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Formation and thermal decomposition studies of thermostable aminoplastics

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Abstract

The thermostable aminoplastics containing 2,4,6-triamino-1,3,5-triazine and hexamethylenetetramine units, respectively, in the presence of a silicon-derived coupling agent, have been prepared. Their structures were confirmed by FTIR spectroscopy. The thermal decomposition of these aminoplastics has been studied by TG and DTA methods and by FTIR and ESR spectroscopy.

INTRODUCTION

Several techniques, including the addition of stabilisers and crosslinking, have been employed to improve the thermal stability of polymers [1,2]. It has been established that the presence of nitrogen in a polymer generally leads to improved thermal stability [3,4]. It has also been shown that titanium and silicon-derived coupling agents used as molecular bridges between the interface of an inorganic surface and the organic polymer matrix lead to increased flame resistance of composites [4–7].

The complex polycondensation formation of urea, formaldehyde, 2,4,6-triamino-1,3,5-triazine or hexamethylenetetramine with silicon(IV) oxide coupling agent is described in this paper. The structures of these aminoplastics were confirmed by Fourier transform (FT) infrared spectroscopy. Thermoanalytical data obtained by thermogravimetry (TG) and differential thermal analysis (DTA), together with FTIR and electron spin resonance (ESR) spectral data, may be used to interpret the physicochemical changes and the radical processes occurring during thermal treatment of the aminoplastics in question.

EXPERIMENTAL

Preparation

A 1.2×10^{-1} M solution of 35% formaldehyde was adjusted to pH 8 with sodium hydroxide and 1.0×10^{-1} M urea, 1.5×10^{-2} M 2,4,6-triamino-

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1,3,5-triazine (UFTT) or 1.5×10^{-2} M hexamethylenetetramine (UFHT) and 9.1×10^{-2} silicon(IV) oxide were added. The mixture was stirred at 353 K for 2.4×10^3 s. After this period, the pH of the mixtures was adjusted to 5 by adding an acid catalyst and was stirred at 363 K for 3.6×10^3 s. After adjusting to pH 7.5, it was cooled to 298 K. The aminoplastics were filtered off and dried at 373 K.

Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of the aminoplastics were recorded on a Perkin–Elmer 1600 FTIR spectrophotometer using the potassium bromide (KBr) pellet (1 mg/150 mg KBr) technique. The samples were also heated to a desired temperature between 493 and 773 K for 1.2×10^3 s, cooled to room temperature and their FTIR spectra were examined to study the chemical changes during heating.

Thermogravimetry (TG) and differential thermal analysis (DTA)

TG and DTA curves were recorded on a Du Pont 951 thermogravimetric analyser and a 407 Netzsch derivatograph in a dynamic atmosphere of pure air. Thermal analyses were made under the following conditions: the aminoplastics were heated in the temperature range 293–1273 K, with a heating rate of 10 K $\min^{-1}$; the reference material was Al_2O_3.

Electron spin resonance (ESR)

The pure solid-state aminoplastics were pyrolysed by heating to the desired temperature between 493 and 873 K for 1.2×10^3 s in air. ESR spectra were recorded on a Bruker 200 D ESR spectrometer employing 100 kHz modulation and nominal frequency of 9.5 GHz. Linewidths were measured from the first-derivative curves (peak-to-peak). Signal intensities (proportional to the spin concentrations) were calculated by double integration of the first-derivative spectrum. These two ESR parameters were measured at room temperature.

RESULTS AND DISCUSSION

The combination of urea and formaldehyde begins with a series of addition reactions followed by condensation of methylol groups in methylol bridges to form methylene-ether bridges at higher temperatures [8–10]. However, the mechanism of a reaction system such as urea, formaldehyde, 2,4,6-triamino-1,3,5-triazine (UFTT) or hexamethylenetetramine (UFHT) with silicon oxide involves a series of complex polycondensation processes. In this way the aminoplastics have less formaldehyde and any ecological

TABLE 1

FTIR spectral data of aminoplastics UFTT and UFHT (cm^{-1})

Assignment of band [a]	UFTT	UFHT
ν(NH)	3370 (s)	3375 (s)
ν(CH)	2970 (w)	2970 (w)
	2820 (w)	2850 (w)
ν(CO) + δ(NH) + ν(CN)	1638 (s)	1640 (s)
	1550 (s)	1560 (s)
δ(CH)	1438 (w)	1438 (w)
ν(SCN)	1370 (m)	1380 (m)
ν(CN)	1250 (m)	1255 (m)
τ(NH) + ρ(NH) + ϕ(CH) +	1138 (m)	1140 (m)
+ ϕ(CN)	1038 (m)	1040 (m)
	775 (w)	825 (w)
	650 (m)	650 (w)
	570 (m)	575 (m)

[a] s = strong, m = medium, w = weak.

problems in the application step are reduced. The products were characterised by FTIR (Table 1).

In order to study the physicochemical changes that occur during thermal treatment, the variations in the FTIR spectra of the aminoplastics at various different temperatures were studied. For recording the effect of temperature on IR absorption bands, the samples were kept at 493, 533, 573, 623, 673, 723 and 773 K for 1.2×10^3 s. It can be seen (Table 1) that the intensities of the functional group IR bands (Table 1) of samples at 3370 or 3375 cm^{-1} (ν(NH)), 1638 or 1640 cm^{-1} and 1550 or 1560 cm^{-1} (ν(NHCO), amide I and II), 1438 cm^{-1} (δ(CH)), 1375 or 1380 cm^{-1} (ν(SCN)), 1250 or 1255 cm^{-1} (ν(CN)) and 1138 or 1140 cm^{-1} (ν(NCH_2O)) decrease on heating and disappear at about 573 K. At higher temperatures, above 773 K, the aromatic ring bands appear [7].

Figures 1 and 2 show the TG, DTG and DTA thermograms of the aminoplastics UFTT and UFHT obtained under the dynamic heating program.

The thermal analyses (Table 2) show that the thermal decomposition of the samples occurs in several reaction stages of weight loss of different natures, followed by exo- and endothermic effects. At each stage, partial volatisation took place while the aminoplastics underwent chemical modification. The thermoanalytical data indicate that the second stages show the major weight loss (22 and 53%) with indistinct separation, and that the temperature at which the main exothermic decomposition process takes place is 523 K for sample UFTT and 513 K for sample UFHT [11,12].

Based on the results of the thermal analyses, supported by the FTIR spectral data, it is proposed that the aminoplastic UFTT, which has 2,4,6-

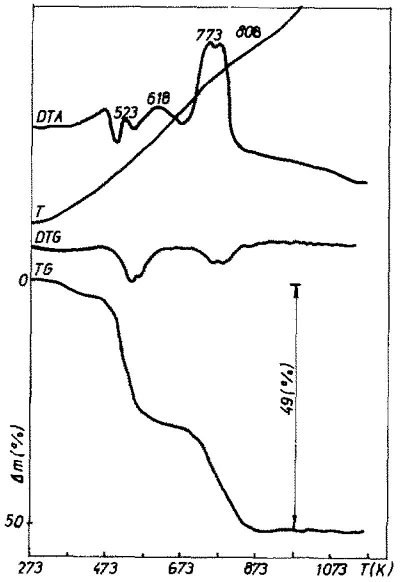

Fig. 1. TG, DTG and DTA traces for aminoplastic UFTT.

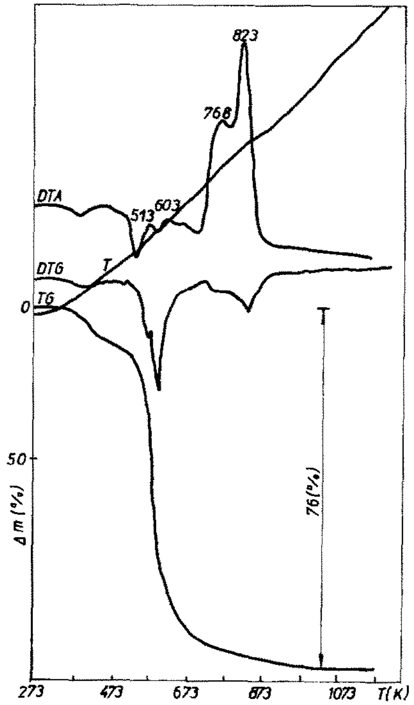

Fig. 2. TG, DTG and DTA traces for aminoplastic UFHT.

TABLE 2

TG, DTG and DTA reaction stages of aminoplastics UFTT and UFHT

Thermal reaction stage	UFTT	UFHT
First		
Temperature range (K)	313–488	315–513
Weight loss (%)	4	12
DTA peak (K)	363 (endo)	373 (endo)
Second		
Temperature range (K)	488–573	513–593
Weight loss (%)	22	53
DTA peak (K)	523 (exo)	513 (endo)
Third		
Temperature range (K)	573–743	593–840
Weight loss (%)	4	11
DTA peak (K)	618 (exo)	603 (exo) 768 (exo) 823 (exo)
Fourth		
Temperature range (K)	743–888	
Weight loss (%)	19	
DTA peak (K)	773 (exo) 803 (exo)	

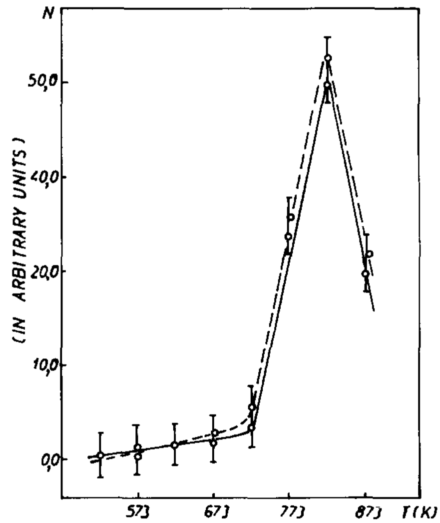

Fig. 3. Variations of normalised ESR intensities, *N* (in arbitrary units) vs. Temperature, *T* (K): ——, aminoplastic UFTT free radicals; ----, aminoplastic UFHT free radicals.

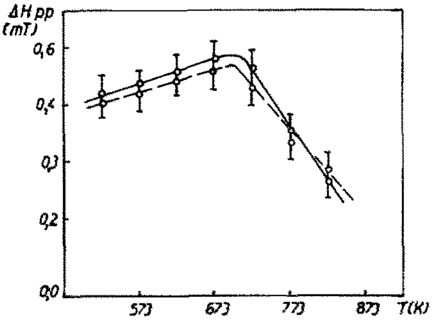

Fig. 4. Variation of the ESR linewidths, Δ*H*pp (mT) vs. temperature, *T* (K): ——, aminoplastic UFTT free radicals; – – –, aminoplastic UFHT free radicals.

triamino-1,3,5-triazine as the thermostabilising component, shows better thermal stability than the aminoplastic UFHT which has hexamethylenetetramine. It appears that the aminoplastic UFTT as polymeric matrix is better attached to the surface of the silicon coupling agent.

As the thermal decomposition of the polymers is generally considered a free radical process, the variations in the ESR spectra of the pyrolysed samples were analysed. In Fig. 3, the change in concentrations of free radicals (relative ESR signal intensities, *N*) of the pyrolysed aminoplastics are shown as a function of temperature. The intermediate molecular species appear above 523 K, and in the range from 523 to 873 K relative ESR signal intensities increase with increasing temperature to about 823 K.

The decrease in the ESR linewidths with increasing temperature (Fig. 4) shows that conjugation is being extended between the chains [13]. The ESR study indicated that at higher temperatures intermolecular condensation reactions in the synthesised aminoplastics proceed by free radical mechanisms.

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