Formation and Investigation of Epoxy Intumescent Compositions Modified by Active Additives

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Received 5 February 2001; revised 13 November 2001

ABSTRACT: Results are reported of research on intumescent composites based on epoxy resin cross-linked with polyethylene polyamine and containing ammonium polyphosphate and such modifying additives as calcium borate, manganese dioxide, nickel, and chromium, containing tubulenes as gas-formers and carbonization stimulators. The changes in composition and physicochemical properties of modified compositions under conditions of heat and fire were investigated by X-ray photo-electron spectroscopy, atomic force microscopy, and local force spectroscopy. Ammonium polyphosphate mainly stimulates carbonization processes on the inner surface of a bubble being formed during foam coke formation. The introduction of metal-containing tubulenes leads to the formation of fire-retardant and low flammability-compositions with high coke and carbon structures content. The use of calcium borate in the compositions considerably increases the strength of foam coke being formed. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1477–1483, 2002

Keywords: epoxy resins; coatings; flame-retardants; atomic force microscopy (AFM)

INTRODUCTION

Intumescent fireproof coatings are of great interest for civil construction industry, machine building, and transport because the main characteristics of the materials used do not practically get worse. Compositions for intumescent coatings containing ammonium polyphosphate as foam-coke-formation stimulator were suggested in an earlier report.[1] A mathematical model for foam coke formation was developed on the basis of this coating.[2,3] However, despite the good coating adhesion to polymer materials,[4] the foam cokes formed could not bear mechanical loads. It is also of interest to predict the structure of foam cokes being formed to rank regulated foams with certain strength and porosity. Therefore, it is advisable to use modifying additives, that can be active structure formers.

The purpose of this paper is to provide the results of composition formation and to investigate their structures and properties during stepped temperature growth.

EXPERIMENTAL

Objects and Methods

Epoxy resin ED-20 modified by ammonium polyphosphate (APP), calcium borate, and phenan-

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Journal of Applied Polymer Science, Vol. 85, 1477–1483 (2002)

Table I Component Content of the Composites Investigated

	Composition (fraction of total mass)											
Component	**1**	**1b**	**2**	**3**	**3b**	**4**	**4b**	**5**	**5b**	**6**	**7**	**8**
ED-20	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
APP	2.0	3.0	2.0	2.0	3.0	2.0	3.0	2.0	3.0	3.0	3.0	3.0
Tubules (Ni)												0.8
Tubules (Cr)										0.4	0.8	
Calcium borate	0.4	0.4		0.4	0.4	0.4	0.4					
MnO_2				0.4	0.4					0.4	0.8	0.8
PEPA	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

threne dehydropolycondensation product containing chromium (tubulene T-Cr) and nickel (T-Ni) was used as epoxy intumescent compositions. Epoxy resin was crosslinked by polyethylene polyamine.

The intumescent compositions were prepared in the components mixture ratios shown in Table I. Components mixing was carried out under normal conditions as follows: powder components were successively introduced into the vessel containing the measured quantity of epoxy resin without a hardener and thoroughly mixed after each component was added. Then, the hardener was introduced into the vessel and stirred for 2 min. The prepared system, the vitality of which is 1.5–2.0 h, was protected from moisture and stored not more than 30 min before application.

The flash temperature was measured by high-temperature pyrolysis. The device allows synchronous-registration of the continuous sample mass changes during pyrolysis and combustion, as well as the temperatures in the surface layer of the polymer under pyrolysis action and in the flame of the burning sample. These measurements included the time of inflammation delay of various polymer materials depending on external conditions. Thermal investigations were carried out in the open flame mode; the temperature increased up to 1073 K during first 10 s. The time of heat resistance testing was 2 min. The changes in surface chemical composition and intumescent systems volume were investigated by X-ray photoelectron spectroscopy (XPS) with an ES-2401 spectrometer (Mg$K\alpha$ radiation) and magnetic photoelectron spectrometer (A1$K\alpha$ radiation). The samples were subjected to pyrolysis in accordance with the following method: A sample was placed into molybdenum cell and then put into a tube quartz furnace. The pyrolysis temperature was provided by an electronic control block with a feedback. The accuracy of temperature support was 2%. The pyrolysis was carried out step by step in nitrogen atmosphere cleaned from oxygen additives. The pyrolysis temperature was chosen according to differential thermogravimetry (DTG) and thermogravimetry (TG) data. The investigation of heat-physical properties of materials was carried out with the help of a standard calorimeter (IT-S-400). The samples for the investigation were obtained by pouring the composition into the cylinders of the corresponding sizes.

Atomic force microscopy (AFM) investigations were carried out with a scanning probe microscope (P4-NT-MDT; Moscow) under the following conditions: contact mode, silicon triangle cantilever, spring constant, 1 N/m; and tip radii <10 nm.

RESULTS AND DISCUSSION

Modification of the compositions, based on epoxy resin hardened by polyethylene polyamine and containing fine APP; was carried out by the introduction of manganese dioxide and calcium borate into the compositions to form mineral net structures in surface layers, and also by the use of carbon-metal-containing tubulenes favoring the formation of foam cokes of a certain structure.

The foam cokes formation process consists of successive stages during the composition heating, so it can be assumed that because of the difference in thermal spreading, microcracks are formed near the particles of APP. Ammonium and water vapor enter these cracks and, simultaneously, polyphosphoric acid is formed at the walls. The latter can act as a dehydrating agent and carbonization stimulator. Therefore, the formation of a carbon (close to graphite-like) layer on

Table II Binding Energies (E_b) of C1s, O1s, N1s, and P2p Lines and Atomic Content (AC) during the Pyrolysis of Epoxy Composites Containing Ammonium Polyphosphate

	C1s		O1s		N1s		P2p	
Temperature	E_b (eV)	AC (%)[a]	E_b (eV)	AC (%)[a]	E_b (eV)	AC (%)[a]	E_b (eV)	AC (%)[a]
20 °C surface	285	46.48	533.6	12.6	398.9	1.18	134.1	0.7
	286.5	28.22			400.5	1.67		
	288	8.3			402.4	0.6		
					403.9	0.25		
20 °C crack surface	285	41.9	533.6	16.3	399.8	1.98	133.3	1.6
	286.5	27.16			401.8	1.35		
	288	8.54			403.8	1.17		
150 °C surface	285	48.1	533.2	19.6	400.7	2.42	134.4	2.0
	286.5	21.46			401.9	1.98		
	288	4.44						
150 °C crack surface	285	38.12	533.4	22.0	400	3.19	134.3	3.0
	286.5	24.94			401.8	2.5		
	288	6.24						
260 °C surface	285	31.42	532.8	10.37	400.7	3.23	134.6	9.2
	286	15.15	533.7	16.27	402.1	5.06		
	288	9.54						
260 °C crack surface	285	38.02	533.7	13.5	401.3	2.2	134.7	2.5
	286.5	24.55			402.1	5.06		
	288	12.68						
	290	3.96						
300 °C surface	285	47.04	531.9	15.7	400.5	3.07	134.4	5.0
	286.5	22.05			402.4	2.72		
	288	4.41						
300 °C surface	283.7	7.24	531.3	9.27	401.7	4.03	134.5	8.1
	285	27.74	533.3	15.13	403.4	3.17		
	286.5	22.92						
	289.4	2.41						

[a] Determined by XPS.

the inner surface of a bubble is possible. In fact, according to XPS spectra (C1s; Table II), a graphite-like layer was formed on a bubble inner surface at a certain stage of a temperature heating (E_b = 283.5–284 eV). Because this layer acts as the surface and boundary layers of a hardened resin, its thermolysis products and residues of materials pyrolysis were investigated by XPS. According to the results of the initial resin investigation there are no differences in bond energy of elements in boundary and surface layers. Carbon is shown in the spectra by the lines with bond energies C1s 285.0, 286.0, and 288 eV, which correspond to epoxy resin fragments $CH_2(CH)$, C—OR, and –O–C–O, respectively. Two lines, 400.0–400.2; (nitrogen in polyethylene polyamine) and 402.1 (nitrogen in APP) are observed in the nitrogen spectrum. In accordance with the scheme of chemical shifts, the nitrogen bond energy N1s in APP should not have such a great value. Apparently, the formation of RNH_3^+ groups took place in APP. The adjunct of this nitrogen line to APP is proved by the fact that it is found in volume layers of epoxy resin together with phosphorus, with bond energy P2p 134.5–134.6 eV ($P^+–O^-+NH_3R$), which is characteristic of phosphorus with a maximum oxidation degree. A high content of oxygen due to the presence of APP was observed on the crack surface, compared with the sample surface of the initial sample (Table II).

When the sample was heated to pyrolysis temperature (533 K), egress of phosphorus-containing substances was observed on the sample surface (ammonium salts of polyphosphoric acid are formed). It should be noted that the temperature of the onset of APP decomposition was 463 K. The nitrogen line with bond energy N1s 402.1 eV was

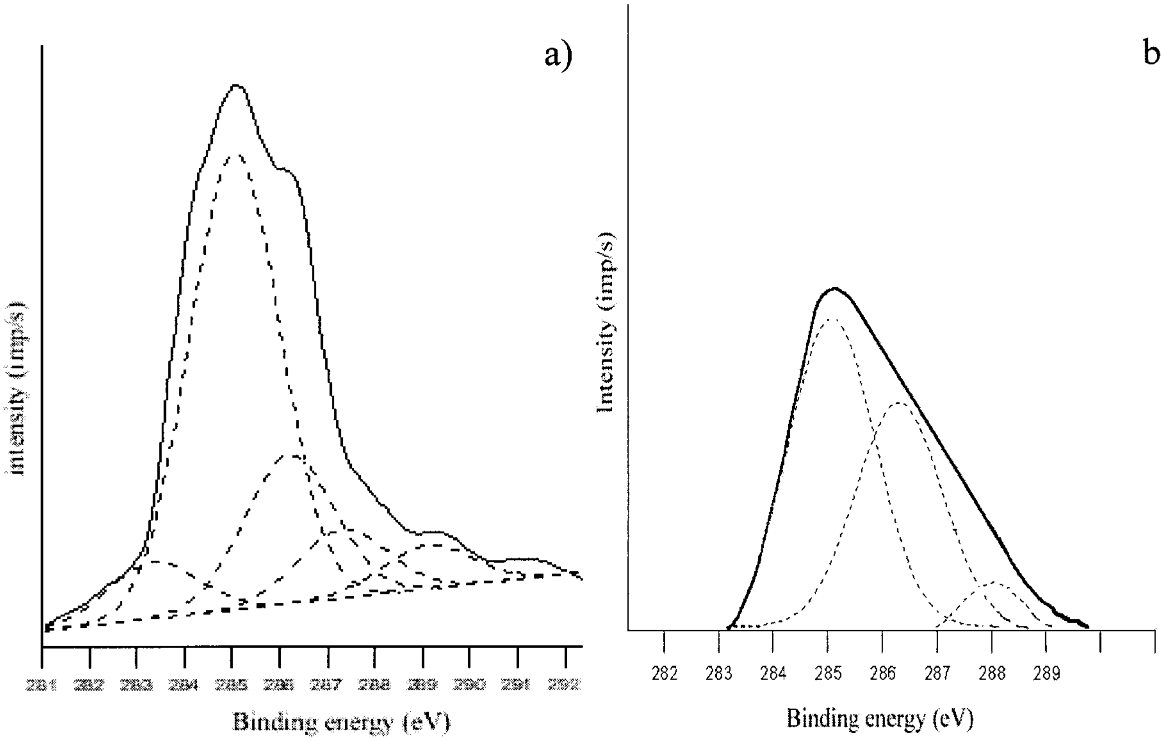

Figure 1 XPS data on 1Cs line for surface samples after pyrolysis of epoxy compositions containing (a) ammonium polyphosphate with T-Ni and (b) ammonium polyphosphate.

the same in the spectra up to 573 K, indicating that the decomposition reaction has a more complex character. It is possible that total APP deamination and, consequently, its total decomposition are difficult in a polymer because of the high density of the polymer and its destruction products even at very high temperatures. The data obtained were confirmed during the determination of temperature dependence of heat capacity of materials investigated.

The egress of phosphorus-containing products was followed by an increase in the phosphorus concentration on the surface and by the redistribution of nitrogen line intensity in the XPS spectrum (an increase in the most high energy line). When the temperature was increased in boundary layers, decreases in relative quantities of C–OR groups and carboxyl groups in the material volume were observed (Table II).

Intensive formation of liquid pyrolysis products started at 573 K (pyrolysis onset temperature), as indicated by a sharp increase in the C1s line intensity that is attributed to CH groups. Carbon products accumulated on the surface of the sample, masking all other fragments of pyrolysis products. Therefore, it is assumed that the process of coke formation starts at 573 K. No more than 7.24% of the total content of carbon was found on the crack surface of the samples. Apparently, the interaction of APP with a polymer continued at the temperature mentioned because the nitrogen line-intensity with E_b = 402.1 eV decreased as the phosphorus bond energy decreased.

In comparison with the results obtained, the introduction of nickel-containing tubulenes into the composition in APP and Ni-T (10:1 ratio) led to an increase of ~ 2 times in the carbon—carbon and carbon—metal groups (Figure 1). Thus, nickel-containing carbon tubules are active precursors of a new carbon phase, and structural additives that stimulate the proportional distribution of NH_3 bubbles into the foam cokes were formed. In turn these additives promote the growth of initial composite heat capacity and the increase in foam coke strength.

The increase in carbon products content in foam coke led to a considerable change in the character of heat capacity dependence on temperature (Figure 2). First, the heat capacity of com-

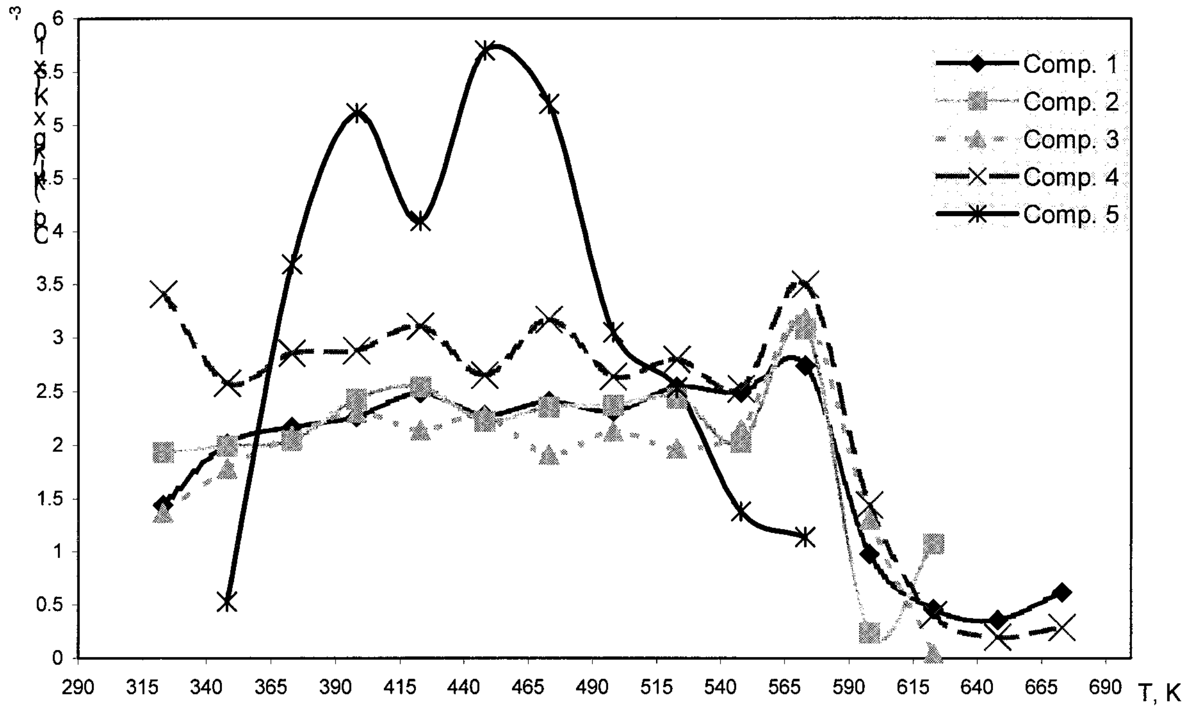

Figure 2 Heat capacity dependence on temperature.

positions modified by structure formers was 3–7 times higher than the heat capacity of composition containing only APP; this result can be explained by different structure formation degree of the compositions. Secondly, the heat capacity of composition containing APP increased sharply, by 10–11 times, at 373–403 and 430–480 K; this result is apparently due to the evolution of water and ammonium vapor into the bubbles being formed and the pressure increase in the bubbles. In contrast to the picture presented, the heat capacity in modified compositions changed without any considerable change in peaks because of a smoother gas-formation process. Furthermore, when calcium borate was introduced into the composition, heat capacity deviations were practically not observed because of the net formation of calcium-phosphorus-borate. Greater heat capacity changes (2–3 times) were seen when manganese dioxide was introduced with calcium borate. In our opinion, this result can be explained by competing thermal destruction processes of samples containing manganese dioxide with the formation of volatile, easily inflammable products. The intumescent degree of this composition is 16 times and the flash temperature is 463 K.

Heat–physical characteristics and XPS data agree with the results obtained during the exam-

Table III **Change of Reaction (C_p^f/C_p^{in}), Intumescence Degree (β), and Temperature for the Composition Flash (T_{fl})**

	Composite Number							
Parameter	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
C_p^f/C_p^{in}	1.90	1.60	2.30	1.03	(11.5)[a]			
β, times	4		16	6	12	9	10 (6)[b]	7 (3)[b]
T_{fl}, K	643		463	583	603	523	593	513

[a] C_p^f/C_p^{in}, maximum on the curve of Figure 2.

[b] The intumescence degree after coolness.

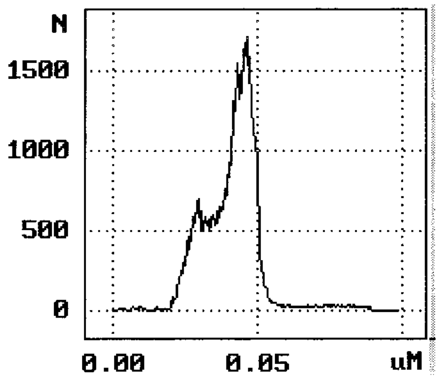

Figure 3 Distribution of irregularities on foam coke surface of composition **2**.

ination of flash temperature, coke intumescence, and strength degree. For the investigated compositions, the flash temperature (T_{fl}), intumescence degree (β), and relation of final (573 K) and initial (323 K) heat capacities (C_p^f/C_p^{in}) were determined (Table III). In the compositions into which manganese dioxide was introduced, the flash temperature decreased in most cases. This result could indicate the formation of considerable concentrations of combustible gases at low temperatures. The cokes obtained lose their shape with the increase of intumescence degree when removed from flame (samples 7 and 8). The introduction of chromium- and nickel-containing tubulenes decreased the intumescence degree, but led to an increase of flash temperature. The increase of ignition time and the decrease of self-combustion time of samples, including metal-containing tubulenes and/or calcium borate, should also be noted.

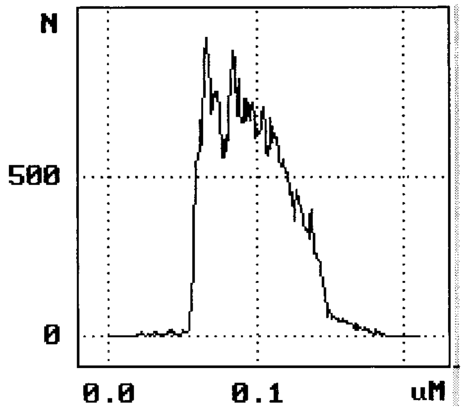

Figure 4 Distribution of irregularities on foam coke inner surface of composition **2**.

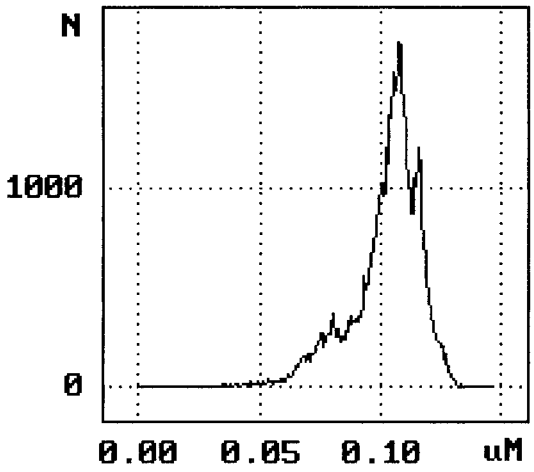

Figure 5 Distribution of irregularities on foam coke surface of composition **4b**.

The topography of inner and outer layers of foam cokes formed was determined by AFM on the foam cokes obtained from compositions **2** and **4b** (composition **4b** differs from composition **4** by the increased, 1.7×, calcium borate content). The differences in topography of the samples being investigated and in the topography of outer and inner layers of the same foam coke were registered. The root mean square roughness (R_q) of sample **2** outer surfaces is 9.769 nm (Figure 3) and the analogous parameter for inner layers is 0.015 nm (Figure 4). For sample **4b**, R_q for the outer surface is 0.026 nm (Figure 5) and that for inner layers is 0.011 nm (Figure 6). The destruction of the outer surface and inner layers of foam coke samples studied was dif-

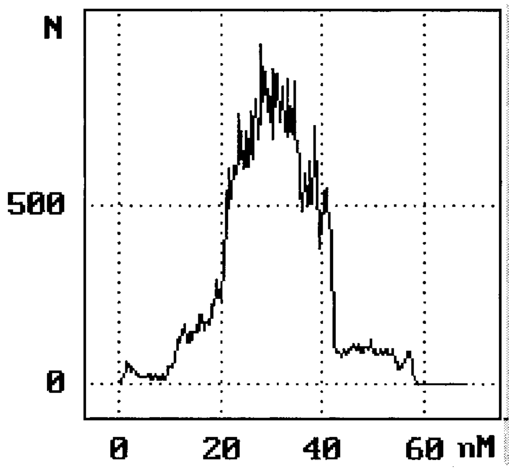

Figure 6 Distribution of irregularities on foam coke inner surface composition **4b**.

ferent: the outer surface of sample **2** did not destruct at maximum loads and the inner layer was damaged at a load $F_u = 2.7$ mcN, whereas weak destruction traces were observed on the inner surface of sample **4** and there was no any destruction of outer surface at minimal load. The presence of polar surface of the foam coke obtained from composition **4** and the results just presented prove the presence of a net structure of calcium-phosphorus-borate in surface layers.

Thus, on the basis of the results given, it is possible to declare that calcium borate- and metal-containing tubulenes are effective as structure formers during foam coke formation. It is also possible to assume that the introduction of metal-containing tubulenes influences the changes of stimulator and gas-former structures and the effect of a hardening polymer on promoting the formation of foam cokes of a certain surface structure and composition.

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