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A comparative study of the mechanism of action of ammonium polyphosphate and expandable graphite in polyurethane

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Abstract

The present work is dedicated to the development of a new method, which enables a better understanding of the intumescence process. Many studies have investigated char formation from a chemical aspect but the foaming and strength of the char have not been well studied before. Thermal scanning measurements using a rheometer as a fire reactor enable a correlation between the fire behaviour and thermal behaviour and the visco-elastic properties of the material. This study investigates the rheological modifications of polyurethane thermoset coatings with or without fire-retardant. The rheological and mechanical destruction properties of the protective char layer have been correlated with their fire retardant performance for two additives: ammonium polyphosphate and expandable graphite. In a first part, the expansion of pure PU and of intumescent materials under normal force is studied. Then, the visco-elastic behaviour is investigated in order to evaluate the different steps of the intumescent process (development, stability and destruction). Finally, mechanical properties of the intumescent chars are discussed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Intumescence; Charring; Dynamic properties; Rheology; Mechanical strength

1. Introduction

Polyurethanes (PUs) have a large variety of forms (foams, adhesives, coatings etc.) which find applications in both industry and daily life [1]. The use of polyurethanes, which are combustible [2], leads to an increase in fire risks and thus to growing importance of flame retardancy. Several approaches may be used to flame retard polymers, in particular intumescence [3,4]. When heated, intumescent materials form a charred protective layer which limits the heat transfer from the heat source to the substrate and the mass transfer from the substrate to the heat source resulting in protection of the underlying material [5,6].

The fire retardant performance of ammonium polyphosphate (APP) and expandable graphite (EG) in polyurethane have been previously reported [7]. The flame retardant mechanisms of both additives have been investigated from a chemical aspect. When APP is added to PU [8], char formation is favoured. The char from PU/APP formulation results from interactions between the additive and the polymer and consists of polymer chains trapped by phosphate links in the carbonaceous shield. In the case of PU/EG [9], it has previously been demonstrated that there is no chemical reaction between the additive and the polymer. Consequently less char is formed (compared with PU/APP). The protective shield from PU/EG consists of expanded "worms" of graphite embedded in the tarry degraded matrix of polyurethane. Thus, the chemical structures of the charred materials are different.

Since the intumescent shield consists of a mixture of a solid (char) and a liquid phase (tar), the importance of the visco-elastic properties of this layer is evident [10–13]. A visco-elastic material possesses a complex dynamic viscosity. Its storage modulus G′ is associated with the energy stored in elastic deformation and its loss modulus G″ is associated with the viscous energy dissipation. The ratio of G″ and G′ gives another parameter called the dissipation factor or the loss tangent which is a probe of the ability of the material to deform.

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Investigation of these parameters as a function of temperature or strain gives important information on the fire performance particularly on the intumescence process of various materials. When the temperature increases and under a strain effect, the material may either deform or split. In the case of crack formation, the material rapidly degrades via oxygen diffusion and mass/heat transfer between the virgin material and the flame in degradation conditions. Consequently, for the charred layer, when formed, to be effective it has to deform without crack formation to preserve the protective character of the carbonaceous shield. Previous studies on thermoplastic polymers have shown good correlation between the different steps of intumescent structure formation and degradation, and measurements of the apparent viscosity [14–17]. This technique, recently developed, is a powerful tool in the study of char formation because it enables characterisation of both the intumescent process and the char strength. The loss of the protective character related to the superficial foam morphology may be explained by change in the viscosity of the charred material under stress. Moreover, the mechanical destruction of the intumescent char is also an important task of investigation. If a char has good structural, morphological and heat insulating properties but is easily destroyed under mechanical action, its efficiency is totally lost [13].

This study investigates the rheological and mechanical destruction properties of the protective charred layer resulting from PU/APP and PU/EG thermoset coatings. Because these layers are chemically different, it is of interest to investigate and to compare the rheological behaviour of the carbonaceous shields formed from PU/APP and PU/EG and to correlate this behaviour with the fire retardant performance of the coatings.

2. Experimental

2.1. Materials

Raw materials were polymeric diisocyanate diphenylmethane and polyester polyol. PU coatings are obtained by polycondensation of the isocyanate with the polyol. The molar ratio NCO/OH has been fixed equal to two. Ammonium polyphosphate (APP, $(NH_4PO_3)_n$, $n = 700$, Hoechst Hostaflam AP422, soluble fraction in $H_2O < 1$ wt.%) was incorporated in PU at a 40 wt.% loading and Expandable Graphite (EG, Callotek 500, Graphitwerk Krophfmühl) at a 15 wt.% loading.

Initial mixing of monomers with the additives is first carried out using a Turbo Turrax mixer (8000 πRad/min). Then, the components are stirred (1000 πRad/min) in disposable paper cups (500 ml) at room temperature for 1 min and allowed to polymerise for 24 h.

2.2. Thermal scanning rheometer

Rheological measurements were carried out using a Rheometric Scientific ARES-20A thermal scanning rheometer (TSR) in a parallel plates configuration (Fig. 1). A dynamic viscometer is a special type of rotational viscometer used for characterising viscoelastic fluids. It measures elastic together with viscous behaviour by determining the response to both steady rate and oscillatory shear. The thermal scanning rheometer is designed (using the RHIOS V6–4.3 instrument configuration) for monitoring the changes in the rheological properties versus temperature and/or time.

Coating samples ($25 \times 25 \times 1$ mm^3) were placed between the two plates (25 mm diameter) with a starting gap around 1mm. A constant normal force was systematically applied in order to obtain good adhesion between sample and plates, and also to assure the validity of the results. First, the viscosity measurements were carried out varying the value of the stress, of the normal force and of the frequency in order to define the best operating conditions for determining the viscosity values over the complete temperature range (20–500 °C). The determined conditions are: normal force: 100 g (i.e. 2000 Pa relative pressure), strain value: 5% (i.e. 2.9°), frequency: 10 rad s^{-1}. These conditions enable preservation of the material during the formation of intumescence. An initial test was performed over the complete temperature range (heating rate: 10 °C/min) to determine the characteristic temperatures corresponding to changes in the visco-elastic behaviour. Then the measurement of viscosity was carried out at the corresponding temperatures with a time in the reactor of 2 min before applying the normal force and the strain.

This apparatus also enables determination of the char strength. With that aim, a sample is placed in the reactor 4 min before measurement in order to enable the development of the intumescence without any perturbation, as shown by TGA in isothermal conditions. Then the upper plate is put in contact with the material and is linearly (0.02 mm/s) forced down, with the force

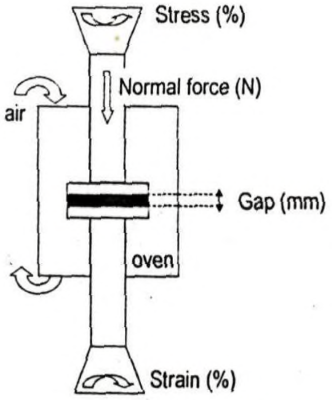


Fig. 1. Scheme of the rheometer in the parallel plates configuration.

being followed versus the distance between the two plates. This is illustrated in Fig. 2.

The upper plate used in these experiments has a diameter of 5 mm in order to increase the pressure on the sample and so to ensure the total char destruction.

Blowing measurements without strain were carried out using the same apparatus (plates of 25 mm diameter). A low constant normal force (30 g i.e. 600 Pa relative pressure) was applied to the sample in order to avoid crushing the char, and also to assure the validity of the results. The heating rate was also 10 °C/min in the range 20–500 °C.

2.3. *Thermogravimetric analysis*

TG analyses were performed using a Setaram MTB 10–8 thermobalance from 20 to 800 °C at 10 °C/min under air flow (Air Liquide grade. 5×10^{-7} m^3/s measured in standard conditions). Samples (about 10 mg) were placed in vitreous silica pans. Precision on temperature measurements is ±1.5 °C.

2.4. *Differential scanning calorimetry*

Differential scanning calorimetry was carried out under nitrogen flow (N45 Air Liquide grade, 5×10^{-7} m^3/s measured in standard conditions) in aluminium pans using Setaram DSC 92 instrument (sample weight 10–20 mg). The thermogram was obtained at a heating rate of 10 °C/min from −20 to 100 °C. Glass transition temperature (T_g) is determined according to DSC experiment.

2.5. *Thermal volatilisation analysis (tva)*

TVA experiments consist of measuring the pressure (via Pirani Gauge) of substances undergoing transfer from one point to another in an initially evacuated system, which is continuously pumped. These experiments give the rate of volatilisation versus temperature (or time). TVA experiments have been carried out with a heating rate of 10 °C/min in the temperature range 20–500 °C.

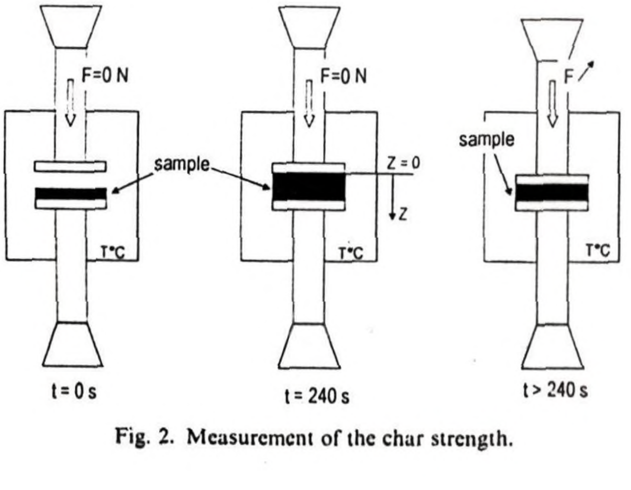


Fig. 2. Measurement of the char strength.

2.6. *Optical microscopy*

Optical microscopy was carried out using an Olympus BX60 microscope equipped with a Sony digital Hyper HAD colour video camera. Pictures were treated using the Olympus Microimage software.

3. Results and discussion

Good correlation may be obtained between the blowing measurement without stress, the weight loss (TGA) and the emission of gases (TVA). Figs. 3–5 report these data for PU, PU/EG and PU/APP coatings.

In the case of pure PU, the blowing as well as the weight loss and the evolution of gases start at 250 °C. The rate of blowing is very high and the maximum gap (≈150%) is reached around 300 °C. When the temperature increases, the charred material degrades: the gap decreases rapidly between 300 and 370 °C and then slowly up to 500 °C. It is of interest to note that 370 °C corresponds to the end of the first step of degradation (change of the TGA slope, end of the first peak of TVA). According to these data, we may assume that the char which is formed between 250 and 300 °C is not stable at high temperature.

The curves for PU/EG coating are also significant. At 200 °C the material starts its expansion. This temperature also corresponds to the beginning of the weight loss and of the emission of gases. The expansion is very quick and is maximum at 300 °C. For higher temperatures, the gap slowly decreases but remains relatively high (≈250% at 500 °C). So, in contrast to PU coating, the carbonaceous layer which is formed during the degradation of PU/EG i.e. between 200 and 300 °C is stable in the high temperature range. This is interesting in terms of fire retardancy because it is this layer which enables insulation of the virgin material in a fire or in the degradation conditions from the action of the heat source and which consequently imparts fire retardant properties to polymeric material.

In the case of PU/APP, no blowing is observed in the conditions of the experiment (10 °C/min). However, a small increase in the gap value is observed at 270 °C.

In fire conditions (Fig. 6), the blowing behaviour is different. In the case of PU/EG formulation, expansion up to 10 times its original thickness occurs. The mixture PU/EG generates an intumescent layer with a "worm-like" structure. In the case of APP, the blowing of the sample is less important (about 3 times its original thickness).

The viscosity of an intumescent system is an important parameter which influences the formation of the char and its physical properties [10,18,19]. It is generally accepted that the viscosity of the char has to be low enough to accommodate the stress induced by the pres-

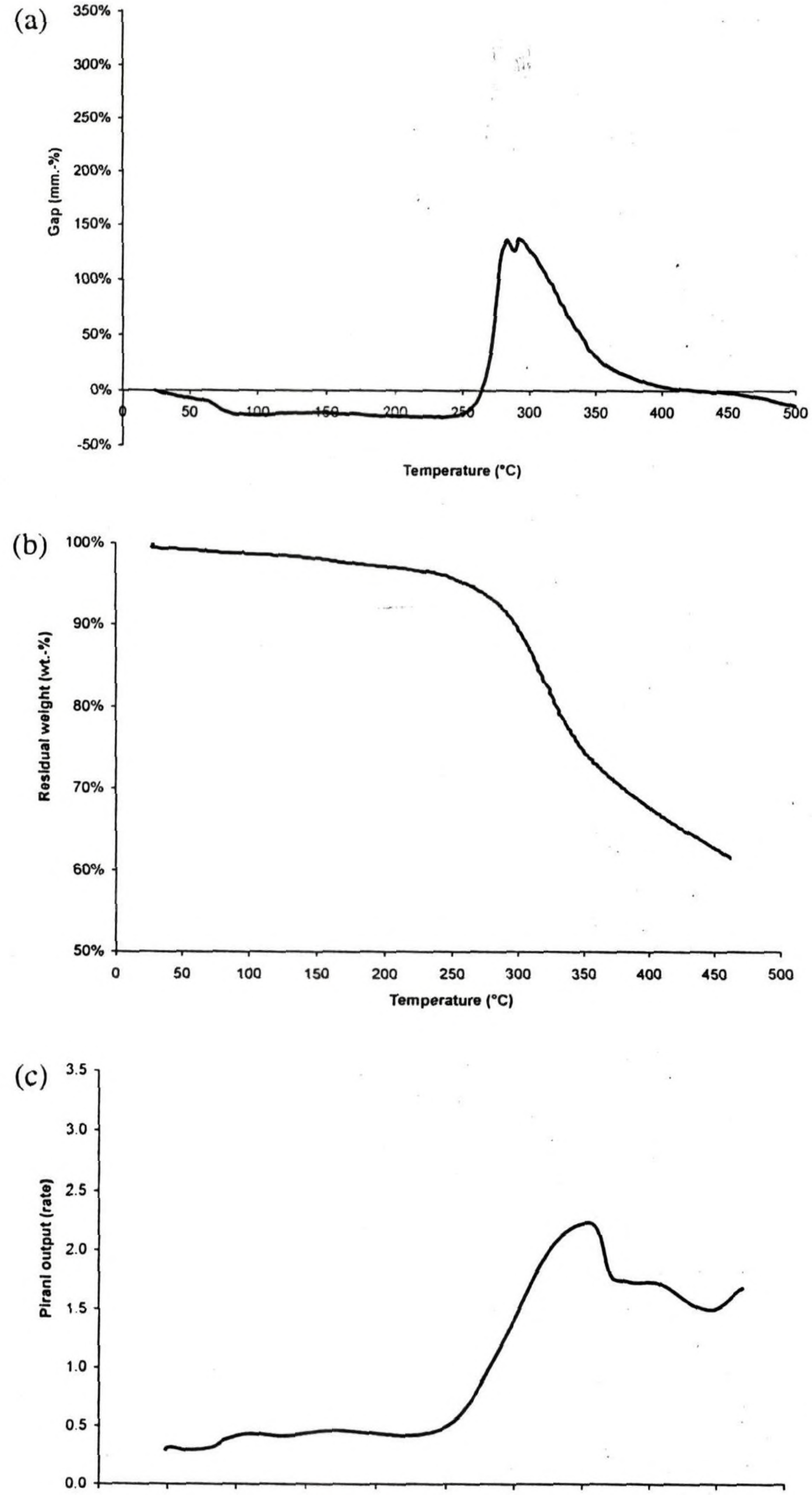


Fig. 3. Gap variation (a), TGA (b) and TVA (c) for PU coating.

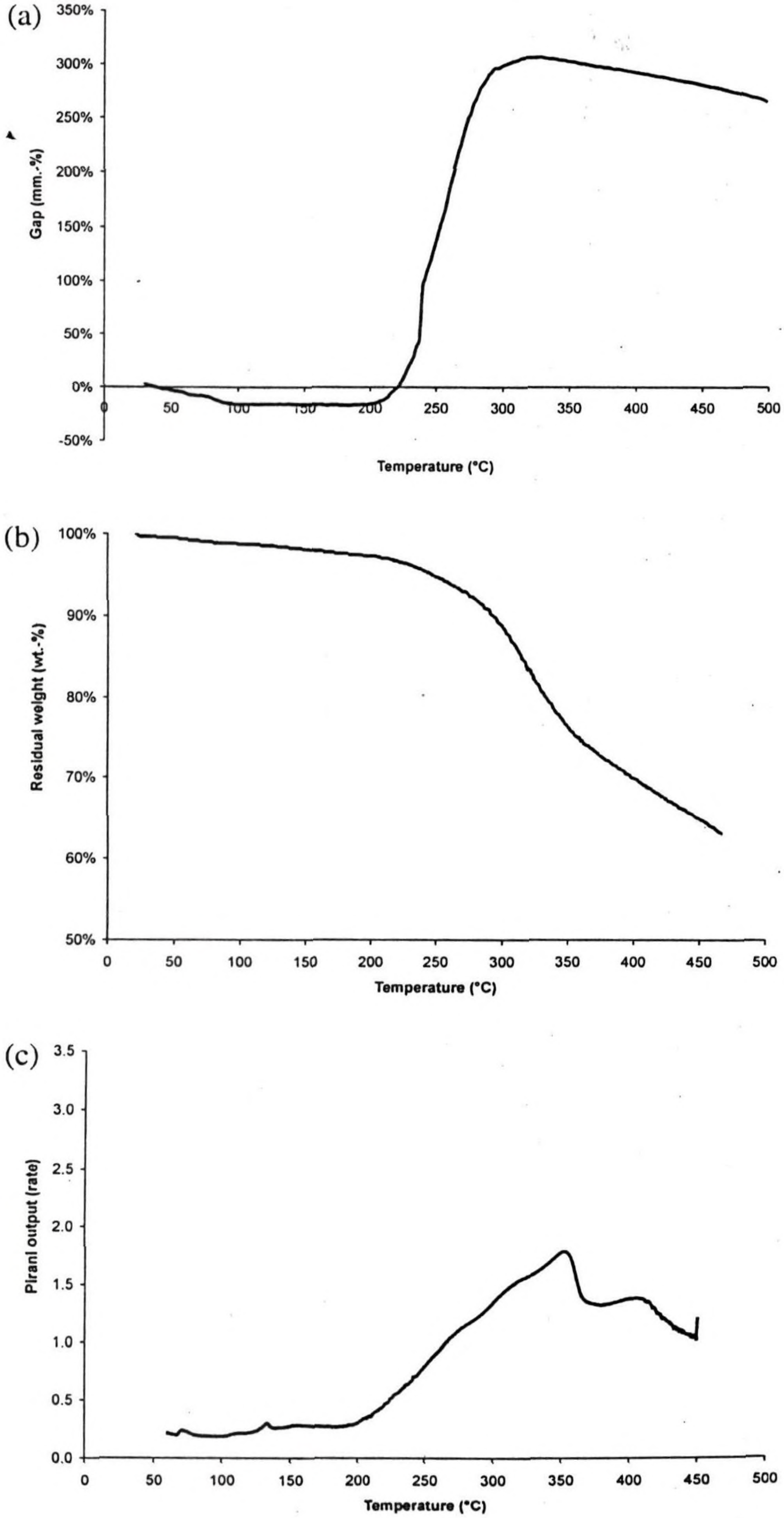
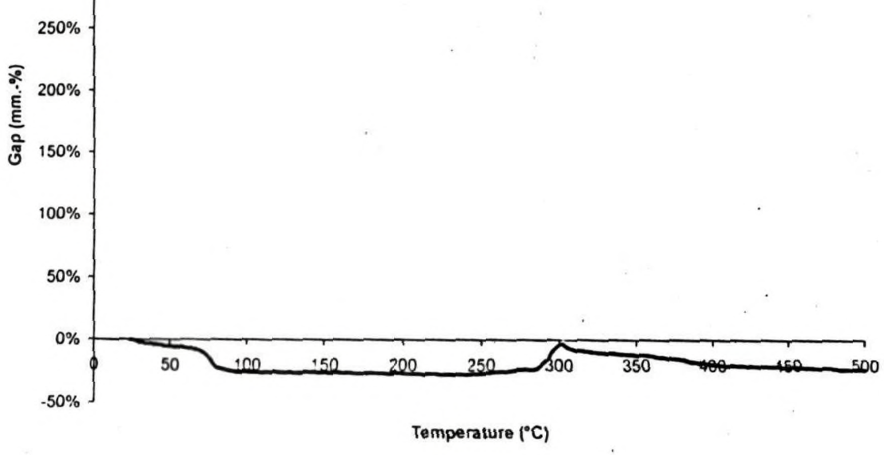
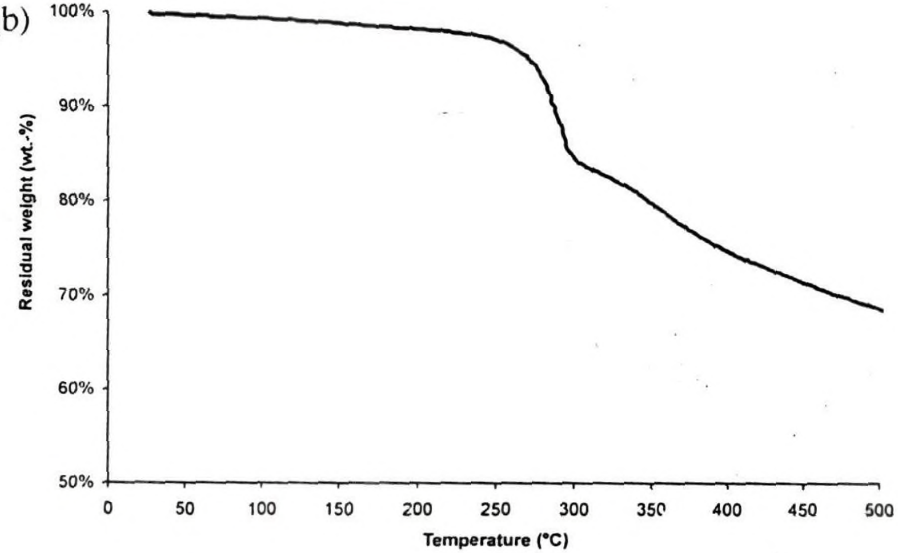


Fig. 4. Gap variation (a), TGA (b) and TVA (c) for PU/EG coating.


250%
200%
150%
100%
50%
0%
-50%
Gap (mm.-%)
0
50
100
150
200
250
300
350
400
450
500
Temperature (°C)

(b)


100%
90%
80%
70%
60%
50%
Residual weight (wt.-%)
0
50
100
150
200
250
300
350
400
450
500
Temperature (°C)

(c)


3.5
3.0
2.5
2.0
1.5
1.0
0.5
Pirani output (rate)

sure of the trapped gases, and high enough to encapsulate these gases and consequently provide expansion of the material. Fig. 7 reports the dynamic viscosity versus temperature for PU, PU/EG and PU/APP coatings versus temperature.

In a thermoplastic polymer [14–17], the intumescence process can be divided in three steps: melt flow, volatilisation and solidification. The viscosity data are only valid for the melt flow stage before decomposition. In the two last steps, the phenomenon which occurs between the two plates is complicated and the viscosity measurements are not valid. In fact, emission of gases may result in problems of contact between the plate and the material. In the solidification step, shear and impact damage of the material may occur. Even if the parameters of the experiment (Normal force, shear angle...) are adjusted in order to avoid these problems, the viscosity values can not be taken into account by themselves but relative variation of these data can be considered.

In the case of thermoset polymers, for which carbonisation occurs before melting, the intumescence process is different and more complex. Only solidification/volatilisation steps are observed. In the case of pure PU, the dynamic viscosity increases between 250 and 500 °C and is lower than the one of the fire retarded systems (Fig. 7). For PU/EG coating, the intumescent process may be divided in three steps:

- a slow increase in the viscosity between 200 and 300 °C, -
- a rapid increase in the viscosity between 300 and 400 °C,
- a decrease in the viscosity between 400 and 500 °C.

The first step corresponds to the expansion zone i.e. to the formation of the intumescent layer as was demonstrated earlier. At this step, the material consists at the same time, of gaseous, liquid and solid phases resulting in a slow increase in the viscosity. When the layer is formed, the carbonisation is still going on. It leads to a sharp increase of the viscosity. The last step of η^* may be attributed to the destruction of the intumescent layer. At high temperature, the PU matrix degrades but the expanded graphite is stable. The graphite planes may slip over each other resulting in a decrease of the viscosity.

In the case of PU/APP, the development of the intumescence process is more complicated: the viscosity increases between 170 and 270 °C, then it decreases between 270 and 300 °C, it remains nearly stable between 300 and 400 °C and finally it increases sharply at higher temperature. The phospho-carbonaceous layer, which is formed during the degradation of PU/APP is composed of aromatic stacks linked by some phosphorous bridges [8]. The bridges have been demonstrated to be present between 290 and 320 °C. The formation and the subsequent destruction of the bridges could explain the successive increase and the decrease in the viscosity between 170 and 300 °C. Spectroscopic investigation [8] of the intumescent char has also showed the presence of phosphoric acid in the temperature range 290–400 °C. The structure of the sample could explain the plateau between 300 and 400 °C. A pasty intumescent shield is formed in which a liquid (the major part) and a solid coexists [15]. This liquid phase may be responsible of the stabilisation of the viscosity values. The sharp increase in the viscosity for a temperature higher than 400 °C may be explained by a final charring process. The carbonaceous char layer is then composed mainly by a solid phase.

The dissipation factor or loss tangent (Fig. 8) also gives important information on the intumescence. A first peak of tan δ is observed for the three coatings with a maximum around 60 °C. DSC analyses (Table 1) show that this temperature corresponds to the glass transition. Moreover, FTIR spectra [Fig. 9(a)] of the coatings at ambient temperature demonstrate that the polymerisation reaction is not complete. The N=C=O band around 2270 cm^{-1} is still observed whatever the coating. The mobility of the polymer chains which occurs during the glass transition enables the polymerisation to finish. This is demonstrated by the decrease in the intensity of the isocyanate band in the FTIR spectra of the coatings after a heat gradient [Fig. 9(b)].

Table 1
Glass transition temperature of PU coatings (DSC measurement)

Coating	PU	PU EG	PU/APP
T_g (°C)	46	52	52

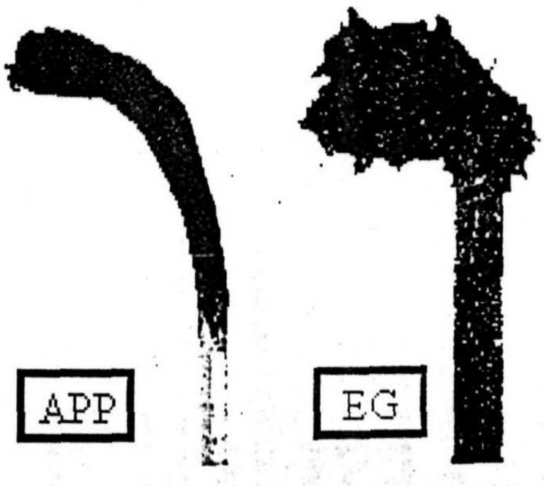


Fig. 6. PU-based samples after LOI test (42 and 29 vol.% oxygen content, respectively (for PU/APP and PU/EG).

A second peak of loss tangent is observed for pure PU and for both intumescent materials. This peak of tan δ for pure PU occurs between 200 and 370 °C with a maximum at 330 °C. In that temperature range, development of the intumescent occurs as was demonstrated earlier. The structure of the material in this range includes both a solid phase and a liquid phase which leads to variation of loss tangent.

The second peak of tan δ is similar for PU/EG coating but the maximum occurs earlier (around at 310 °C i.e. when the expansion of PU/EG is total) and is lower (around 0.3). This may be correlated with the presence of the expandable graphite. The graphite contributes to the solid phase in the intumescent shield and consequently leads to a loss of the elasticity of the material. It results in a comparative decrease in tan δ.

In the case of PU/APP, the value of the maximum of loss tangent is more important. Its decrease is very fast and occurs around 300 °C with a maximum at 290 °C, corresponding to a maximum of the apparent viscosity (Fig. 4). A plateau is observed between 300 and 400 °C, as for the dynamic viscosity data. In contrast to EG, APP evolves phosphoric acid when it degrades and thus contributes to the liquid phase of the intumescent shield. Moreover, the phosphorus bridges present in the char confer a "flexibility" which is not observed for

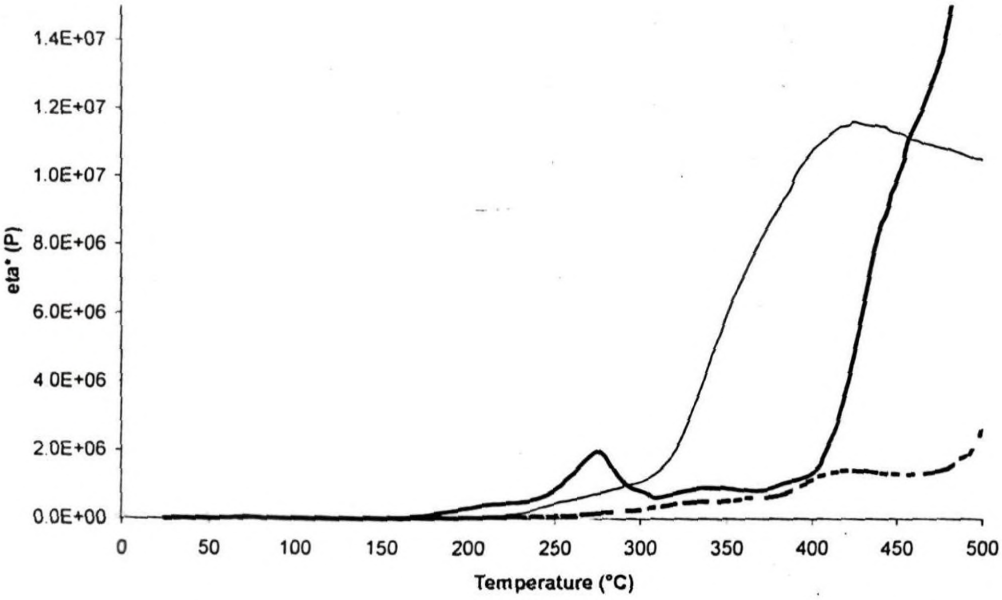


Fig. 7. Variation of the dynamic viscosity versus temperature for PU (– –), PU/EG (—) and PU/APP (—) coatings.

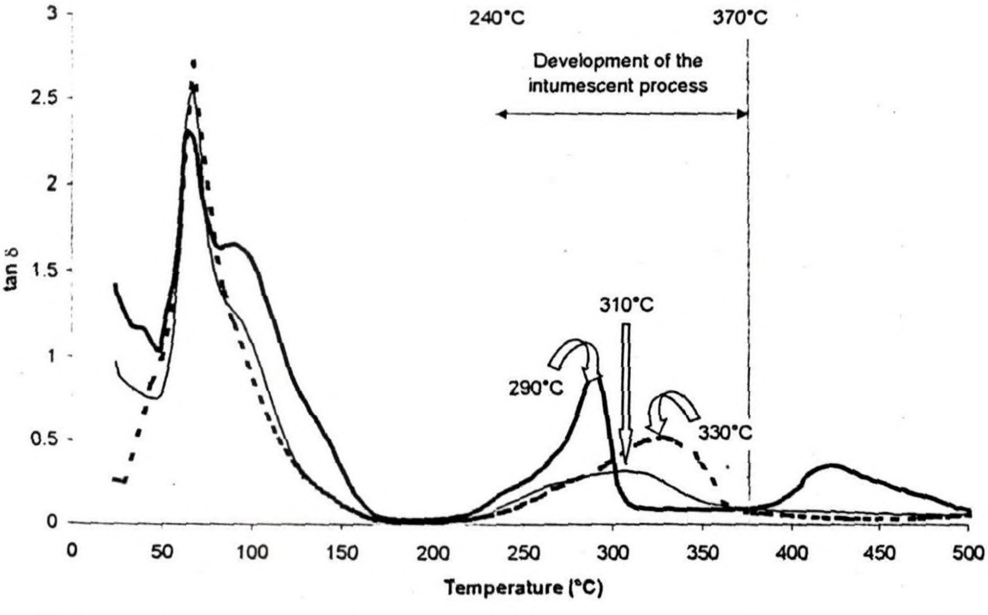


Fig. 8. Variation of tan δ versus temperature for PU (– –)PU/EG (—) and PU/APP (—) coatings.

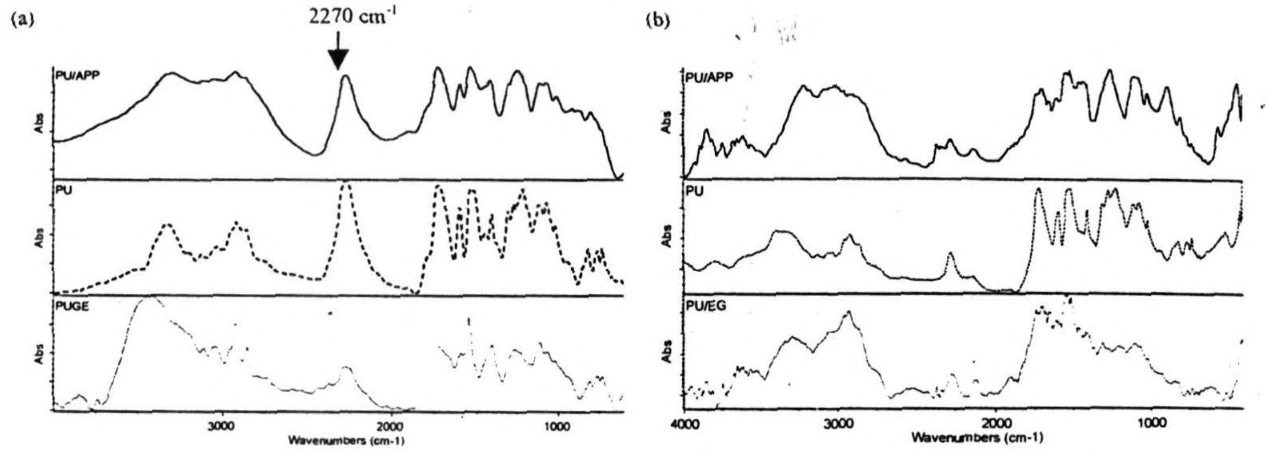


Fig. 9. FTIR spectra of PU (– –), PU/EG (—) and PU/APP (—) coatings before (a) and after (b) a temperature gradient (from ambient to 150 °C with a heating rate of 10 °C/min).

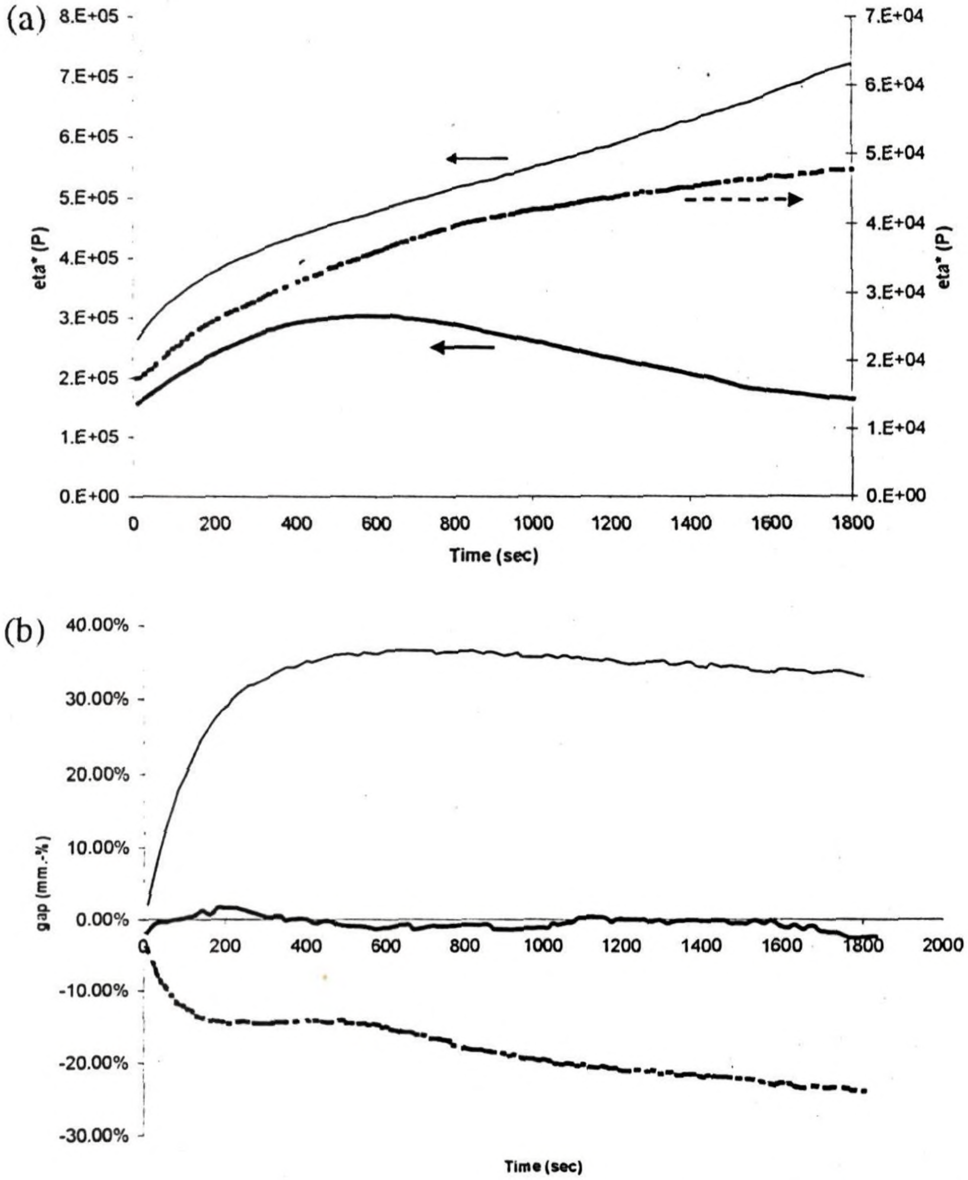


Fig. 10. Change of the viscosity (a) and of the gap (b) versus time at the beginning of the development of the intumescence process ($T = 240$ °C) for PU (– –), PU/EG (—) and PU/APP (—) coatings.

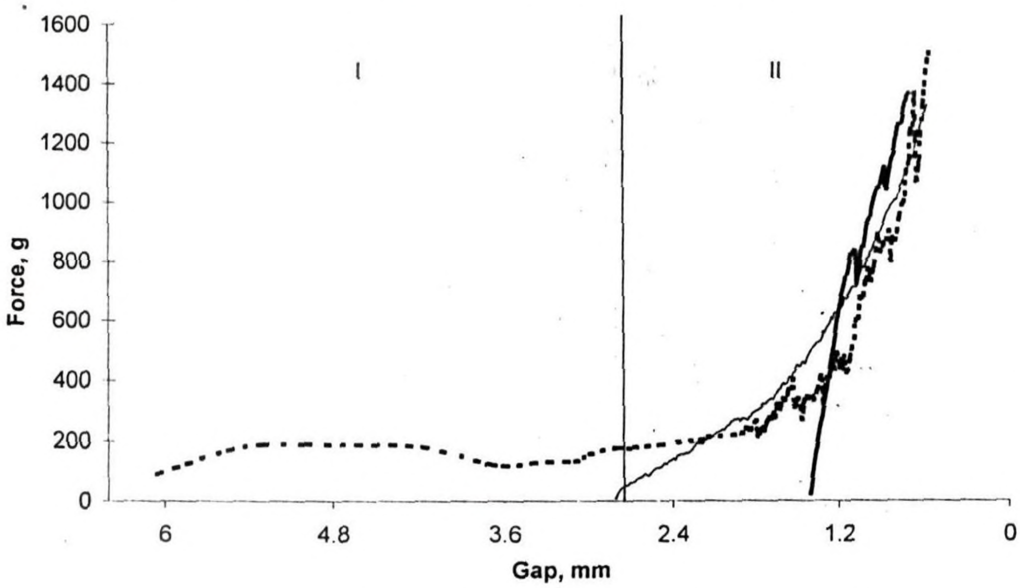


Fig. 11. Evolution of the char strength for PU (– –), PU/EG (—) and PU/APP (—) coatings at a temperature of 450 °C.

pure PU. This may explain the difference in the variation of tan δ between PU, PU/EG and PU/APP.

Finally, a third peak of tan δ is observed only for PU/APP in the temperature range 400–500 °C. It corresponds to the carbonisation process (sharp increase in the viscosity; Fig. 7). This visco-elastic behaviour is of interest in terms of fire retardancy since, at high temperature, the intumescent shield may accommodate the stress due to internal pressure of gases without crack formation. So, the insulating properties are maintained in a high temperature range.

According to these data, it is of interest to analyse the visco-elastic behaviour of the coatings at the beginning of the development of the intumescence i.e. at 240 °C. Fig. 10 represents the variation of the viscosity and of the gap versus time at 240 °C. The apparent viscosity is always lower than that of intumescent materials for pure PU as it has been previously observed in the whole temperature range. However, its evolution is similar to that of PU/EG coating; the viscosity increases as a function of time. In the case of PU/APP, the viscosity increases and then decreases after 600 s. This behaviour is interesting in terms of fire retardancy because when intumescence develops, the carbonaceous shield may deform without crack formation.

The gap change versus time also gives interesting information on the char strength and on its foaming behaviour. Indeed, in the case of PU/EG, a thick layer is formed and is maintained throughout the experiment (30 min). This layer is thick enough to ensure fire protection. In the case of PU/APP, no blowing is observed but the layer is preserved up to 30 min and it was demonstrated earlier that its visco-elastic behaviour enables us to explain the fire performance of PU/APP coating. Finally, in the case of PU, the strength of the carbonaceous layer is very low. In fact, the shear involves destruction of the shield which consequently leads to a decrease in the gap value versus time.

The mechanical properties of the char are also an important task of investigation because the efficiency of the fire protection depends up on these factors.

Fig. 11 represents the dependence between the destruction force and the distance for pure PU and for the intumescent formulations. The apparatus enables us to study the char properties in the degradation conditions. It is important because the properties of the char are different in the flame and after cooling.

The curve for PU is typical curve of destruction in conditions of the compressional rheometer [14]. The curve may be divided into two parts: the destruction of the char (I—the force is almost constant) and the destruction of the pyrolysis zone (II—the force increases

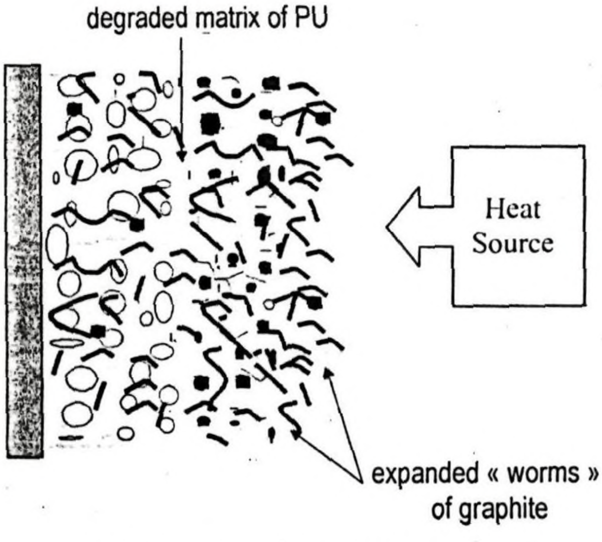
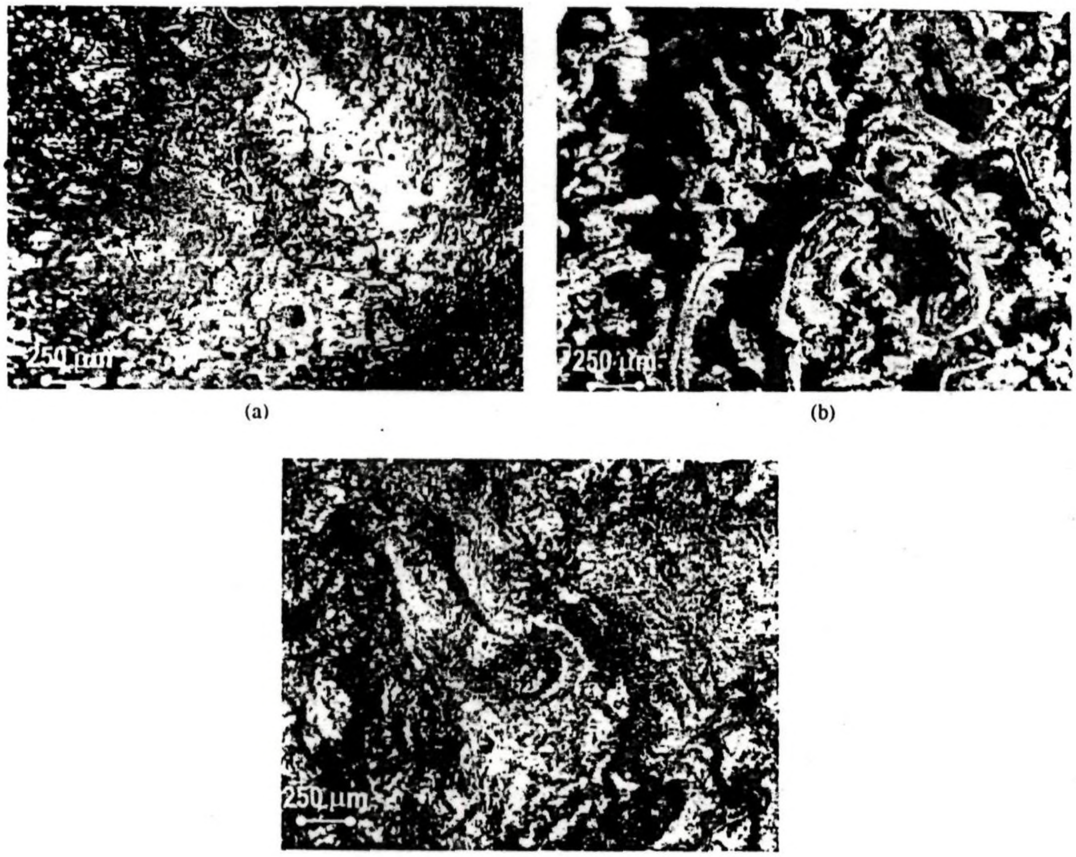


Fig. 12. Structure of PU/EG after expansion.



(a) (b)

(c)

Fig. 13. Optical microscopy picture of the surface of PU (a), PU/EG (b) and PU/APP (c) samples after exposure at 800 °C during 15 min magnfication: ×40).

sharply). In the case of intumescent materials, the behaviour is different.

For PU/EG coating, the curve consists of two linear parts which may be attributed to a first compression of he expanded graphite worms followed by a compression of the degraded matrix of PU including expanded graphite. In fact, the blowing of graphite is very imporant and is larger than the expansion of the matrix. Consequently, the expanded material will present on its surface a zone rich in graphite particles but poor in degraded matrix. The core of the material will present a higher proportion of degraded matrix trapping expanded graphite "worms". This structure is illustrated in Fig. 12. The zone which is poor in degraded PU matrix s the easiest to compress. Consequently, the slope is ower in this part of the curve.

In the case of PU/APP, the blowing is very poor as demonstrated earlier. Consequently, the compressional force is linear and very high which corresponds to the compression of a thin but resistant carbonaceous shield. The curve does not present a part corresponding to the destruction of the any foamed char.

The optical microscopic pictures of the surface of the coatings (Fig. 13) after heat treatment are in good agreement with previous results. Indeed, cracks are presented on the surface in the case of PU whereas large domains of deformation are observed for PU/APP coating. In that case, a "hills and valleys" topography is observed. This confirms that the rheological properties of the char enable deformation rather than cracking of the surface which favours the fire retardant performance. In the case of PU/EG coating, the structure of the surface is mainly composed of expanded graphite flakes as previously assumed.

4. Conclusion

This study develops an original technique for the characterisation of the intumescence process in the case of thermoset polyurethane coatings. It enables us to obtain at the same time information on the foaming process and on the strength of the char. This method is in a preliminary stage of development but interesting results have already been obtained.

In combination with spectroscopic study, this study enables us to better understand the fire retardant action of APP and EG in PU coating. As was previously assumed, the modes of action of both additives are different. In the case of PU/EG, a very thick layer is obtained. This layer combines low density and heat insulative properties. This enables it to impart fire performance of interest to the coating. In the case of PU/APP, the carbonaceous layer is not expanded but presents a visco-elastic behaviour which ensures the fire protection in a large range of temperatures. Indeed, in fire conditions, deformation of the shield occurs rather than crack formation, which limits heat and mass (oxygen as well as fuel) transfer between the virgin polymer and the flame. It results in fire performance of interest.

Acknowledgements

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