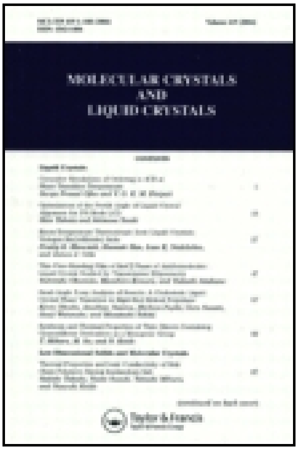

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# Elaboration and Grafting of Cold Plasma Organo-Phosphorus Copolymers on Polyamide 6: New Approach to Flame Retardancy

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# Elaboration and Grafting of Cold Plasma Organo-Phosphorus Copolymers on Polyamide 6: New Approach to Flame Retardancy

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*Argon plasma-induced graft polymerization of (ethylene glycol) methacrylate phosphate (EGMAP) was performed on the polyamide-6 (PA6) surface to improve the fire retardancy properties. The surface composition and morphologies of the PA6-g-poly(EGMAP) surfaces were then characterized by Attenuated total reflection-Infrared and Scanning electron microscopy. The thermal properties were investigated by using Thermogravimetry analysis. It was found that weight loss rate of the grafted substrates was lower, as compared to the virgin PA6. The results obtained showed also that the grafting allows to obtaining a residue of about 30% at 600°C, temperature at which the virgin PA-6 was totally decomposed.*

**Keywords:** (Ethylene glycol) methacrylate phosphate; plasma polymerization; polyamide-6; thermo-degradation

## INTRODUCTION

Polyamides (PA) are engineering resins that exhibit high strength over a broad temperature range, wear and abrasion resistance and chemical resistance. Due to these mechanical properties, polyamide was used in a broad range of high performance applications in automotive, electrical, electronic and industrial markets. The PA should be flame retarded in most of the application.

Traditionally, the flame retardation properties of a polymer can be activated by several methods, such as copolymerisation or blending, as well as by treatment with flame retardant finishes. But these methods have inherent disadvantages. For example, the mechanical properties

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of the polymer materials is reduced, transparency is decreased (in case of transparent materials). Cold Plasma is a new technology, which can be used to modify the surface properties of macromolecular materials to obtain certain requirements, e.g. adhesion, printing ability of polymer film, dyeing ability, hydrophilicity or hydrophobicity. Moreover, plasma treatment has the advantage of modifying only the surface properties of a polymer without affecting the bulk properties.

Grafting is an effective tool to modify the interfacial adhesion of polymer blends or composites [1–6]. Various kinds of grafting polymerization techniques have been developed in the last few decades. The grafting is generally carried out using photo-induced graft polymerization such as UV, chemical initiator, plasma-induced graft polymerisation, plasma polymerization and others [7,8].

The fire retardation of polymers and textiles has been performed by using cold plasma polymerization or plasma induced graft-polymerization [9–15]. Phosphorus-containing compounds are promising flame retardants as they release less toxic gases and smoke during combustion compared to conventional halogen-based compounds. These phosphorus-based flame retardants lead to the formation of foamed cellular crusts when it burns. It has also been reported in the literature that the amount of the charred residue increases with increasing the phosphorus content in the polymer [16]. The formed char act as a barrier between the flame and the underlying polymer, which results in a large decrease of rate of heat released leading to a reduction of the rate of fire growth.

In this article, the cold plasma process is used to induce graft-polymerization of the ethylene glycol methacrylate phosphate (EGMAP) onto the polyamide-6 (PA6) surface with the aim of improving its fire retardancy properties. The PA6 treated has been characterized by scanning electron microscopy (SEM) and ATR- spectroscopy. The thermal stability was by thermogravimetry (TG) analyses. The influence of NaOH rinsing on thermal stability of PA6-g-poly(EGMAP) is also studied.

## EXPERIMENTAL

### Materials

Polyamide-6 plates ($10 \times 10 \times 0.3\,\mathrm{cm}^3$) were prepared by pellets provided from Radilon Company using darragon press at 260°C under a pressure of $10^6$ Pa. The monomer ethylene glycol methacrylate phosphate (EGMAP), the photo-initiator 2-hydroxy-2 methylpropiophenone (Darocur1173), the cross-linking agent ethylene glycol dimethacrylate

(EGDMA) and the solvent ethanol were supplied from Aldrich Company. Argon and oxygen were obtained from Air Liquide Company.

## Cold Plasma Process

Argon glow discharge was generated in an Aluminium reactor chamber (27 l) at 2.45 GHz with a continuous out power ranging from 0 to 600 W. The chamber was pumped down to 10.7 Pa using a pump (E2M28 PEPE, Edwards), and the Argon gas was introduced into the chamber. When the pressure become constant, the generator was switched on and adjusted to a certain power value, which gives rise to continuous glow discharge.

## Homopolymerization

(Ethylene glycol) methacrylate phosphate monomer mixed with 2.5% (w/w) of the photoinitiator was placed onto a Teflon plates to obtain liquid films of three different thicknesses (0.1, 0.5 and 1 mm). The coated plate was then introduced in the plasma reactor, the sample to generator window distance being 15 cm. Before treatment, the reactor was pumped down using a vacuum pump to achieve a pressure of 10.7 Pa. The Ar gas was released in the reaction chamber with the flow rate of 500 sccm. The discharge was then initiated by adjusting the power of the generator at 100 W. The treatment time was fixed at 10 min. The poly(EGMAP) film was washed with ethanol to remove the non polymerized monomer and dried at 70°C. The polymerization of EGMAP induced by Ar -plasma was carried out according to the following reaction scheme: (Fig. 1)

## Graft Polymerization Process

In the first step, the polyamide plates were cleaned with ethanol for 5 min in an ultrasonic bath and then dried at 70°C for 5 h. These plates

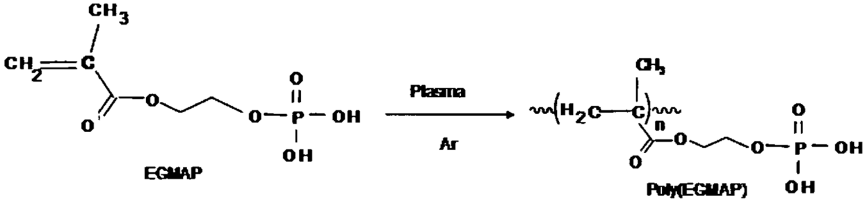


**FIGURE 1** Reaction of plasma induced polymerization of EGMAP.

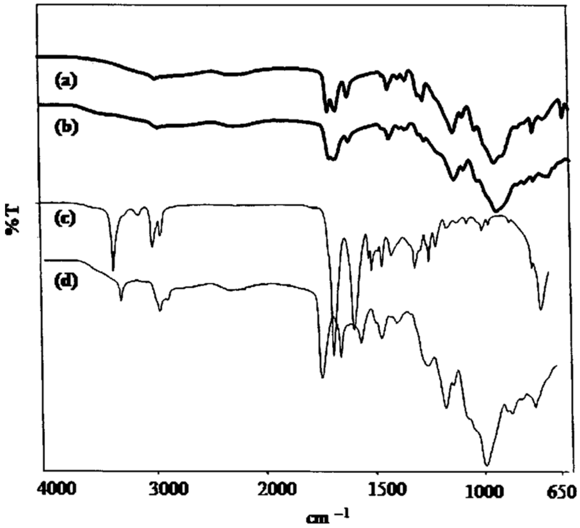


**FIGURE 2** ATR-FTIR spectra of EGMAP monomer (a), poly(EGMAP (b), virgin PA6 (c) and PA6-g-poly(EGMAP) (d).

were then pre-treated using a microwave oxygen plasma (Oxygen flow rate: 0.5 l/min; P = 100 W, t = 10 min) and subsequently immersed in a solution containing 100 g/l of EGMAP in the presence of 2.5% and 3.5% by weight of the Darocure 1173 and the cross-linking agent (EGDMA), respectively in ethanol at room temperature for 3 min. After that the immersed samples were treated by Ar plasma (Argon flow rate: 0.5 l/min; P = 100 W, t = 10 min). Finally, the treated plates were placed in ethanol for 7 h at room temperature in order to take off the residual monomer and the non graft homopolymer and subsequently dried at 60°C.

The surface morphology of untreated and treated PA6 was studied by SEM (LEO 982 ZEISS microscope). The electron beam was operated at low voltage 1 kV. Virgin PA6, and PA6 grafted poly(EGMAP) plates were directly coated with gold (Au) onto a conductive surface before SEM analysis. The ATR-FTIR (Perkin-Elmer spectrometer one) spectra of the EGMAP, poly(EGMAP), virgin PA6 and PA6-g-poly(EGMAP) were recorded.

Thermogravimetric (TG) analyses were performed with a Setaram apparatus in the temperature range 20 to 800°C at a heating rate of 10°C/min in presence of air flow (Air Liquide grade, $5 \times 10^{-7}$ m$^3$/s measured in standard conditions). Samples were placed in open vitreous silica pans. Thermal analyses were carried out on treated and untreated PA6 in the pellets form ($\sim$10 mg).

# RESULTS AND DISCUSSIONS

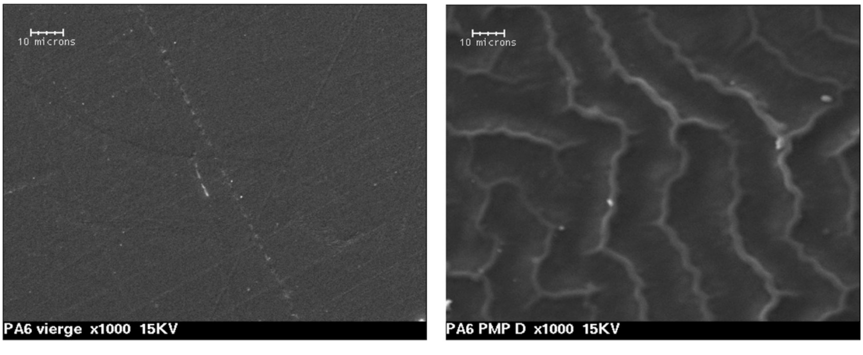
## Surface Characterization of Treated PA6

### *ATR-FTIR Spectroscopy*

The ATR-FTIR spectra of EGMAP, poly(EGMAP), untreated PA6 and the PA6-g-poly(EGMAP) after washing with ethanol for 7 hours are depicted in Figure 2. The ATR-FTIR spectra of EGMAP (Fig. 2a) exhibits the peak at 980, 1066 and 1240 cm$^{-1}$, which assigned for $\nu$(P−O−H), $\nu$(P−O−C) and $\nu$(P=O), respectively. The bands at 813, 948 and 1634 cm$^{-1}$ are assigned for methacrylate group ($\delta$(=CH2)$_{\text{twisting}}$, $\delta$(=CH2)$_{\text{waging}}$ and $\nu$(C=C)), respectively. The disappearance of the 813, 948 and 1634 cm$^{-1}$ indicate the polymerization as shown in Figure 2b. It is apparent from Figure 2d that there are strong and broad band at 971 cm$^{-1}$ and 1156 cm$^{-1}$ due to (P−O)H and P=O stretching respectively which are absent in Figure 2c. Additionally, the absorption band at 1724 cm$^{-1}$ is due to the stretching of C=O unit of the methacrylate group.

## SEM Study

The SEM images of the Virgin PA6 and PA6-g-poly(EGMAP are shown in Figure 3. A comparative morphological image of PA6-g-poly-(EGMAP) and virgin PA6 were presented in Figure 3. As a result, the morphology of the surface of the PA6-g-poly(EGMAP) shows a well



(a) (b)

**FIGURE 3** SEM micrographs of virgin PA6 (a), PA6-g-poly(EGMAP) (b).

covering surface of the film which has a "labyrinths" like structure form with broad ways on average of 13 µm.

## Thermal Properties

Figure 4 shows TGA curves for virgin PA6 (a), poly(EGMAP) (b) and PA6-g-poly(EGMAP) (c). It is observed that, a weight loss of about 2% occurred in case of virgin PA-6 at the first stage around 50°C, which could be probably due to the loss of water in the sample, in other words, powder dehydratation occurred. A weight loss of about 86% occurred at the second stage between 315 and 478°C that might be attributed to the thermal depolymerization of PA-6 leading to ε-caprolactam as reported in the literature [17–19]. Many authors reported the analysis of the PA6 decomposition products [20–21].

In a third step from 450°C to 600°C which may be due to the oxidative char degradation of the virgin PA6 powder. The degradation process for poly(EGMAP) can be divided in two stages (Fig. 4 curve c). The maximum decomposition temperature $T_{max}$, and rate, $r_{max}$, for the two-stages of degradation were found to be around 292°C ($T_{max1}$) and 0.20 wt%/°C ($r_{max1}$) for the first stage and around 625°C ($T_{max2}$) and 0.12%/°C ($r_{max2}$) for the second stage. The solid residual weight formed are ~51% and ~21% at 500°C and 800°C, respectively. The two degradation process can be explained by initial hydrolysis mechanism of the phosphate ester group to evolve hydroxyethyl

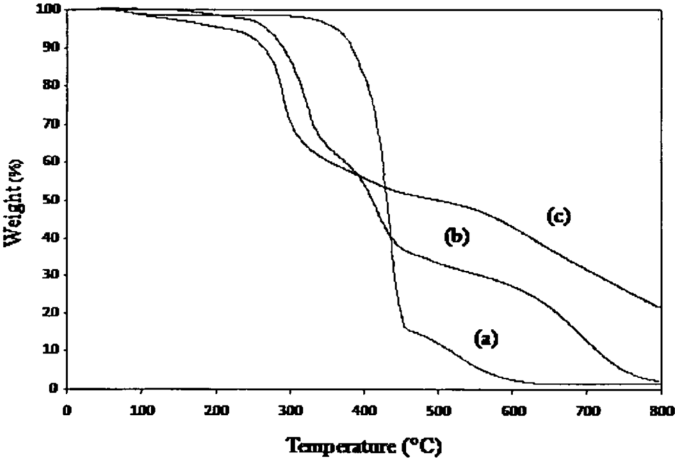


**FIGURE 4** TGA curves of virgin PA6 (a), PA6-g-poly(EGMAP) (b), and poly-(EGMAP) (c).

methacrylate (HEMA) and phosphoric acid $H_3PO_4$; then, subsequently, the dominant mechanism occurring in the second stage was a main-chain random scission to form acetaldehyde and water as major products along with carbonization of about 20% char yield of a solid residue at 800°C. The formation and the stability of the char residue over 800°C has been explained by the fact that the phosphorus-containing moieties degraded at low temperature are able to react further with the polynuclear aromatic carbon formed during degradation to give a thermally stable phosphorus-carbon structure by grafting, or linking different aromatic carbons as reported in the literature [22–24]. It is observed from Figure 4b that the weight loss starts at a temperature of 150°C at a very slow rate and relatively higher than the virgin PA6 which may be due to the presence of moisture in the PA6-g poly(EGMAP) as this weight loss is very low ($<5\%$). Above 210°C the rate of weight loss is increased but less than the virgin PA6. After 440°C the weight loss rate was further slowed down. The total weight loss is 63% at 460°C, this significantly much lower than the virgin PA6 where it is 83%. This may be due to increased char formation of the PA6-g-poly(EGMAP) in presence of phosphorus polymers, as evidenced from the residue char yield of 25% at 635°C for PA6-g-poly(EGMAP) where it is about 2% in the case of virgin PA6. This indicates that the grafted PA6 was thermally stabilized. Phosphorous products have the ability to increase the conversion of

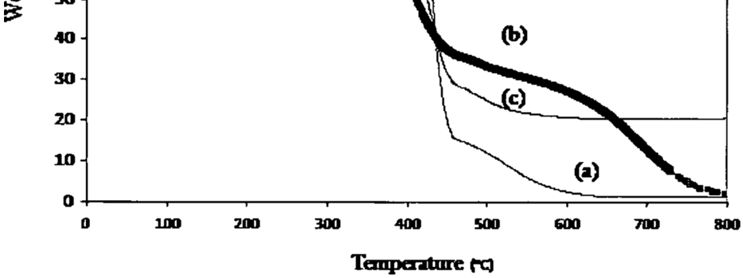


**FIGURE 5** TGA curves of virgin PA6 (a), PA6-g-poly(EGMAP) (b) and PA6-g-poly(EGMAP) treated b0.5 M NaOH (c).

polymeric materials into a char residue during degradation and thus reduce the formation of flammable carbon-containing gases. The char could lead to the formation of a mass transfer barrier to the release of volatile gases i.e. fuel which induce increase of flame retardancy performance.

The powder of PA6-g-poly(EGMAP) was washed by an aqueous solution of NaOH (0.5 M), and rinsed with ethanol to eliminate the excess of NaOH and dried at 70°C. It is apparent from Figure 5c that a clear decrease of the rate of weight loss at 325°C. This result suggest that the condensation reactions of the phosphoric acid groups may be inhibited through the formation of $P(O)O^{-}Na^{+}$ groups. Above 500°C, a residue representing 20% of the initial mass is obtained. This residue is very thermally stable since its mass remains stable up to a temperature of 800°C.

## CONCLUSION

The Ar-plasma-induced polymerization of (ethylene glycol) methacrylate phosphate (EGMAP) monomer on the polyamide-6 (PA6) was successfully carried out. ATR-FTIR and SEM images indicates the chemical and morphological changes on the PA6-g-poly(EGMAP). Thermogravimetric analysis of virgin PA6 and PA6-g-poly(EGMAP) and PA6-g-poly(EGMAP) treated by NaOH solution shows that the grafting decreases the initial temperature decomposition of polyamide 6 due to the catalytic effect of $H_3PO_4$ released during the degradation. However, the weight loss rate of the grafted substrates was less compared to the virgin PA6. This investigation shows that the grafting allows to obtaining a residue of about 30% at 600°C, temperature at which the virgin PA-6 was totally decomposed. When the grafted PA6 powder was washed by Sodium hydroxide (0.5 M), the residue was stabilized up to a temperature up to 800°C.

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