

# Synthesis and characterization of Organic-Inorganic Hybrid Materials

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**Abstract-** Organic-inorganic hybrid containing Al<sub>2</sub>O<sub>3</sub> and PCTFE were prepared successfully by the solvent-cast process. The hybrid systems have network structure and inorganic phases have a size of less than 100nm. The scanning electron microscope also confirms the homogeneous surface of the resulting hybrid for low concentration of Al<sub>2</sub>O<sub>3</sub> in PCTFE. At 10wt% of Al<sub>2</sub>O<sub>3</sub> the hybrids show non-homogeneous surface morphology. Crystallinity of the hybrid is found to decrease with increasing Al<sub>2</sub>O<sub>3</sub> concentration. The glass transition temperature of hybrids initially decreases and then increases with increasing Al<sub>2</sub>O<sub>3</sub> concentration.

**Keywords:** XRD, Hybrid, Crystallinity, Morphology.

## I. INTRODUCTION

Nano-structured composite materials, when using organic polymer and inorganic fillers, represent a merger between traditional organic and inorganic materials, resulting in compositions that are truly hybrid. Hybrid materials are composites consisting of two constituents at the nano-meter or molecular level. Commonly one of these compounds is inorganic and the other one organic in nature. Thus, they differ from traditional composites where the constituents are at the macroscopic (micrometer to millimeter) level. Mixing at the microscopic scale leads to a more homogeneous material that either shows characteristics in between the two original phases or even new properties.

Hybrid organic-inorganic materials can be defined as nano-composites made of organic and inorganic components combined over length scales ranging from a few Angstroms to a few tens of nanometres. The relative properties of hybrid organic-inorganic materials certainly depend on the chemical nature of their components. Thus, a simple classification based on the nature of the links and interactions between the organic and inorganic components exchange has been proposed [1]. Class I corresponds to systems where both phases exchange only weak interactions such as vander Waals forces, hydrogen bondings or electrostatic forces. In class II materials, the organic and the inorganic components are linked by strong chemical bonds such as covalent or ionic-covalent bonds. Class I materials can also be obtained by the simultaneous formation of the two components generally leading to high interpenetrating networks [2-3]. In Class II organic-

inorganic hybrids the two phases are totally or partly linked together through strong chemical bonds characterized by strong orbital overlap (covalent or ionic-covalent bonds).

Many hybrid materials display both types of interactions and have the possibility to be classified either as Class I or Class II hybrids [4]. The analysis of hybrids or nano-composites can be made on the basis of structural, mechanical and thermal. Experimental techniques used for the characterization of nano-composites include X-ray diffraction (due to ease and availability), scanning electron microscope [5-6] (SEM- allows a qualitative understanding of the internal structure) and differential scanning calorimetry [7-8] (DSC- to understand the nature of crystallization taking place in the matrix). Morphologies are controlled by many factors, such as the miscibility, modifier concentration, curing temperature and reaction rate [9]. The properties of a polymer-reinforced composite are mostly influenced by the size, shape, composition, state of agglomeration, and degree of matrix-filler adhesion [10] as well as processing parameters. Optimum surface curvature at the polymer-filler interface can be realized when large surface areas are created, which is possible when the filler particles are sufficiently small [11].

Polychlorotrifluoroethylene (PCTFE), synthetic resin formed by the polymerization of chlorotrifluoroethylene. It is a moldable, temperature-resistant, and chemical-resistant plastic that finds specialty applications in the chemical, electrical, and aerospace industries. PCTFE can be prepared as a powder by treating an aqueous suspension or emulsion of chlorotrifluoroethylene with polymerization catalysts. PCTFE powder can be melted and then shaped by molding or by extrusion into solid articles. The plastic remains ductile at temperatures as low as -200°C (-330°F) and is stable at temperatures above 200°C (390°F). The general properties of PCTFE are appearance as white granule or powder, specific gravity 2.10-2.17, bulk density 2.10-2.14, glass transition temperature is around (T<sub>g</sub>) 45°C, melting point 210-215°C, good thermal stability and nonflammable.

PCTFE has a higher tensile strength, hardness and resistance to creep. The crystallinity of PCTFE and its composites by DSC and XRD have been reported. The

properties of this poly-composites using the techniques of differential scanning calorimeter, scanning electron microscopy and X-ray diffraction have been investigated.

## II. EXPERIMENTAL DETAILS

For preparing various samples of different weight percentage commercially available polymer PCTFE and inorganic material  $\text{Al}_2\text{O}_3$  were used. The polymer granules of PCTFE was procured from M/S Chemical Industries, Mumbai, India. Analytical grade  $\text{Al}_2\text{O}_3$  was supplied by Aldrich, USA. The glass transition temperature of PCTFE are  $45^\circ\text{C}$ .

The solution casting technique was utilized for preparing the composites of different compositional percentage of the inorganic material.  $\text{Al}_2\text{O}_3$  was added in 2, 5 and 10 wt% ratio in the pure PCTFE individually for preparing the nanocomposites. For this, pure PCTFE and  $\text{Al}_2\text{O}_3$  were weighted for their desired ratio. These were then mixed and dissolved in common solvent. This solution was stirred at  $60^\circ\text{C}$  in a magnetic stirrer. The solution was poured in a glass mould and it was kept inside the temperature controlled oven for 6 h at  $80^\circ\text{C}$ . After the film was formed the glass plates were taken out carefully; and films were detached from the glass plates using a sharp edge knife or blade. The films were preserved for further characterization.

The X-ray diffraction studies of prepared pure PCTFE and  $\text{Al}_2\text{O}_3$  reinforced PCTFE nano-composites were carried out with PANalytical Empyrean X-ray diffractometer with  $\text{CuK}\alpha$  radiation. The X-ray powder diffraction pattern was recorded in the  $2\theta$  range from  $0^\circ$  to  $60^\circ$  with scanning speed of  $0.2^\circ$  per minute.

Differential Scanning Calorimetry (DSC) measurements are carried out using DSC PYRIS 6000 instrument for which 1-2 mg of sample is used. The samples are heated at a rate of  $10^\circ\text{C}/\text{min}$  over a temperature range  $10^\circ\text{C}$ - $200^\circ\text{C}$  in heating cycles for pure PCTFE and its hybrids.

The SEM studies of prepared pure PCTFE and  $\text{Al}_2\text{O}_3$  reinforced PCTFE nanocomposites were carried out with JEOL-JJM-5600LV electron microscope

## III. RESULT AND DISCUSSION

The DSC profile for pure PCTFE and hybrid nano-composites are observed. In the present system, the DSC measurements are carried out in order to investigate the effect of varying filler concentration (2-10wt%  $\text{Al}_2\text{O}_3$ ) on thermal characteristic of the nano-composite matrix. The glass transition temperature of the pure PCTFE is found to be  $45^\circ\text{C}$  (fig.1.1). The DSC thermograms of various  $\text{Al}_2\text{O}_3$  reinforced PCTFE nanocomposites are also shown in fig.1.2 to 1.4. It is evident that the glass transition temperature of  $\text{Al}_2\text{O}_3$  reinforced PCTFE nanocomposites initially decreases from  $45^\circ\text{C}$  to  $39.7^\circ\text{C}$  for sample with (2wt%  $\text{Al}_2\text{O}_3$ +PCTFE). However, when

the concentration of  $\text{Al}_2\text{O}_3$  is increased to 5 weight percent (5wt%  $\text{Al}_2\text{O}_3$ +PCTFE), the glass transition temperature increases to  $48^\circ\text{C}$ . On further increasing the concentration of  $\text{Al}_2\text{O}_3$ , the glass transition temperature successively increases to  $55^\circ\text{C}$  for specimen with 10wt%  $\text{Al}_2\text{O}_3$ . The increase in the glass transition temperature with increase in the wt% of  $\text{Al}_2\text{O}_3$  in the hybrid nanocomposite of PCTFE shows the increase in crystallinity with the developed morphology in the hybrid system. Such variations observed in the DSC scans of the composite may be due to interaction amongst the composite constituents (between PCTFE and  $\text{Al}_2\text{O}_3$ ). The maximum value of  $T_g$  obtained for the hybrid sample with 10wt% of  $\text{Al}_2\text{O}_3$  in PCTFE which exhibits the maximum crystallinity.

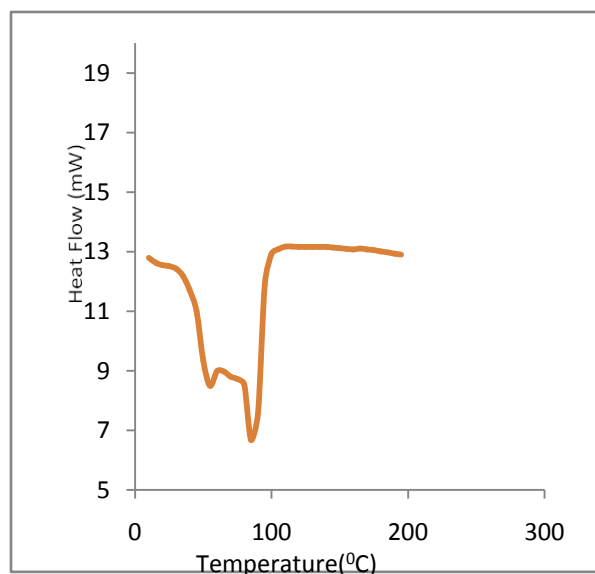


Figure 1.1: DSC thermogram of the Pure PCTFE

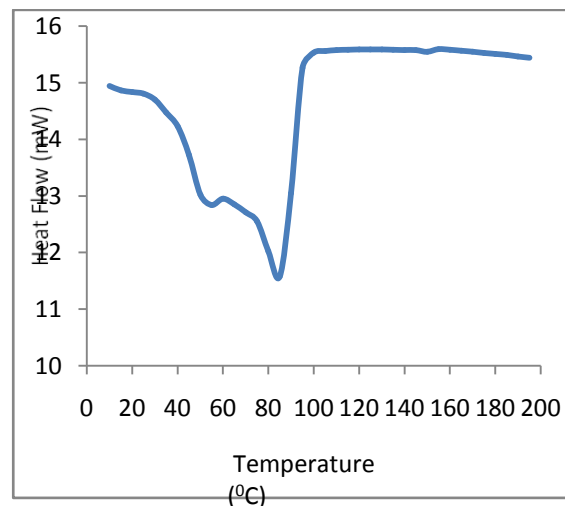


Figure 1.2: DSC thermogram of the 2wt%  $\text{Al}_2\text{O}_3$ +PCTFE .

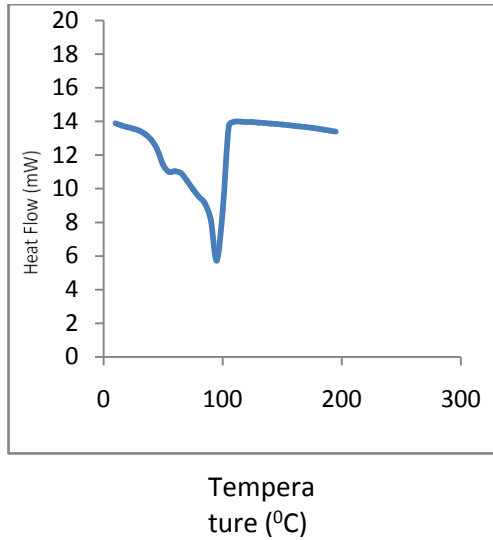


Figure 1.3: DSC thermogram of the 5wt% Al<sub>2</sub>O<sub>3</sub>+PCTFE .

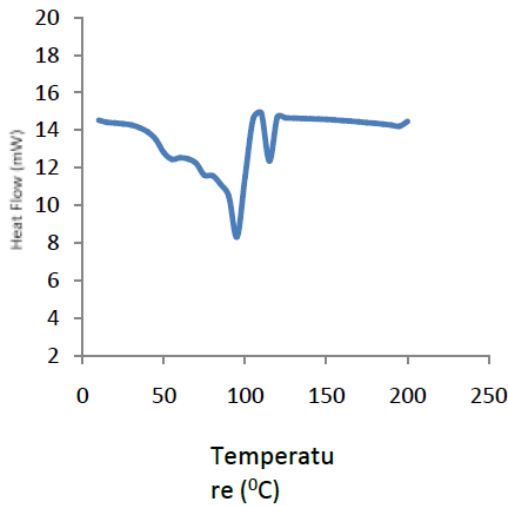


Figure 1.4: DSC thermogram of the 10wt% Al<sub>2</sub>O<sub>3</sub>+PCTFE

Table 1: Glass transition temperature of various polymer nano-composites of PCTFE and Al<sub>2</sub>O<sub>3</sub>

Sample	T <sub>g</sub> (in °C)
Pure PCTFE	45
2% Al <sub>2</sub> O <sub>3</sub> +PCTFE	39.7
5% Al <sub>2</sub> O <sub>3</sub> +PCTFE	48
10% Al <sub>2</sub> O <sub>3</sub> +PCTFE	55

For pure PCTFE , the crystalline peak is observed at 21.1<sup>0</sup>, which yields crystallinity 26.92%, interplanar

distance  $d = 4.205A^0$  and crystallite size  $D = 19.581A^0$ . As a result of the addition of Al<sub>2</sub>O<sub>3</sub> in PCTFE shifts in crystalline peak is observed. The peak is shift towards the higher glancing angle. For 2% Al<sub>2</sub>O<sub>3</sub>+ PCTFE nanocomposite film, crystalline peak is observed at  $2\theta = 21.2^0$ , which yields crystallinity of 21.05%, interplaner distance  $d=4.185 A^0$  and crystallite size  $D=17.408A^0$ . For 5 weight percent Al<sub>2</sub>O<sub>3</sub> nanocomposite film similar increase in various properties have been observed. In the case of 10wt% nanocomposite film, a decrease in various properties has been observed; the crystalline peak at  $2\theta=21^0$ , the calculated crystallinity value is 32.81%, interplanar distance  $d=4.225A^0$ , crystallite size  $D=19.577A^0$ . It is clear from the crystallinity variation profile that the crystallinity increases up to the 5 weight percentage concentration of Al<sub>2</sub>O<sub>3</sub> and decreases thereafter.

It is clear from the XRD profile that the value of crystallinity index is maximum for the hybrid sample with 10wt% of Al<sub>2</sub>O<sub>3</sub> in PCTFE. However, the crystallite size relatively decreases for hybrid samples in comparison to pure PCTFE. It is also possible to observe from the X-ray diffractograms that the intensity of diffracted X-rays increases with increasing wt% ratio of Al<sub>2</sub>O<sub>3</sub> in PCTFE matrix. Moreover, the crystallite size progressively increases with the increase in wt% of Al<sub>2</sub>O<sub>3</sub> in the hybrid samples. The maximum value for crystallinity index and crystallite size is thus obtained for the hybrid samples with 10wt% of Al<sub>2</sub>O<sub>3</sub> in PCTFE. The XRD study reveals that the crystalline nature of PCTFE is obtained in the developed hybrid nanocomposites with Al<sub>2</sub>O<sub>3</sub>. However, the level of crystallinity varies with wt% incorporation of Al<sub>2</sub>O<sub>3</sub> in PCTFE.

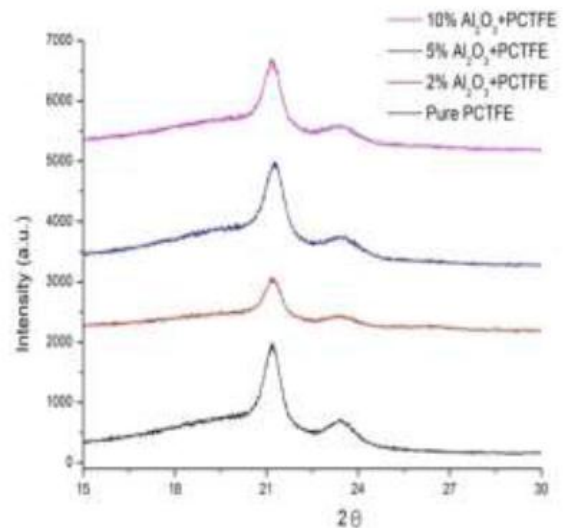
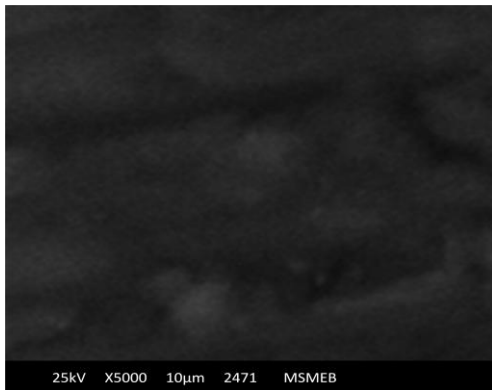


Figure 1.5: X-Ray diffraction pattern of pure PCTFE, 2%Al<sub>2</sub>O<sub>3</sub>+PCTFE, 5% Al<sub>2</sub>O<sub>3</sub>+PCTFE, 10%Al<sub>2</sub>O<sub>3</sub>+PES

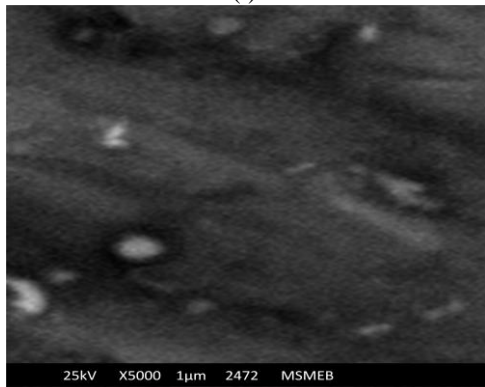
**Table 2:** Crystallinity, Peaks at  $2\theta$  ( $^{\circ}$ ), Interplanar distance ‘d’ and Crystallite Size ‘D’ ( $\text{\AA}$ )

S. No.	Sample with weight percentage of $\text{Al}_2\text{O}_3$	Crystallinity Index C <sub>r</sub> I (%)	Peaks at $2\theta$ ( $^{\circ}$ )	Interplanar Distance ‘d’ ( $\text{\AA}$ )	Crystallite size ‘D’ ( $\text{\AA}$ )
1.	Pure PCTFE	26.92	21.1	4.205	19.581
2.	2% $\text{Al}_2\text{O}_3$ +PCTFE	21.05	21.2	4.185	17.408
3.	5% $\text{Al}_2\text{O}_3$ +PCTFE	18.18	21.3	4.166	17.411
4.	10% $\text{Al}_2\text{O}_3$ +PCTFE	23.81	21	4.225	19.577

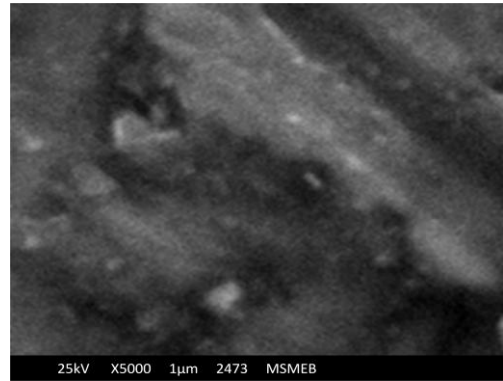
In order to confirm the nanocomposite hybrid structures, the dispersibility of the oxide in selected hybrids was observed using SEM. Figs (3.27 to 3.30) present micrograph of Pure PCTFE polymer, 2wt%, 5wt% and 10wt%  $\text{Al}_2\text{O}_3$  reinforced nanocomposite. From the figures of SEM, different types of dispersion structure of nanoparticle were observed in the nanocomposite films. SEM micrograph of pure PCTFE in fig.3.27, describes the morphological interaction and formation of a single phase with a smooth surface. In the 2wt% and 5wt%  $\text{Al}_2\text{O}_3$  reinforced PCTFE films (Figs 3.28 and 3.30), a clear homogeneous distribution of the oxide nanoparticles within the polymeric network is evident. The advantage of this insitu oxide nanoparticle formation allows the avoidance of any macroscopic agglomeration, thus achieving a uniform size of nanoparticles that are homogeneously dispersed within the polymeric matrix. But in 10wt%  $\text{Al}_2\text{O}_3$  reinforced PCTFE (fig. 3.30) the particles are agglomerated and nonhomogeneous dispersion is obtained.



(i)



(ii)



(iii)



(iv)

Fig.1.6: Scanning Electron Micrograph of Pure PCTFE PCTFE: $\text{Al}_2\text{O}_3$  (i) Pure PCTFE (ii) 2wt% (iii) 5wt% (iv) 10wt% of  $\text{Al}_2\text{O}_3$

#### IV. CONCLUSION

The aim of this study was to explore new polymeric nanocomposites. XRD spectra can be used to determine the onset of crystallization i.e. the transition from a non-crystalline or amorphous film to a crystalline or partially crystallized film. The SEM, AFM, XRD and DSC studies of the PCTFE:  $\text{Al}_2\text{O}_3$  hybrid nanocomposites reveal similar information regarding the morphology and structure of the composites. The SEM and AFM shows that  $\text{Al}_2\text{O}_3$  particles are homogeneously mix in the composite. The homogeneous mixture of the two polymeric constituents is confirmed by DSC and XRD technique as well. The two components are mixing with each other in a homogeneous manner and the composite specimen shows that the one  $T_g$  value for hybrid nanocomposite.

## V. ACKNOWLEDGEMENT

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