

# PEBAX<sup>TM</sup>-Silanized Al<sub>2</sub>O<sub>3</sub> Composite, Synthesis and Characterization

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## ABSTRACT

Alumina nanoparticles were dispersed in poly(amide 12-b-tetramethylene oxide) copolymer through extrusion. The alumina particles were functionalized with 3-(2 trimethoxysilylethyl) cyclohexene oxide. The following PEBAX<sup>TM</sup>/Al<sub>2</sub>O<sub>3</sub> proportions were prepared: 0.1, 1.0, 5.0, and 10.0% w/w. The thermal stability of the nanocomposites was evaluated by thermogravimetric analysis under N<sub>2</sub> and was comparable to the neat PEBAX<sup>TM</sup> polymer. The thermo-oxidative degradation of the polymeric matrix by oxygen was strongly hindered by the functionalized alumina. The rule of mixture would predict that the thermal degradation should be strongly dominated by PEBAX<sup>TM</sup> matrix. Therefore, the physical mixture of PEBAX<sup>TM</sup> and silanized alumina should be almost as stable as pure PEBAX<sup>TM</sup>. However, the experimental results suggest that the nanocomposites are more stable than the mixture of their components. This stabilization effect is evident in the temperature range between 300°C and 400°C, in which the degradation of the PA12 block takes place.

**Keywords:** Nanocomposites; Alumina; Functionalization; Thermoplastic Elastomers; Thermal Behavior

## 1. Introduction

In the past decades the development of organic-inorganic composites containing polymeric phases as the organic component [1-5] and further on polymer nanocomposites [6-10] has been receiving a great deal of attention due to the unique combination of light weight, processability of polymers with the outstanding chemical and thermal stabilities of the inorganic components. This technology was extended to different fields, which includes, reinforced polymeric materials, polymeric membranes for several application as for instance: gas-separation [11], fuel cell applications [9,12], pervaporation [13,14]; protecting coatings [1,15] to name a few. One of the key issues is to assure a good dispersion and distribution of the inorganic phase in the polymeric matrix [16]. When dealing with organic-inorganic hybrids prepared by the sol-gel method, the controlled hydrolysis and condensation of metal alkoxides in polymeric solutions are paramount to achieve the desired properties (enhanced mechanical stability, higher resistance against liquid and vapors) [17]. Even though this method enables the control of the size of inorganic domains; it requires the use of solvents and drying steps, which are drawbacks for the

development of polymer-based materials for industrial applications. On the other hand, the surface of inorganic and carbon-based nanoparticles can be modified in order to enhance the compatibility between the polymeric and the inorganic phases and ensure an optimal improvement of the mechanical, chemical and thermal properties of the final functional materials [18-20]. Gas separation using polymeric membranes has drawn a great deal of interest from researchers because it offers advantages such as low energy costs and environmental benignity. This is especially true for hydrocarbon separations performed in the petrochemical industry, which generally incur heavy operating costs. The membrane-based method is particularly attractive for the removal of heavier species present in dilute concentrations, such as CO<sub>2</sub> and H<sub>2</sub>S from the lighter but major constituent, CH<sub>4</sub>, in natural gas [21-23]. In the last decades, increasing interest has been turned to design new functional polymeric membranes in order to control interfacial phenomena, traditionally affecting separation and purification processes. It is well known, the first step of each membrane separation process involves chemical interactions at the membrane-feed interface, directing positively or negatively the productivity and efficiency of the overall transport [24]. Specifically, the behavior of CO<sub>2</sub> in relation to water vapor and other

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non-polar gases (CH<sub>4</sub>, O<sub>2</sub>, and N<sub>2</sub>) was evaluated, after introducing different chemical moieties in an elastomeric block co-polyamide (Pebaxw2533: 80PTMO/PA). Many studies, devoted to gas separations based on membrane processes, elucidated the importance to correlate the characteristics of polymers, as free volume, polymer chain packing and intersegment distance, with their transport properties, emphasizing the role of the microstructure of the polymers in gas/vapor permeability and selectivity [25-30]. PEBAX polyether block amides are a new family of engineering thermoplastic elastomer, their general structure is (A-B)<sub>n</sub>; they consist of linear and regular chains of hard polyamide segments having molecular weight between 600 and 4000, and soft polyether segments of molecular weight between 600 and 2000, the soft and hard segments are relatively short blocks. In the temperature region of exploitation, the soft segment component is viscous or rubbery while the hard segment is glassy or semi-crystalline. The ratio of the polyamide and polyether blocks controls the hardness. The length of the polyamide block influences the melting point of the polymer. Since polyamide and polyether segments are not miscible, the polyether block amides have a morphology characterized by phase separation (bi-phase separation) [31-33]. PEBAX is a group of copolymers including hard polyamide segments and soft polyether segments. These copolymers have extremely high polar/non polar (e.g. H<sub>2</sub>S/CH<sub>4</sub>, or CO<sub>2</sub>/N<sub>2</sub>) gas selectivity coefficients, making them interesting candidates for the removal of CO<sub>2</sub> from synthesis gas, natural gas, and flue gas. Crystalline amides block in PEBAX<sup>TM</sup> works as impermeable phase, whereas soft ether block in PEBAX<sup>TM</sup> acts as a permeable phase due to its high chain mobility. The permeability of membranes can be also tailored through the dispersion of inorganic particles [34]. During the past decades, different inorganic phases (e.g. SiO<sub>2</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub>) were in situ generated during the casting of PEBAX<sup>TM</sup> membranes from solutions using alkoxides as precursors [35,36]. The incorporation of inorganic phase in a polymer matrix leads also to improved solvent resistance and thermal stability of PEBAX<sup>TM</sup> polymer [37-41]. In the present work we report the preparation of PEBAX<sup>TM</sup>/Alumina nanocomposites obtained by extrusion process. The properties of the nanocomposites are discussed in terms of thermal stability, crystallinity degree and interactions between the filler and the soft and hard segments of the PEBAX<sup>TM</sup> matrix.

## 2. Experimental

### 2.1. Materials

Alumina: Al<sub>2</sub>O<sub>3</sub> supplied by Sasol South Africa. Silane coupling agent: 3-(2 trimethoxysilylethyl) cyclohexene oxide

oxide (**Figure 1**) from Aldrich Germany. PEBAX<sup>TM</sup> (**Figure 1**) supplied by Arkema (France) is a polyamide-12, poly(tetramethylene oxide) multi-block copolymer (**Figure 1**). The polymer was supplied as a black powder, due to the presence of pigments.

### 2.2. Silanization Process

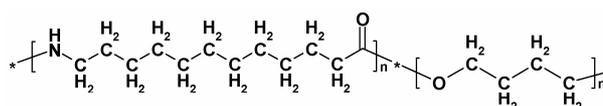
A suspension containing 15 g of alumina (Sasol, South Africa) 15 mL hexane and 5 g alkoxysilane were stirred during 24 h at room temperature. After 8 h, the formation of spherical yellowish agglomerates of silanized alumina could be observed. The precipitate was recovered by filtration and dried overnight at 100°C.

### 2.3. Manufacturing of the Nanocomposite

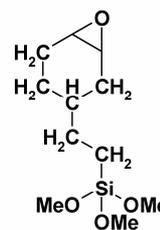
Neat PEBAX<sup>TM</sup> powder and mixtures of 0.1, 1.0, 5.0, and 10.0% w/w PEBAX<sup>TM</sup> /modified alumina were extruded in a Haake Poly lab system twin-screw extruder using the conditions summarized in **Table 1**. The extruded nanocomposites were polluted at room temperature and milled at -120°C in a cryo-milling machine (**Table 1**).

### 2.4. Measurements

Differential Scanning Calorimetry (DSC) of each composite were carry out in a DSC calorimeter under nitrogen at 10°C/min temperature ramp from -100°C to 200°C



PEBAX<sup>TM</sup>: Poly(amide 12 -b- tetramethylene oxide)



3-(2 Trimethoxysilylethyl) cyclohexene oxide

**Figure 1.** Chemical structure of PEBAX<sup>TM</sup> and 3-(2 Trimethoxysilylethyl) cyclohexene oxide.

**Table 1.** Conditions for the extrusion of PEBAX<sup>TM</sup> and composites thereof.

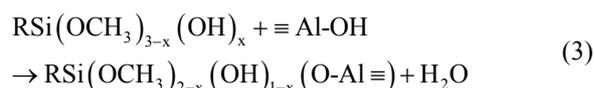
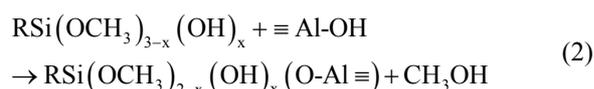
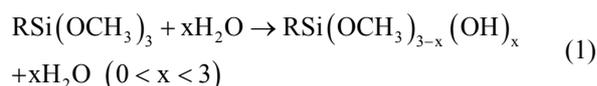
Parameter	Value (°C)
Temperature at heating zone 1	205
Temperature at heating zone 2	215
Temperature at heating zone 3	225
Temperature at die	240

(SEIKO: Japan). The decomposition temperatures in nitrogen and air were determined from the thermogravimetric analysis carried out in a TGA Q500 (TA Instruments, New Castle, DE).

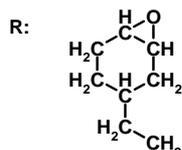
### 3. Results and Discussion

#### Alumina Functionalization

The fictionalization of alumina took place through condensation reaction involving the species produced from the hydrolysis of 3-(2 trimethoxysilylethyl) cyclohexene oxide. This process was accelerated by the moisture adsorbed at the surface of the alumina nanoparticles. The hydrolysis of the methoxy groups attached to the silicon atom yields a silanol groups (as described by Equation (1)) [42,43], which in turn can react with the Al-OH groups at the surface of alumina nanoparticles, as exemplified by the Equations (2) and (3).



where:



Evaluation of the thermal properties of the nanocomposites.

**Table 2** contains the DSC data of the neat PEBAX<sup>TM</sup> and their nanocomposites. The mobility of the soft PTMO segment is strongly hindered by the presence of the silanized nanoparticles, since the glass transition temperature of a nanocomposite containing only 0.10 wt% of nanoparticle exhibits much higher  $T_g$  values for the PTMO block than the neat PEBAX<sup>TM</sup>.

The hard semi-crystalline PA-12 blocks were also influenced by the presence of the nanoparticles. The overall crystallinity degree ( $^{\circ}\text{C}$ ) of the nanocomposites was estimated using the Equation (4), which correlates the crystallinity degree, melting enthalpy ( $\Delta H_m$ ) with the equilibrium melting enthalpy ( $\Delta H_m^0$ ) [44]. The value of  $\Delta H_m^0$  used was 246 J/g [45].

$$C = \frac{\Delta H_m}{\Delta H_m^0} \quad (4)$$

**Table 2. Thermal properties of polymers.**

Filler loading (wt%)	$T_g^a$ PTMO ( $^{\circ}\text{C}$ )	$T_m^b$ PA12 ( $^{\circ}\text{C}$ )	$T_c^c$ PA12 ( $^{\circ}\text{C}$ )	$\Delta H_m^d$ (J/g)	$C^e$ (%)
0	-48	142	110	39.4	16.0
0.1	-47	143	110	12.3	5.0
1.0	-39	140	110	10.5	4.2
5.0	-39	141	110	10.2	4.2
10.0	-39	141	110	8.9	3.6

<sup>a</sup> $T_g$ : Glass transition temperature, <sup>b</sup> $T_m$ : Melting point, <sup>c</sup> $T_c$ : Crystallisation temperature, <sup>d</sup> $\Delta H$ : Melting enthalpy, <sup>e</sup> $C$ : Crystallinity degree (calculated using the Equation (4)).

Although Equation (4) provides an approximation of the crystallinity degree of the PA12 phase of the PEBAX<sup>TM</sup> used in the present work, because it does not take the weight percentage of PA12 in the copolymer, it can be used to evaluate the potential of the filler to enhance or decrease the crystallinity of the PA12 segments.

The values for crystallinity degree of the nanocomposites were significantly lower than of the neat PEBAX<sup>TM</sup>. A 66% reduction of the crystallinity degree was reached at very low filler loadings (0.10 wt% of silanized alumina). This fact can be explained by the partial cross-linking of the PA-12 block by the functionalized alumina nanoparticles.

The crystallisation temperatures ( $T_c$ ), determined during the second cooling cycle, did not change for the nanocomposites. This reflects the little interaction of PA12 with nanoparticles and other fillers, as described in several papers [46-50].

The thermal stability of the PEBAX<sup>TM</sup>/Alumina nanocomposites was evaluated by TGA under  $\text{N}_2$ . Under these constrains, the degradation of polyamides takes place via depolymerisation reaction, *i.e.*, formation of lactams (in the case of polyamide 12, lauryl lactam [51]) or via elimination of alkenes and nitriles [51]. Whereas the de-polymerization involves the end-groups of the polymer, the  $\gamma$ -elimination can take place at any part of the chain. Hence, it is relatively independent of the molecular weight, while the de-polymerization is more extensively observed for polymers having lower molecular weight.

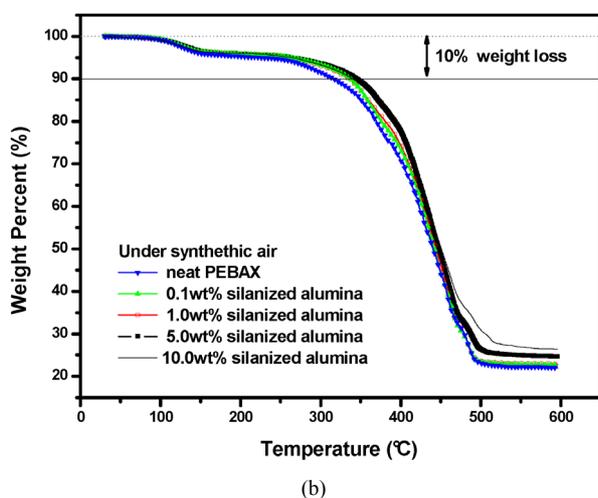
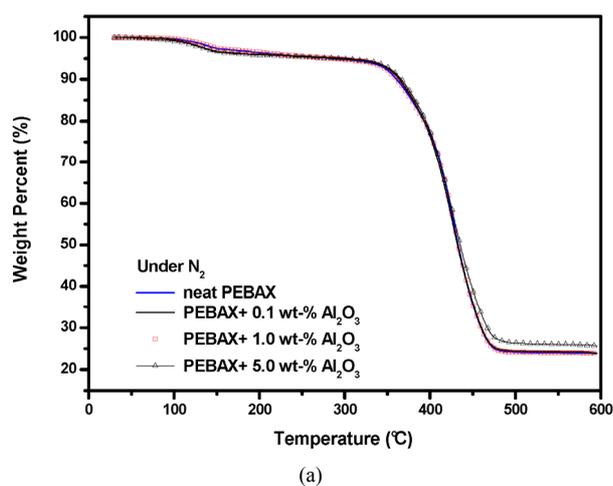
Epoxy and alcohols are prone to react with nitriles at higher temperatures [52]. In this case, after the chain scission into an amide (followed by its dehydration towards a nitrile), the resulting nitrile could be trapped by the fillers bearing epoxy or -OH groups. Therefore, an improvement of the thermal stability should be observed for the PEBAX<sup>TM</sup> nanocomposites containing epoxy-functionalized alumina.

The thermal stability of the nanocomposites was marginally higher than neat PEBAX<sup>TM</sup>. Therefore the filler

does not seem to interfere in the degradation process of this polymer under inert atmosphere.

**Figures 2(a) and 2(b)** depict the TGA curves of the nanocomposites under  $N_2$  and synthetic air, respectively. It can be seen that the incorporation of the silanized alumina nanoparticles with excellent thermal stability under oxidation conditions. It could be observed that the char yield at  $600^\circ C$  increases proportionally to the alumina content. This fact can be explained in terms of higher inertness of alumina at higher temperatures.

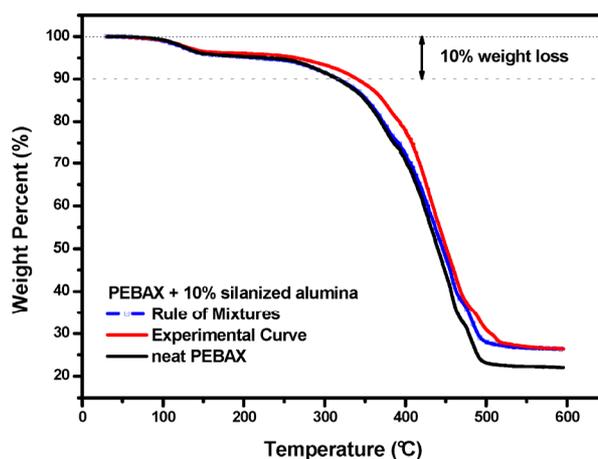
In order to understand and better evaluate this stabilization effect, some calculations were done to estimate the thermal stability of a mixture of PEBAX<sup>TM</sup> and silanized alumina. For example, the TGA curve of PEBAX<sup>TM</sup> nanocomposite containing 10.0 wt% silanized alumina was compared to a calculated TGA curve, which was obtained by adding the TGA curve of pure PEBAX<sup>TM</sup> to the TGA curve of the silanized alumina. It was taken into consideration that there 90 wt% of PEBAX and 10 wt% of



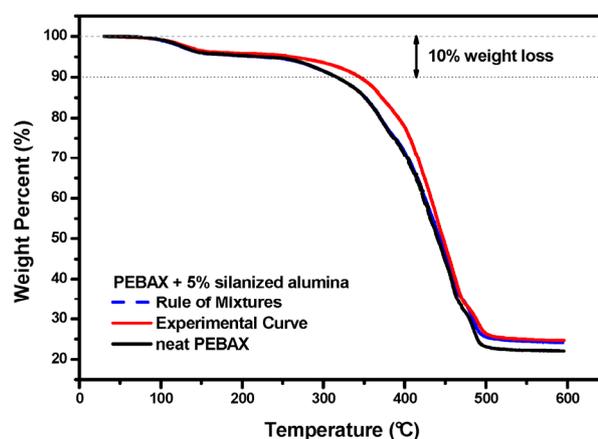
**Figure 2.** TGA traces of the neat PEBAX<sup>TM</sup> and PEBAX<sup>TM</sup>/Al<sub>2</sub>O<sub>3</sub> nanocomposites under  $N_2$  (a); and under synthetic air (b).

silanized alumina in the nanocomposite. Therefore the TGA curves of PEBAX<sup>TM</sup> and the alumina were multiplied by factor of 0.90 and 0.10, respectively. The same procedure was taken for the PEBAX<sup>TM</sup> nanocomposite containing 5 wt% of silanized alumina. These curves as depicted in the **Figures 3 and 4**, respectively.

The rule of mixtures would predict that the thermal degradation should be strongly dominated by the PEBAX<sup>TM</sup> matrix. Therefore, the physical mixture of PEBAX<sup>TM</sup> and silanized alumina should be almost as stable as pure PEBAX<sup>TM</sup>. However, the experimental results suggest that the nanocomposites are more stable than the mixture of their components. This stabilization effect is evident in the temperature range between  $300^\circ C$  and  $400^\circ C$ , in which the degradation of the PA12 blocks takes place. Hence, the alumina nanoparticles did indeed improve the thermo-oxidative stability of the PEBAX<sup>TM</sup> matrix.



**Figure 3.** Experimental and calculated (following a rule of mixtures) TGA curves of PEBAX<sup>TM</sup>/silanized alumina 90/10 w/w. The TGA curve of neat PEBAX<sup>TM</sup> is shown for the sake of comparison.



**Figure 4.** Experimental and calculated (following a rule of mixtures) TGA curves of PEBAX<sup>TM</sup>/silanized alumina 95/5 w/w. The TGA curve of neat PEBAX<sup>TM</sup> is shown for the sake of comparison.

## 4. Conclusion

The dispersion of nanoparticles constituted of silanized alumina in PEBAX<sup>TM</sup> matrix using extrusion process could produce nanocomposites with improved thermo-oxidative stability. The chemical coupling between the PA12 blocks and the functional groups at the surface of the alumina nanoparticles caused a decrease of the crystallinity of the hard PA-12 segments, as well as, constrained the mobility of the soft PTMO segment, as evidenced by the increase in  $T_g$  of this component.

## 5. Acknowledgements

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