Journal of Thermal Analysis and Calorimetry, Vol. 90 (2007) 2, 489–494

FIREPROOFING OF POLYURETHANE BY ORGANOPHOSPHONATES
Study of degradation by simultaneously TG/DSC

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In this work, we have studied the degradation processes of polyurethane containing phosphonate groups used as a fireproofing agent. These studies are undertaken by simultaneous thermogravimetry (TG) and differential scanning calorimetry (DSC) measurements. It is found that fireproofing agents with phosphonate react with oxygen in the air and prevent the complete combustion of the material. It is also found that the energy released during combustion is low when comparison is performed with other fireproofing materials.

Keywords: *DSC, fireproofing, phosphonate, polyurethane, TG*

Introduction

Various fireproofing combinations can be used to delay the burning process of organic materials. These compounds include halogenous (with or without antimony oxide) [1], mineral hydroxides [2] and organophosphorus compounds [3–5]. More recently, the use of silsesquioxanes containing epoxy, amino or alkenyl groups [6–9], boric acid, borates [10] and carboranes [11, 12] were proposed. Among these compounds, the organophosphoruses are known to meet the current requirements of international standards in the field of fire propagation restriction and fire protection [13, 14].

Mechanisms for fireproofing have been the subject of a substantial amount of research [15–25]. For halogenous, at high temperature, halogenous radical are released. These radicals are able to react with polymer radicals leading to the formation of acid (HCl or HBr) or halide (Cl_2 or Br_2). When antimony oxides are included in the material composition some gas as $SbBr_3$ can be produced. These non flammable compounds reduce the concentration of oxygen in the medium surrounding the material. The exothermic process resulting from the reaction of the polymer radicals with oxygen in the air is consequently interrupted. In other words, halogenous compounds can be understood as flame inhibitors [15–18]. When mineral hydroxides are used such as aluminium or magnesium hydroxide, the high temperature decomposes the hydroxide through an endothermic process and as a result, large quantities of water molecules are released and unvolatile compounds are produced. As a consequence, the material is isolated from its surrounding and a large decrease of heat transfer is observed [19, 21].

The mechanisms of reaction of organophosphorus compounds depend on the type used [22–25]. For example, phosphates and polyphosphates are used in the intumescing systems [26]. They allow the formation of carbonaceous foams on the material surface. This foam prevents the progression of the degradation and the combustion mechanisms. By using oxides of triphenylphosphine and *p*-terbutylphosphite, radicals as P·, PO·, HPO· are produced and recombination with free radicals created by the action of the flame can easily be obtained [27–30].

In a previous work, we have presented the synthesis of a diol phosphonate, prepared in order to increase the fireproof properties of a polyurethane based materials prepared from polybutadiene hydroxy telechelic, [31, 32]. In this current work, thermogravimetry (TG) and differential scanning calorimetry (DSC) techniques have been performed under inert and oxidized atmosphere with the objective to evaluate th

e effects of the temperature and time on the material decomposition.

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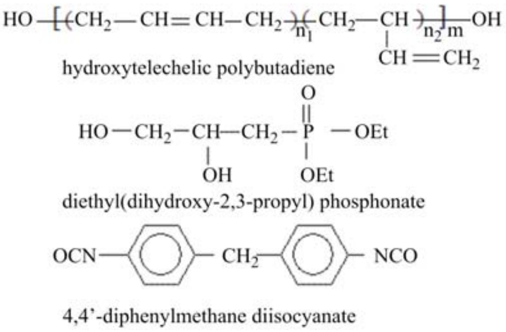

Fig. 1 Chemical formula of the products used to prepared the samples studied in this work

Experimental

Samples of polyurethanes (PU) having, respectively, 0 and 3 mass% of phosphorus were prepared according to the procedure described previously in [31, 32]. The chemical formulas used for the preparation of these samples are given in Fig. 1.

The thermal properties of the different PUs were studied by using a TG-DSC 111 Setaram thermoanalyzer. Samples with 0 mass/mass% of phosphorus and 3 mass/mass% of phosphorus. These tests were done under inert (N_2+Ar) and an oxidizing atmosphere (N_2+O_2). The temperature range from 20° to 600°C was scanned with a heating rate of 5°C min^{-1}. In these measurements, sample masses ranging between 4.5 to 6.8 mg were introduced in open platinum crucibles under a gas flow of 15 mL min^{-1}.

Results and discussion

Let us first present the results obtained under an inert atmosphere. The TG/DSC curves of the sample with 0 mass/mass% of phosphorus are presented in Fig. 2, curve a. Under an inert atmosphere (N_2), the sample is degraded in two steps:

A first degradation process occurs at 230°C. The kinetics is maximum at 310°C (Fig. 2, curve b) and is achieved at 380°C. The mass loss measured is 26 mass/mass% of the total mass of the sample.

A second degradation process occurs at 380°C. The kinetic is maximum at 450°C and is achieved at 600°C. The mass loss is close to 72 mass/mass% of the initial sample mass. Finally at high temperature we find 2 mass/mass% of residue.

These results can be interpreted as follow. At first the urethane bridges decompose giving isocyanates and polyols. In the temperature range (230–380°C) the isocyanate (MDI) breaks up to give volatile products. It is important to note that the initial amount of MDI is 28 mass/mass%. This value is comparable to the 26 mass/mass% found experimentally. Thus we may conclude that practically all the MDI is degraded. During the second stage of degradation, the polyol is completely degraded by giving volatile products [33, 34].

The kinetics of the degradation process is obtained directly from the derived curve of the mass loss *vs*. temperature, which is displayed on Fig. 2, curve b. The kinetics of degradation exhibits a maximum of 1.5% min^{-1} in the first step and of 6% min^{-1} in the second step. An exothermic reaction is associated with the first degradation step (Fig. 2, curve c). After integration of the signal, for this first reaction, we find that the energy given of by the system is 0.28 kJ g^{-1}. For the second reaction an endothermic signal of 0.20 kJ g^{-1} is measured.

For the sample containing 3 mass/mass% of phosphorus the same experiments lead to the data reported on Fig. 3. A first decomposition occurs at 200°C (Fig. 3, curve a). The kinetics is maximum at 255°C and is finished at 355°C. The mass loss measured is 37 mass/mass% of the initial sample mass. No clear evidence for an exothermic reaction is observed in the DSC curve (Fig. 3, curve c). A second decomposition occurs at 350°C. The kinetic is maximum at 430°C (Fig. 3, curve b), and is slowed down after 480°C; a very light drift prolongs the reaction up to 600°C. The mass loss measured is 49 mass/mass% of the initial

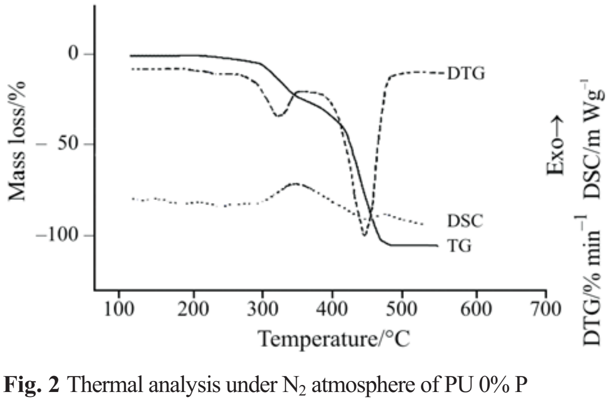

Fig. 2 Thermal analysis under N_2 atmosphere of PU 0% P

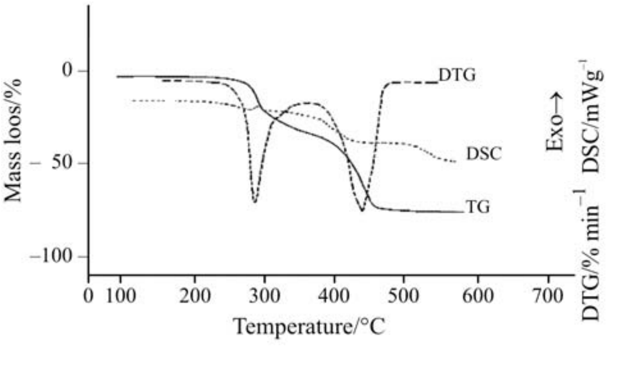

Fig. 3 Thermal analysis under N_2 atmosphere of PU 3% P

sample mass. Finally a residue of 14 mass/mass% of the initial mass is measured at high temperature. For this second degradation, an endothermic energy of 0.15 kJ g^{-1} is measured (Fig. 3, curve c). The kinetics of degradation exhibit a maximum of 5.6% min^{-1} for the first step and 5.7% min^{-1} for the second step.

For the second material, the sum of MDI and phosphonate content represents 65% of the sample mass. Thus, for the first degradation step the measured quantity (37 mass/mass%) allows us to conclude that phosphonate prevents full degradation. There is also a decrease in the characteristic temperature of the first degradation phenomenon when phosphorus is added. This can be explained as follow. During the first stage P–C bonds of the phosphonate are degraded; then, depolymerisation of the urethane bridges with the release of the isocyanate appears. In this temperature range, the volatile isocyanate molecules are drained off by the gaz flow. The addition of phosphorus does not modify the characteristics of the second degradation process. Finally, for the second material the amount of residue at high temperature is greater (14 mass/mass% to be compared to the 3% find for the first one). This confirms that the introduction of phosphonate prevents complete degradation of the material and these results support the idea of a formation of an insulating carbonaceous coating on the sample surface.

Let us now to analyse the data obtained under the presence of oxygen. The curves obtained for the sample with 0 mass/mass% phosphorus are now displayed on Fig. 4. A first degradation of low magnitude begins at 200°C (Fig. 4, curve a) and is followed by a second degradation which is achieved at 385°C. The kinetics is maximum (Fig. 4, curve b) at 300°C with a value of 1% min^{-1}. The sums of mass loss are 16 mass/mass% of the initial sample mass. In spite of the existence of a very small signal on the DSC curve (Fig. 4, curve c), we may assume the existence of an exothermic reaction at 300°C with an energy of 0.43 kJ g^{-1}. Above 385°C a third mass loss of 55 mass/mass% occurs. The kinetics are maximum at 420°C with a value of 5% min^{-1}. A fourth reaction is observed with a maximum at 520°C. These two last reactions are exothermic with a large energy of 14.4 kJ g^{-1}. No residue is left at the high temperatures.

A comparison of the results obtained when experiments are performed with and without oxygen can be made as follows. When oxygen exists, a decrease of the thermal stability of the polyurethane without phosphorus is observed. This result is not truly surprising. The oxygen atoms react strongly with the material leading to a large quantity of heat restored. Finally a full degradation will be obtained at high temperature. In other words, this polyurethane without phosphonate burns easily and consequently must not be considerate as a good fireproofing material.

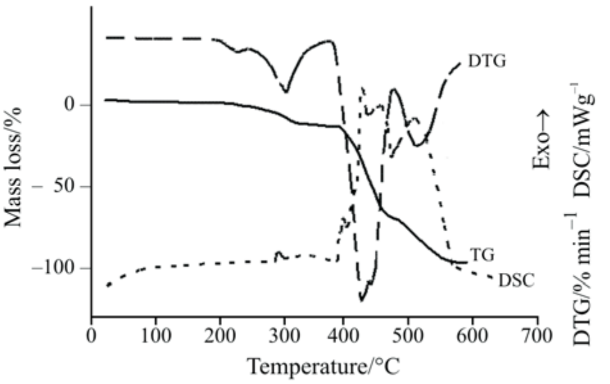

Fig. 4 Thermal analysis under (N_2+O_2) atmosphere of PU 0% P

The results obtained under oxidative atmosphere for the samples with 3 mass/mass% phosphorus are displayed on Fig. 5. A first degradation, still occurs at 180°C, and is finished at 300°C. The corresponding mass loss is 21 mass/mass% (Fig. 5, curve a). The kinetics are maximum at 285°C with a value of 2.7% min^{-1} (Fig. 5, curve b). The reaction is exothermic with an energy of 0.23 kJ g^{-1}. Then, from 285 to 380°C, a second degradation process occurs with a mass loss of 12.6 mass/mass% of the initial sample mass. In this temperature domain, no signal characteristic of an endo- or an exothermic reaction is detected on the DSC curve (Fig. 5, curve c). The degradation kinetics are maximum at 300°C with a value of 0.2% min^{-1}. This is a slow evolution. Then, the degradation of the polyol occurs at 380°C and is finished at 470°C. The corresponding mass loss is 33.5 mass/mass%. The kinetics are maximum at 420°C with a value of 2.2% min^{-1}. The exothermic effect measured from the DSC curve and corresponding to this last degradation gives an energy of 7.5 kJ g^{-1}. Finally, the decomposition continues slowly up to 600°C and a residue of 11.3 mass/mass% is measured.

The main data collected from these measurements are regrouped in Tables 1 and 2. For sample containing

Table 1 Comparison of kinetics of degradation of the materials studied in this work

	Under nitrogen atmosphere		Under oxidative atmosphere	
	0%	3% P	0%	3% P
1st degradation/% min^{-1}	1.5	5.6	1	2.7
2nd degradation/% min^{-1}	6	5.7	5	2.2

Table 2 Results obtained from thermal analysis (TG, DSC) performed on the different samples studied in this work

Sample	Atmosphere	$T_{\mathrm{beginning}}$/°C	T_{end}/°C	Mass/%	$T_{\mathrm{beginning}}$/°C	T_{end}/°C	Mass/%	$T_{\mathrm{beginning}}$/°C	T_{end}/°C	Mass/%	$T_{\mathrm{beginning}}$/°C	T_{end}/°C	Mass/%
PU 0%P	inert				230	380	26.6	385	~500	69.8	very light drift until 600°C		
				Weak exotherm 0.28 kJ g^{-1}						Weak endotherm 0.20 kJ g^{-1}			
							residue 3.6 mass%						
PU 3%P					200	350	37.3	350	~490	48.5	very light drift until 600°C		
				Very weak exotherm 0.02 kJ g^{-1}						Weak endotherm 0.15 kJ g^{-1}			
							residue 14.2 mass%						
PU 0%P	oxidizing	>180	280	6.7	280	385	9.7	385	475	55.3	475	600	28.3
		No thermal effect			Weak exotherm 0.43 kJ g^{-1}					Strong exotherm 14.24 kJ g^{-1}			
							residue 0 mass%						
PU 3%P		180	285	21.1	285	380	12.6	380	470	33.5	470	600	21.5
		Weak exotherm 0.23 kJ g^{-1}			Negligible thermal effect					Strong exotherm 7.5 kJ g^{-1}			
							residue 11.3 mass%						

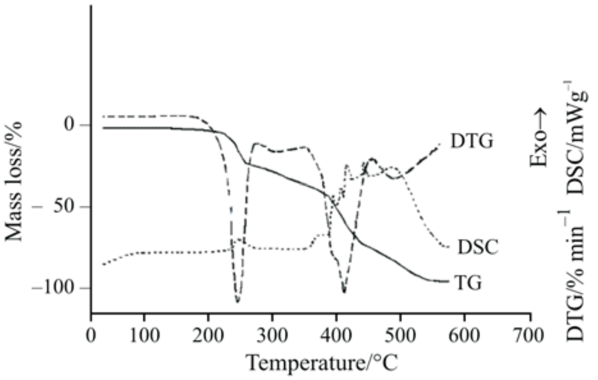

Fig. 5 Thermal analysis under (N_2+O_2) atmosphere of PU 3% P

3 mass/mass% phosphorus we may now add some data obtained previously and concerning expriments carried out by coupling pyrolysis/GC/MS (pyrolysis/gas chromatograph /mass spectrometry). This study has shown that during pyrolysis at 250°C the formed products are those resulting mainly from the phosphonate group. Furthermore, a sample with the same content of phosphorus examined by EPMA (electronic probe mass analyser) in order to identify the elemental concentration in it before and after an isothermal annealing performed during 3 h at 220°C has shown clearly that there is only a significant increase in concentration of the oxygen on the sample surface [29].

Thus, the presence of phosphonate slightly modifies the range of degradation temperature and increases the proportion of mass loss. The phosphonated compound breaks up first and releases volatile products. The negligible heat transfer obtained in this work shows that these volatile products are not reactive with the oxygen in air. The phosphonate during this transformation plays the role of a fireproofing agent, in a chemical way. Moreover it is also found that phosphorous decreases the rate of the degradation process occurring at low temperature.

Conclusions

This study leads to conclude introduction of phosphonate considerably acts on the thermal degradation of the material. The degradation nature of the material shows that the phosphonate group breaks up first; it volatilizes and starts the fireproofing action before the beginning of combustion. This is shown by the decrease of the combustible products at beginning of the decomposition and the considerable reduction of oxidation reactions with oxygen in air. This supports the formation of the carbonaceous residue in the course of combustion which forms a barrier preventing migration of the volatile products. This also confirms that the phosphonates act exclusively in gas phase. This gas screen limits the ability of the oxygen molecules to be in contact with the polyurethane and increases the fire protection.

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Received: September 25, 2006
Accepted: April 12, 2007
OnlineFirst: June 1, 2007

DOI: 10.1007/s10973-006-7971-x