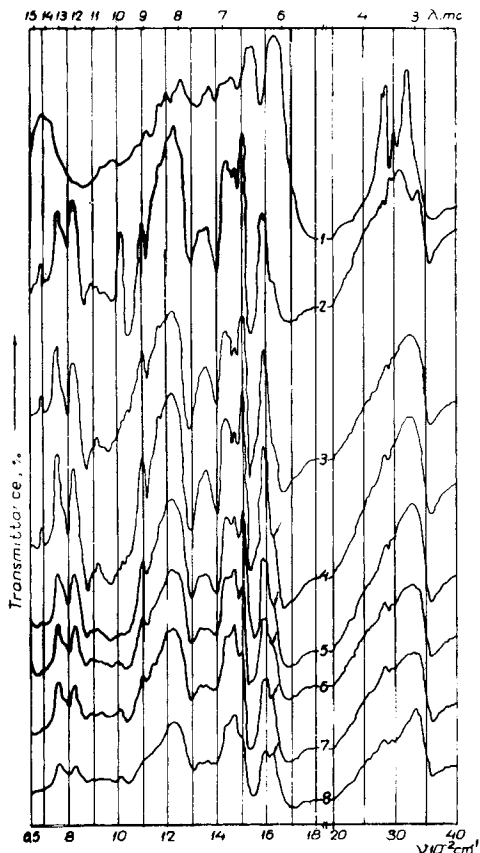EST spectra were obtained by means of a Japanese apparatus IES 3BS-X[14] with carbon as reference material.

Fig. 1. Infared spectra of PC and Novolak PFR modified with 10% PC and hardened with various quantities of HMTA: (1) PC; (2) PFR with 10% HMTA; (3) MPFR; (4) MPFR with 1% HMTA; (5) MPFR with 5% HMTA; (6) MPFR with 10% HMTA; (7) MPFR with 15% HMTA; (8) MPFR with 20% HMTA.

DISCUSSION

IR spectra were prepared (Figs. 1 and 2) for elucidating and correct interpretation of processes taking place in curing the synthetized various types of modified phenolformaldehyde resins (MPFR) with varying quantities of HMTA.

These processes can be interpreted in the following manner. The frequency range of 3500–3000 cm^{-1} corresponds to the valence vibrations of the OH group. In the initial PFR spectra (Fig. 1, curve 2), two absorption bands are clearly observed—at 3450 cm^{-1} and 3200 cm^{-1}. The absorption band at 3450 cm^{-1} is generally related to the dimeric hydrogen bond, while the band at 3200 cm^{-1} is related to the polymer hydrogen bond.[15] The high content of intermolecular hydrogen bonds formed between the —NH and OH groups results in masking the other absorption in this interval. Absorption bands at 2950 and 2860 cm^{-1} are the result of asymmetric and symmetric vibrations of —CH_3 and —CH_2 groups, and this is also confirmed by their deformative vibrations at 1380 and 1460 cm^{-1}. The results thus obtained (Fig. 2) show that the intensity of these bands grows with increasing the quantity of the modifying additive. This is a result of the increased number of —CH_2 groups in the studied polymers.
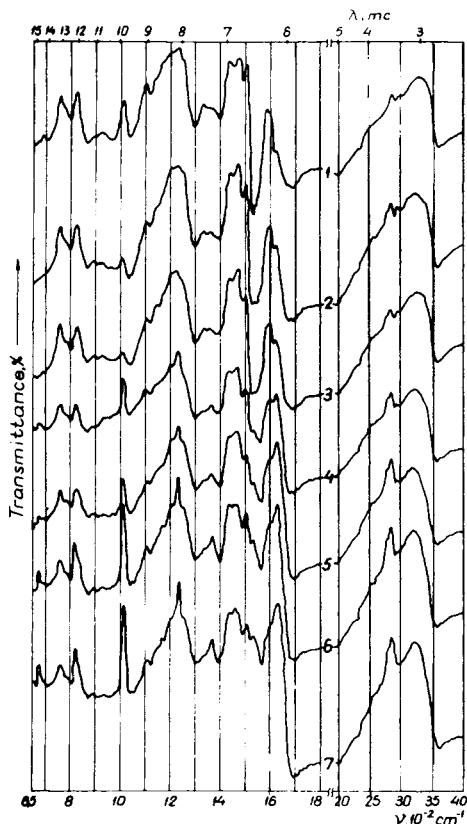

Fig. 2. Infrared spectra of Novolak PFR modified with various amounts of PC and hardened with 15% HMTA: (1) PFR; (2) MPFR with 5% PC; (3) MPFR with 10% PC; (4) MPFR with 20% PC; (5) MPFR with 30% PC; (6) MPFR with 40% PC; (7) MPFR with 50% PC.

TABLE I
Elemental Composition of Some of the Tested Polymers

Polymer no.	Type of polymer	MPFR Hardened with HMTA, %	Content of, %		
			C	H	N
1	PFR modified with 10% PC	0	76.69	6.09	2.23
2	PFR modified with 10% PC	5	77.00	7.08	3.08
3	PFR modified with 10% PC	10	73.01	6.06	4.09
4	PFR modified with 10% PC	15	73.04	6.58	6.01

A typical absorption is also observed at 1530 and 1630 cm^{-1} (known as II amide) which corresponds to the deformative vibrations of the —NH groups.[15] The absorption band at 1630–1640 cm^{-1} is due to a typical vibration of substituted amides.[16] The results obtained indicate that intensity of these bands grows with increasing the quantity of the modifying agent (Fig. 2). This is influenced also by the quantity of the added HMTA hardener (Fig. 1).

In curing the tested polymers under selected temperature conditions, HMTA degrades into dimethylenimine (—CH$_2$—NH—CH$_2$—) and other groups which cause a deeper spatial crosslinking of the polymers. The elemental analysis made (Table I) as well as the observed rise of typical absorption at 1630 cm^{-1} with increasing the quantity of HMTA (Fig. 1) are both an indication of the incorporation of nitrogen in the structure of the studied polymers.
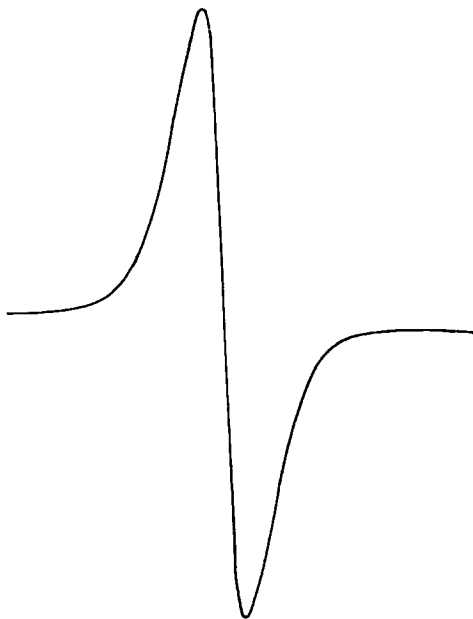

Fig. 3. ESP spectrum of PFR modified with 10% PC and hardened with 10% of HMTA.

The 1600 and 1510 cm^{-1} band typical of a phenolic nuclei is easily distinguished in all spectra.[15] The absorption band at 1270–1220 cm^{-1} corresponds to an aromatic ether bond as well as to the valence vibration of —C=O bonds.[17,18] Absorption at 1015 cm^{-1} typical of aromatic ethers is also an evidence of this. Data indicate that the intensity of these bands also considerably grows with increasing the quantity of the modifying additive (Fig. 2). This can be explained by the intensive formation of ether groups and consequently the increase of the content of spatial polymer. In support of this are also the gravimetric tests, the definite rate of curing the cross-linked MPFR being above 97%.

In all tested polymers typical absorption at 760 and 820 cm^{-1} is observed, which corresponds to the out-of-plane vibrations of the hydrogen atoms in 1,2,6- and 1,2,4,6-substituted benzene nucleus.[15] Data indicate that with increasing the amount of the modifying agent (Fig. 2), the absorption band also increases at 860 cm^{-1}. This can be due to the intensive formation of 1,2,4,6-substitutions in the aromatic cycle and hence to an increase of the spacial polymer content.
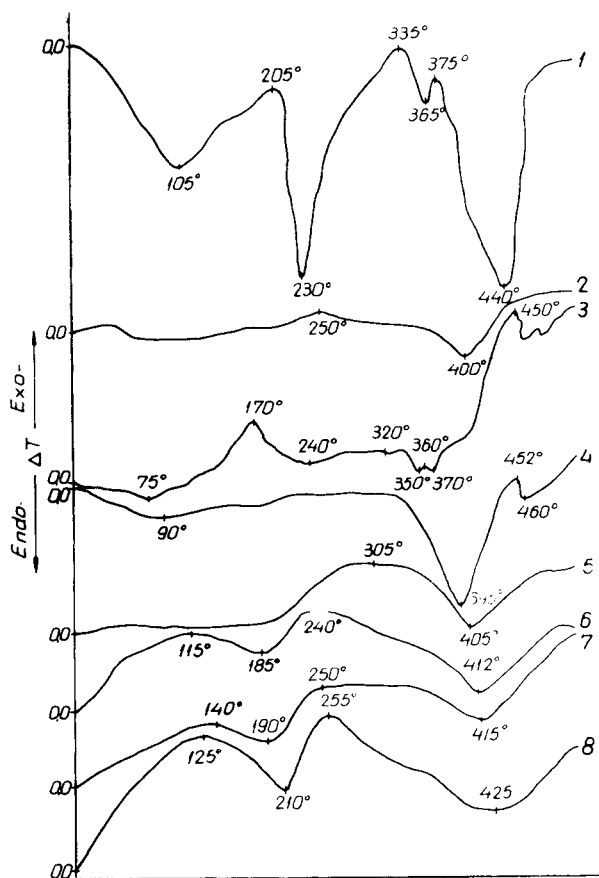

Fig. 4. Thermograms of PC and PFR modified with 10% PC and hardened with various quantities of HMTA. The indications are the same as in Fig. 1.
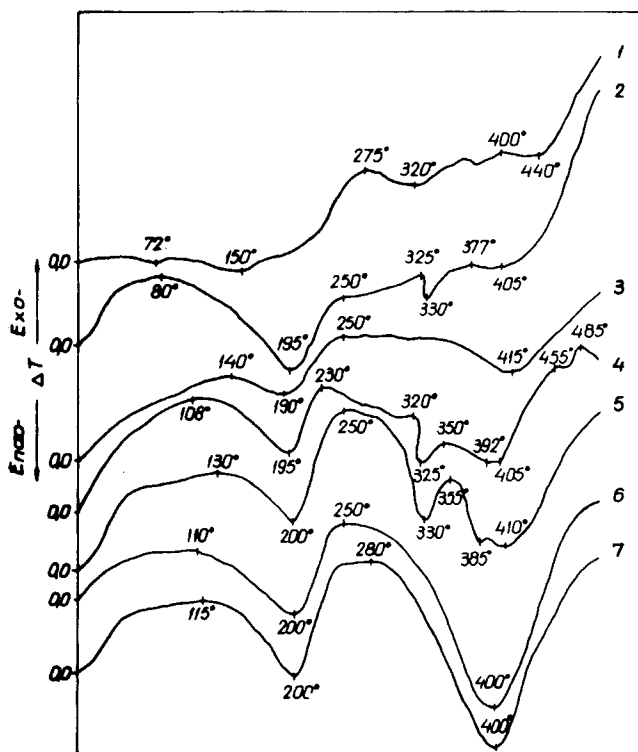
Fig. 5. Thermograms of PFR modified with various amounts of PC and hardened with 15% HMTA. The indications are the same as in Fig. 2.

The ESR spectra of the studied polymers are almost of the same nature, differing only in intensity. They are an indication of the content of long-lived radicals in the cured polymers. A typical ESR spectrum is shown in Figure 3. It appears as a symmetrical singlet with a g-factor close to that of the free electron 2.00395.[13,14] The paramagnetic units (PMU) concentration fluctuates from 0.51×10^{14} to 0.202×10^{15} spin/g, while the signal width varies from 11.1 to 6.78 gauss. A higher number of PMU is observed with increased quantity of the HMTA hardener. Since in ambient temperature the polymers studied are in a glass-like state, i.e., below the glass transition temperature (T_g), their viscosity is of a very high level. This makes them a proper medium for stabilization of free radicals emerging in the curing process.

It is assumed on the ground of the results obtained that in the process of curing curing PFR modified with PC and hardened with a varying amount of HMTA, an essential part is played also by free-radical processes.

For elucidating the processes taking place at a higher temperature, the synthetized MPFR's hardened with varying amounts of HMTA were studied also by means of a derivatograph (Figs. 4 and 5). DTA curves of PC and of the pure PFR thus obtained and cured under the same conditions as the other polymers are given for comparison. The thermogram of PC which was used as a modifying agent is slightly different from that published in the literature.[19,20]
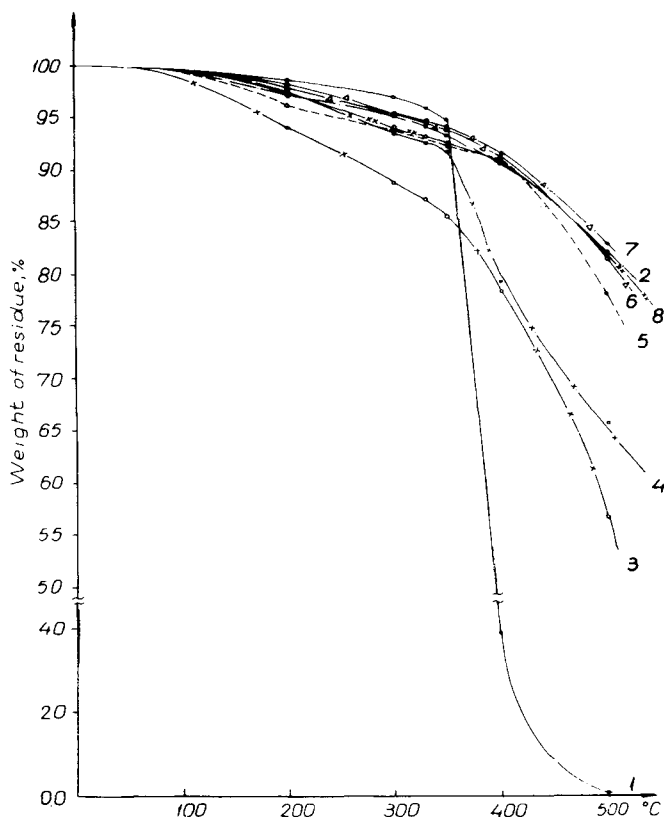
Fig. 6. Temperature dependence of the weight residue of PFR modified with 10% PC and hardened with various quantities of HMTA. The indications are the same as in Fig. 1.

The endothermal peak observed with its maximum at 105°C is due to the separation of physical water from the polymer. The exothermal effect with a maximum at 205°C is obviously a result of PC crystallization. A typical endothermal peak with its maximum at 230°C characterizes the melting process of the polymer crystal phase.

DTA curves make it possible to ascertain measurable endothermal effects at 60–90°C resulting from the differing way of the polymer transition from a glassy into a viscous-liquid state. The fact that endothermal effect is not observed with MPFR cured with 5%, 10%, and 15% HMTA indicates that in these cases T_g values are probably higher than 185–210°C (Fig. 4) and 190–200°C (Fig. 5), and that transition from a glassy into a viscous-liquid state takes place in a larger range of temperatures. Proceeding chemical processes give rise to exothermal effects with a maximum at 115–170°C (Fig. 4) and 80–140°C (Fig. 5), which are related to a deeper crosslinking of the polymers. The structurizing process taking place as a result of the formation of crosslinks is always accompanied by a heat release.

The endothermal effects at 350–440°C (Fig. 4) and 320–415°C (Fig. 5) are most characteristic since they are related to thermal destruction of the studied polymers. The nature and magnitude of these peaks depend, too, on the amount of both the modifying agent and the HMTA hardener (Figs. 4 and 5).
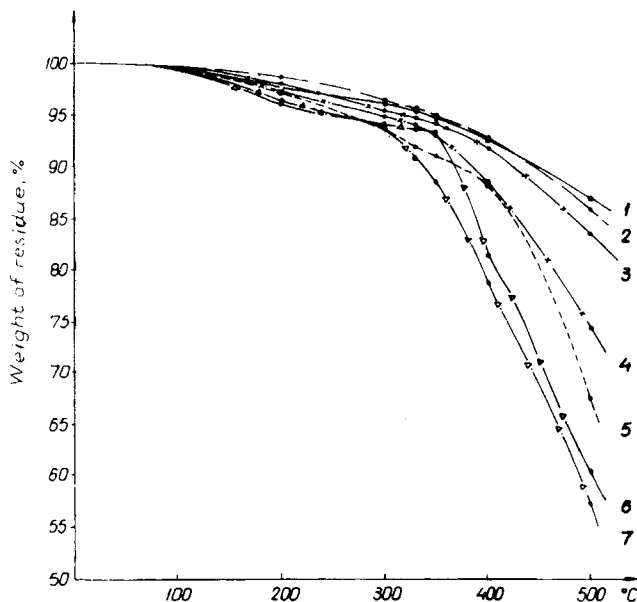
Fig. 7. Temperature dependence of the weight residue of PFR modified with various amounts of PC and hardened with 15% HMTA. The indications are the same as in Fig. 2.

The results thus obtained indicate that in heating the tested polymers to 500°C competitive processes of structurizing and destruction of the polymer chains take place.

Up to 350°C, the lowest rate of destruction is that of PC, while at higher temperatures, the opposite is true (Fig. 6). The PC losses at 400°C are 61% and reach 99% at 500°C. The highest losses among PFR modified with PC are those of samples with no addition of HMTA (Fig. 6, curve 3). The losses decrease when HMTA hardener is added (Fig. 6, curves 4 to 8). For synthesized MPFR, they are from 8.25% to 23.2% at 400°C and as high as 14.5% to 43% at 500°C (Figs. 6 and 7).

The results obtained indicate that the new type of synthesized MPFR are considerably more thermostable than PC. PFR modified with 5% and 10% PC have the highest thermostability. These results are of an essential practical importance. They show that the properties of the commercially produced PFR can be considerably improved by modification with PC.

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