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Thermal stability and flammability studies of coated polymer powders using a plasma fluidized bed process

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In this work, the thermal stability of organosilicon coatings, polyamide-6 powders and polyamide-6 clay nanocomposite powders coated with organosilicon are studied. The coatings were obtained from polymerization of 1.1.3.3-tetramethyldisiloxane (TMDS) monomer doped with oxygen using a cold remote nitrogen plasma (CRNP) process. A fluidized bed reactor using CRNP assisted polymerization was used to coat the polymer powders. The effect of oxygen addition to TMDS on the thermal stability was investigated. Oxygen addition to TMDS promotes the formation of more thermally stable coated polymers. In the case of the polyamide-6 clay nanocomposite, the Limiting Oxygen Index values were much improved. This shows that the deposits are effective fire retardant coatings. © *2002 Kluwer Academic Publishers*

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1. Introduction

The increasing use of polymers in many fields such as housing, transport and electrical engineering applications poses a problem because of their high flammability. Several ways have been investigated to reduce fire risks. The classical way to flame retard a polymer

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is to incorporate additives. This causes problems as it reduces mechanical properties. Moreover, it leads to ecological problems concerning for example the incineration of polymers loaded with halogenated flame-retardants [1]. Chemical modification of the macromolecule and surface modification (γ-ray radiation) are two other possible ways [2–4]. Chemical modification presents difficulties in processing on the industrial scale. Thus, surface modification is an attractive method.

Here, surface modification is investigated by laying down a thin film on the polymer using a plasma assisted polymerization technique. A plasma deposition process induced by cold remote nitrogen plasma (CRNP) has been developed. This process has the advantage of not damaging the substrate by high-energy particle bombardment from the plasma, in comparison to the traditional plasma enhanced chemical vapor deposition.

In the CRNP process, the substrate is removed from the plasma as the plasma and the reaction chamber are spatially separated [5–9]. The main reactive species of the CRNP are nitrogen atoms in the ground electronic state and electronically and vibrationally excited nitrogen molecules. The CRNP is then a non-ionized reactive zone and is characterized by an nonequilibrium thermodynamic state. CRNP assisted polymerization of organosilicon compounds is an interesting preparation technique for thin polysiloxane based films [5–10]. These polymers are known to have good thermal stability. Specific industrial aspects of CRNP assisted polymerization have been protected by industrial patents [10–12].

In preliminary work [13, 14], results on the fire retardancy performances of polyamide-6, polyamide-6 clay nanocomposite and polymers coated by the CRNP process were presented.

Here, a CRNP process is used to coat polymer sheets or powders. As powder is difficult to handle in the classical plasma treatment because of the aggregation phenomenon, a fluidized bed reactor using CRNP assisted polymerization has been developed in order to coat polyamide-6 (PA-6) and polyamide-6 clay nanocomposite (PA-6 nano) powders with thin polysiloxane based films. Fluidized bed reactors are characterized by perfect mixing of the particles, high rate of transfer phenomena and very reactive chemical species [15]. The thermal stability of organosilicon coatings, obtained from the polymerization of 1.1.3.3-tetramethyldisiloxane (TMDS) monomer doped with oxygen and coated polymers are studied. Fire retardancy performances are evaluated using Limiting Oxygen Index (LOI). The effect of oxygen addition to TMDS monomer on the thermal stability of the coated polymer is also discussed.

2. Experimental

2.1. Materials

The monomer was 1.1.3.3-tetramethyldisiloxane 97% (TMDS) which was supplied by Aldrich Chemical Co. Raw materials were polyamide-6 (PA-6, as pellets supplied by UBE Industries) and polyamide-6 clay nanocomposite (PA-6 nano, as pellets supplied by UBE Industries, clay mass fraction of 2 wt%). Polymer sheets used for Limiting Oxygen Index tests were made using a Darragon press at 235°C with a pressure of 10^6 Pa. The polymer powder (particle size lower than 200×10^{-6} m) was obtained using a Retzsch cryogenic grinder at about −196°C.

2.2. Experimental set-up

2.2.1. CRNP fluidized bed reactor

Fig. 1 shows the experimental set-up of a CRNP fluidized bed assisted deposition reactor. This reactor was used to deposit an organosilicon film on the surface of the powders. The discharge was created in a 70 cm long, 0.9 cm diameter quartz tube by a Broïda cavity [16] cooled by compressed air and connected to a 2450 MHz microwave generator. The nitrogen flow rate ($\phi(N_2)$) was regulated by an Alphagaz RDM 280 mass flow regulator (MFR). The reactor pressure was controlled by a Pirani type vacuum gauge. The CRNP excited species were extracted from the discharge zone by a primary pump.

The fluidized bed reactor is composed of a 75 cm high and 3.5 cm internal diameter Pyrex tube. The reactive gas (TMDS) and oxygen were injected into the reactor through a coaxial injector. This injector was situated in the fluidization zone at a distance of 65 cm downstream from the discharge. The gas flow rates, ϕ(TMDS) and $\phi(O_2)$, were regulated by MKS mass flow controllers.

Initially, the polymeric powders were fluidized by a flow of nitrogen plasma doped with oxygen in order to modify the chemical composition of their surfaces. An increase of surface functionality and hydrophilic character was observed. Oxygenated and nitrogenated functional groups were incorporated on the surface of the polymers [15]. Nitrogen and oxygen flow rates were respectively 500 sccm and 3.7 sccm (standard cubic centimeter per minute). The incident microwave power was equal to 300 W and the treatment time was 10 min.

Secondly, an organosilicon film was deposited on the surface of PA-6 and PA-6 nano powders by CRNP assisted polymerization. The incident microwave

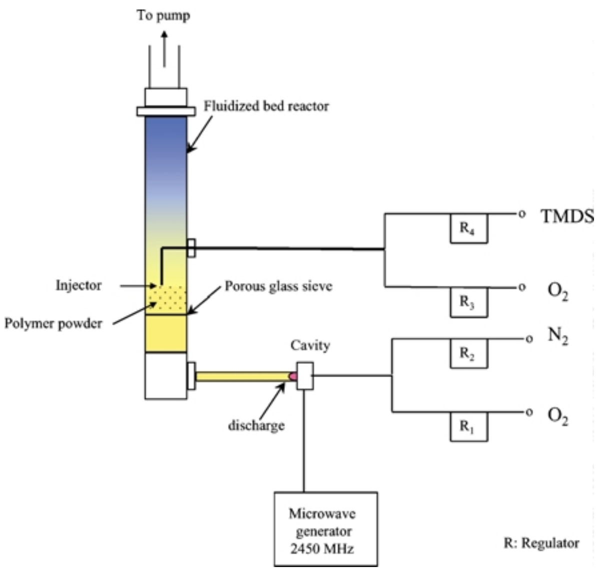

Figure 1 Experimental set-up of a CRNP fluidized bed assisted deposition reactor.

power and nitrogen flow rate were maintained constant and equal respectively to 300 W and 500 sccm. Oxygen flowing at a rate in the range of 10–150 sccm was mixed with a constant TMDS flow rate of 5 sccm. The deposition time was equal to 40 min. In order to investigate the nature of the coatings in the absence of the polymers, deposits were made on aluminum plates and the deposited material removed for analysis.

2.2.2. CRNP assisted deposition reactor

The experimental setup of the CRNP assisted deposition reactor is described elsewhere [5]. This reactor was used to deposit an organosilicon film on PA-6 and PA-6 nano plates for the limiting Oxygen Index tests. Nitrogen was introduced under a pressure of 4.2 hPa at a flow rate of 1800 sccm in a quartz tube of 33 mm outer diameter. The discharge excitation was created by a coaxial coupling device [17] at 2450 MHz. The gas containing excited species was extracted from the discharge zone by a primary pump. The reactive gas, TMDS mixed with oxygen, was injected into the reaction chamber through a coaxial injector at a distance of 1.5 m downstream from the discharge.

Samples were placed horizontally in the reactor and coated successively on each face; the reactor was set to atmospheric pressure between these two steps (few minutes). In order to obtain homogeneous deposits, the substrates were located at a distance of 10 cm from the injector inlet. The incident microwave power was maintained constant and equal to 600 W. Oxygen flowing at a rate in the range of 10–150 sccm was mixed with a constant TMDS flow rate of 5 sccm. The deposition time was 20 min for each face. The thickness of the deposit was about 30 μm at $\phi(O_2) = 50$ sccm.

2.3. Thermogravimetric (TG) analyses

Thermogravimetric analyses were performed using a Setaram apparatus at a heating rate of 7.5°C/min from 20 to 800°C under 30 sccm of air flow (Air Liquide Grade). A sample of either a deposit or a coated polymer powder (about 10 mg) was placed in an open vitreous silica pan. The precision of temperature measurements is ±1.5°C over the whole range selected.

2.4. Limiting oxygen index (LOI) test

LOI was measured using a Stanton Redcroft instrument, according to the standard oxygen index test (ASTM D2863/77) [18]. This test provides a comparative numerical value for research and quality control. It is based on the determination of the limiting percentage of oxygen in a gas mixture which will just sustain the candle like burning of a sample. The main drawback of the test is that it is not directly relevant to a normal fire situation.

3. Results and discussion

3.1. Thermal analyses

3.1.1. PA-6 and PA-6 nano

Fig. 2 shows the TG analyses of PA-6 and PA-6 nano. The first minor weight loss is observed above 50°C and can be assigned to the loss of physically sorbed water. The major stage of the weight loss (about 80%) occurs between about 300 and 470°C. It leads to the formation of a stable carbonaceous material between 450 and 500°C which decomposes above 500°C. In the case of PA-6 nano, a stable charred residue (about 2 wt% above 650°C) is formed. This residual weight is equal to the clay mass fraction in PA-6 nano. Thus, the addition of nanocomposite does not stabilize the polymer above 500°C.

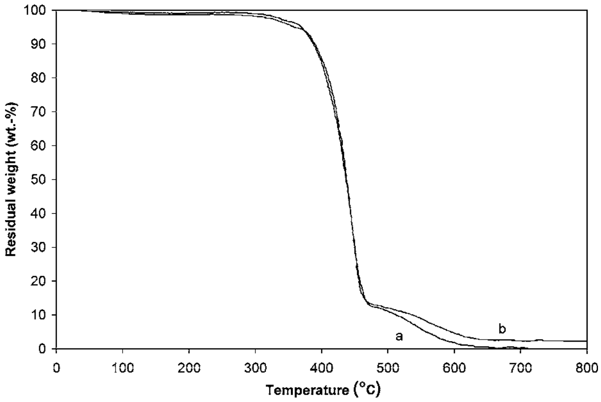

Figure 2 Thermogravimetric curves of PA-6 (a) and PA-6 nano (b).

3.1.2. Organosilicon coatings : effect of oxygen addition

Fig. 3 shows the TG analyses of the organosilicon deposit (i.e. the powdered material removed from the aluminum plate) obtained at different oxygen flow rates. At $\phi(O_2) = 10$ sccm, the main deposit decomposition is between about 320 and 480°C. A 53 wt% solid residue at 800°C results. On increasing $\phi(O_2)$ from 10 to 150 sccm, the degradation begins at a lower temperature (around 290°C) but it finishes at a similar temperature (around 480°C) whatever the $\phi(O_2)$. The residual weight increases sharply when $\phi(O_2)$ is increased from 10 to 50 sccm and continues to increase slightly at higher oxygen flow rates. These data clearly indicate that increasing oxygen flow during the polymerization promotes the formation of more thermally stable coatings.

Infra-red analyses were carried out in order to determine the nature of the deposit and solid residue

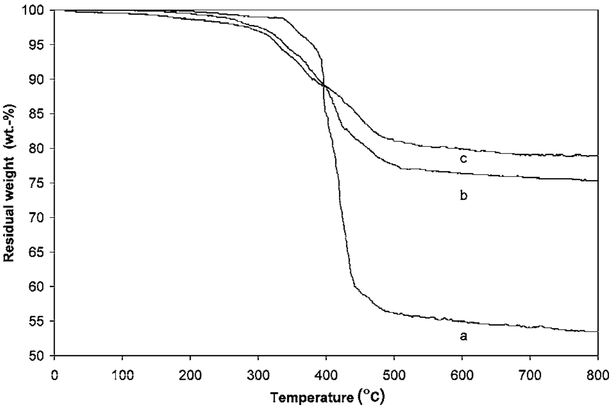

Figure 3 Thermogravimetric curves of organosilicon deposits for three oxygen flow rates (a : 10 sccm, b : 50 sccm, c : 150 sccm).

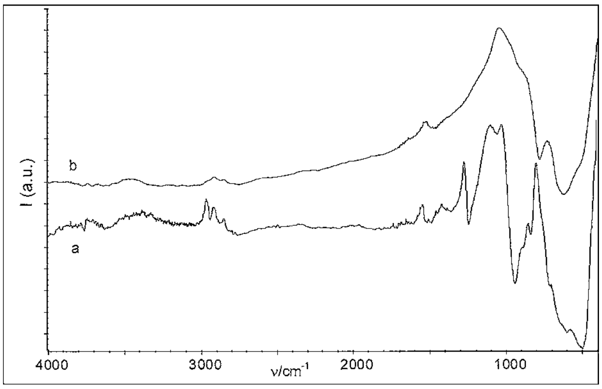

Figure 4 Infrared spectra of the deposit at 25°C (a) and the residue at 800°C (b) for $\phi(O_2) = 50$ sccm.

from TGA. Fig. 4 presents i.r. spectra of the deposit obtained at $\phi(O_2) = 50$ sccm at 25°C and the residue obtained after TGA experiments at 800°C. At 25°C, a sharp band assigned to the CH_3 symmetric bending mode appears around 1300 cm^{-1} and is characteristic of Si-CH_3 in a polysiloxane structure. The band observed around 800 cm^{-1} is characteristic of a H-Si-C bending motion. The polymeric structure is evidenced by a broad band appearing between 1000 and 1100 cm^{-1} which is assigned to the Si-O-Si stretching mode [19]. The spectrum of the residue is distinct from the one of the deposit. It is dominated by a broad band assigned to the Si-O-Si stretching mode. This result indicates that the solid residue obtained at 800°C has a SiO_2 like structure.

3.1.3. Coated polymer powders : effect of oxygen addition

3.1.3.1. Coated PA-6 powder. The TG curves of the PA-6 powder coated at different oxygen flow rates are presented in Fig. 5. The shapes of the TG curves are different to those of PA-6 and deposits. Degradation occurs between about 290°C and 450°C and between about 500°C and 680°C whatever the $\phi(O_2)$. The degradation begins at a similar temperature to the degradation of the coatings obtained with $\phi(O_2) = 50$ sccm or 150 sccm and results in a stable material at 450°C. A 2.5wt% solid residue is formed at 800°C. In the 450–650°C range, the thermal stability increases slightly as $\phi(O_2)$ increases from 10 to 150 sccm, as observed in the case of deposits.

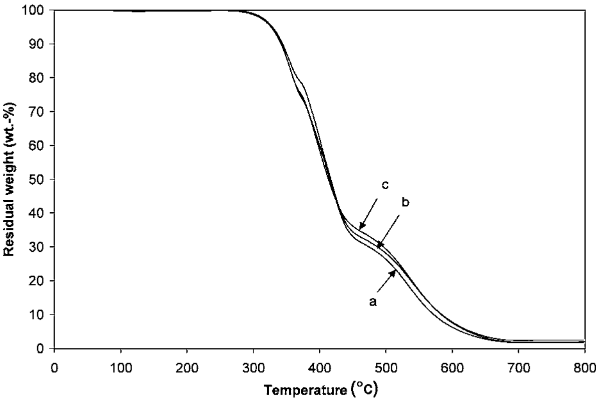

Figure 5 Thermogravimetric curves of coated PA-6 powder for three oxygen flow rates (a : 10 sccm, b : 50 sccm, c : 150 sccm).

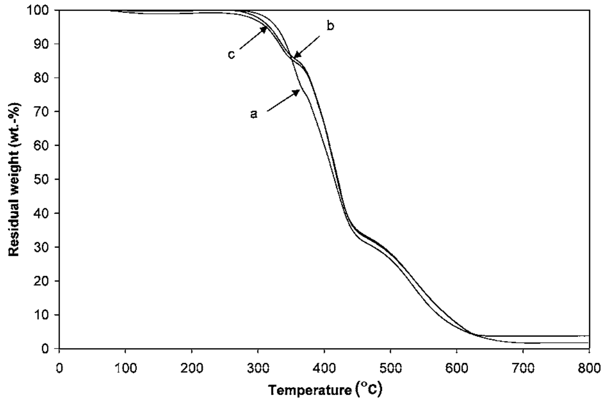

Figure 6 Thermogravimetric curves of coated PA-6 nano powder for three oxygen flow rates (a : 10 sccm, b : 50 sccm, c : 150 sccm).

3.1.3.2. Coated PA-6 nano powders. The TG curves of coated PA-6 nano powders for various oxygen flow rates are presented in Fig. 6. The TG curves have the same shape as those of coated PA-6 powders. The degradation begins at a lower temperature (about 280°C) whatever the $\phi(O_2)$. When $\phi(O_2) = 10$ sccm, it finishes at similar temperature (about 680°C) to the coated PA-6 and gives about 1.8 wt% solid residue at 800°C. On increasing $\phi(O_2)$ from 10 to 150 sccm, the degradation finishes at a lower temperature (around 630°C) and gives about 3.8 wt% at 800°C. In the 290–350°C range, the decomposition is faster for $\phi(O_2) = 50$ sccm and 150 sccm than for $\phi(O_2) = 10$ sccm. The residual weight increases when $\phi(O_2)$ increases from 10 to 50 sccm and it stabilizes at higher oxygen flow rates. The residual weights are in accordance with the residual weights of organosilicon coatings obtained at the different oxygen flow rates. These data are consistent with an increasing oxygen flow promoting the formation of more thermally stable coatings.

3.1.3.3. Comparison. Temperature ranges of degradation and residual weights at 800°C for an $\phi(O_2)$ of 50 sccm are summarized in Table I. The residual weight difference between PA-6 and coated PA-6 (≈2.5 wt%) is of the same order as that of PA-6 nano and coated PA-6 nano (≈2 wt%). This indicates that the deposit plays the same role in the thermal degradation whatever the polymer. The coated polymer decomposes at a lower temperature than the virgin polymer but it gives a more thermally stable residue at 800°C. The first step of the main degradation of the coated polymers occurs between about 290 and 375°C, is relatively slow and may be assigned to the partial degradation of the deposit coupled with a weight loss of about 20% of the

TABLE I Temperature ranges of degradation and residual weights at 800°C at $\phi(O_2) = 50$ sccm

Samples	Range of degradation (°C)	Residual weight (wt%) at 800°C
PA-6	300–630	0
PA-6 nano	300–630	2
Coating	290–480	75
Coated PA-6	290–680	2.5
Coated PA-6 nano	280–630	4

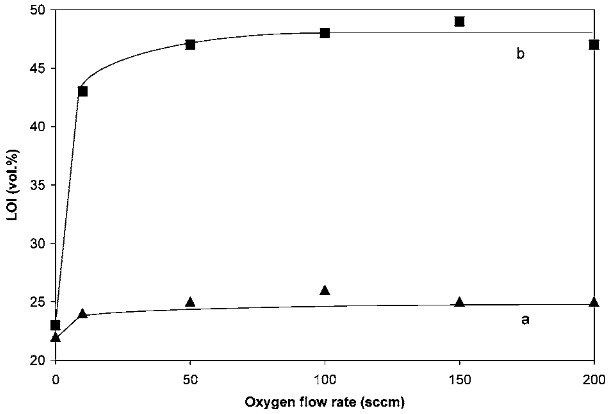

Figure 7 LOI values versus oxygen flow rates for virgin and coated PA-6 (a) and for virgin and coated PA-6 nano (b).

polymer. The second step is between about 375 and 450°C, is faster and may be attributed to the degradation of the polymer with a weight loss of about 45%.

3.2. Fire retardancy performance of coated polymers

3.2.1. Effect of oxygen flow rate

Fig. 7 presents the LOI values versus oxygen flow rates for virgin and coated PA-6 and PA-6 nano substrates. No significant difference is observed between virgin PA-6 and PA-6 nano. A slight increase is observed for coated PA-6 (LOI = 25 vol%) in comparison to the virgin PA-6 (22 vol%). However, a very sharp increase is observed in the case of PA-6 nano. A LOI of 43 vol% is obtained for PA-6 nano coated at $\phi(O_2) = 10$ sccm. Such behavior is slightly accentuated at higher oxygen flow rates. The increase of LOI values with oxygen is agreement with the fact that the oxygen addition to the monomer promotes the formation of more thermally stable coatings as clearly shown in the thermal analysis.

3.2.2. Relationship between LOI and residual weight of the coating

Fig. 8 shows the LOI values versus the residual weight of the deposit obtained at 800°C under air for virgin and coated PA-6 and PA-6 nano substrates. In the case of PA-6, the thermal stability of the deposit has only a very slight effect on the LOI values. However, in the case of PA-6 nano, the LOI values increase as the thermal stability of the coatings increases.

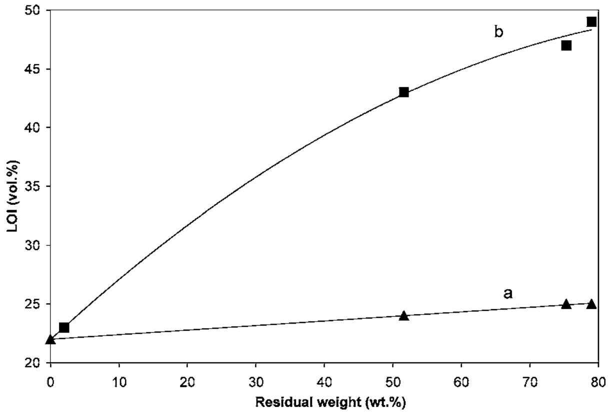

Figure 8 LOI values versus the deposit's residual weight at 800°C for virgin and coated PA-6 (a) and for virgin and coated PA-6 nano (b).

4. Conclusion

In this work, the thermal stability of organosilicon coatings and the fire retardancy performance of coated polyamide-6 and polyamide-6 clay nanocomposite have been studied. The coatings were obtained from polymerization of 1.1.3.3-tetramethyldisiloxane (TMDS) monomer doped with oxygen using a cold remote nitrogen plasma process. A fluidized bed reactor using CRNP assisted polymerization was used to coat the polymer powders. In the case of the polyamide-6 clay nanocomposite, the Limiting Oxygen Index values are much improved.

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