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A Study on Pebax 3533|SiO_2 Polymer Films

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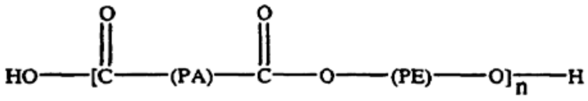
Abstract—*The present work aims to prepare Pebax 3533|SiO_2 nano particle membrane in various weight concentrations by the method of solvent casting and to evaluate their thermal, mechanical and chemical properties. Simulative studies show that nanosilica loading improves the diffusion coefficients for CO_2 and CH_4 gases in Pebax 3533. For this reason, we chose Pebax 3533 and SiO_2 nanoparticles for our characteristic study so that further studies could reveal their gas transport behavior. Solution casting and solvent evaporation techniques were employed for casting of polymeric membranes. Polymeric solution was then poured into Teflon trays for casting. The films thus obtained were found to have thickness around 200 µm and were observed to have pale appearance and smooth surface. SiO_2 nano particles were added in various weight percentages of 1%, 3%, 5% and 7%. It was observed that the addition of nanoparticles make the films more tough and white in color. The films were then subjected to various characterization tests like UTM, SEM, TGA, DSC, FTIR, and XRD. The morphology of the films was obtained from the SEM images whereas the mechanical properties were given by UTM. A TGA and DSC result deals with thermal properties of the polymeric films. The physical properties were confirmed by the XRD results and the chemical composition by FTIR. All the obtained results of the raw polymeric films as well as the composite films were compared and the optimum filler concentration was found. From the characterization tests, 5% is concluded to be the optimum nano filler concentration with the best properties.*

1. INTRODUCTION

Polyether block amide copolymer has drawn lot of attention recently because of its versatile properties. Polyether block amide is an engineering grade copolymer, commercially known as Pebax®, consists of polyether (PE) block which is the amorphous rubbery segment and hard polyamide (PA) block which is the semi-crystalline segment. Hence Pebax® stands for poly ether block amide [1]. A melt polycondensation reaction between amide blocks which are terminated by carboxylic acids and polyoxyalkylene glycols catalyzed by metallic $Ti(OR)_4$ at high vacuum and temperature of 250 °C is utilized to synthesize poly ether block amides [5]. The general structural formula of these block copolymers is shown below.



$$HO-[\overset{O}{\overset{\|}{C}}-(PA)-\overset{O}{\overset{\|}{C}}-O-(PE)-O]_n-H$$

Fig. 1: Structure of Pebax [5]

Characteristics of each copolymer depend upon the relative amount of polyether block and polyamide block present. E.g.: relative amount of PA block determines its chemical resistance and mechanical strength [1] while the polyether region enhances high permeability due to greater chain mobility of the ether linkage. Pebax has a very good performance in terms of mechanical and chemical properties, electrical conductivity, selective molecular diffusion and many more. Their wide field of application includes medical components, sports equipment, power transmission, and gas separation membranes [3].

Polyether block amide was widely investigated upon its gas permeation properties and studies have showed that PE fraction enhances its gas solubility. A series of Pebax materials are available which varies based on the PE and PA content like Pebax 1657, 2533, 3533, 4533, 5533 etc. Among the commercially available Pebax® series, Pebax 3533 was chosen for our work. Pebax® 3533 SA 01 MED is the commercially available grade.

Recently, usage of nanoparticles to increase mechanical or transportation properties of polymeric material has an extremely high rate among researchers. The method of direct addition of nanoparticles is employed in our research work. In previous studies, the addition of SiO_2 and TiO_2 as nanofillers in multiblock terpoly(ester-b-ether-b-amide)s has improved the mechanical properties compared to the terpolymer before modification[4].An increase in the glass transition temperature was also observed. Other studies have shown that mixed matrix membranes of polysulfone containing ordered mesoporous silica speheres or microporous titanosilicates, which are exfoliated layered, could improve the gas transport properties [6].

This work aims at the preparation and characterization Pebax 3533 films with SiO_2 nanoparticles in various concentrations. An integrated theoretical - experimental approach had been adopted for a detailed investigation on the molecular and morphological properties at a nano scale range

2. MATERIALS AND METHODOLOGY

2.1 Materials

N-Butanol of analytical standard was purchased from Chemind Chemicals Ltd. and was used directly as solvent without further purification. The copolymer used in this work

Pebax 3533 was kindly provided by Arkema as pellets and were used as received for film preparation without any further treatment.

Table 1: Properties of Pebax 3533 [3]

Properties of Pebax 3533	Typical value
Density	**1g/cm^3**
Water Absorption at Equilibrium (At 20°C and 50% R.H)	0.4%
Water Absorption (At 23°C and 24 h in water)	1.2%
Melting Point	144
Hardness(*) (Instantaneous)	82/33 Shore A/Shore D
Flexural Modulus(*)	21 Mpa
Vicat point	77 C

(*) Samples conditioned 15 days at 23°C - 50 % R.H.

2.2 Membrane Preparation

N-butanol was chosen as the solvent for Pebax 3533. Method of solution casting and solvent evaporation was employed for casting of polymeric membranes. Initially Pebax 3533 was dissolved in n-butanol to a concentration of 4 wt. % at a heating of 70 °C on reflex and magnetically stirring for around 1 hour to obtain very good polymer solution. SiO_2 nanoparticles were then added, stirring was continued for 1 hour. To obtain a stable suspension, the mixture was then kept in an ultrasonication bath for 2 hours. Finally obtained polymer solution was then casted on Teflon trays. The solution is casted into films immediately after mixing without letting them to cool down to prevent the possibility of gelation. Casted polymer solution in Teflon trays were initially dried in air oven at 70 °C for 24 hrs and later vacuum dried, initially at room temperature for 12 hrs and then at 40 °C to ensure complete removal of solvent.

Prepared polymer films were then subjected to number of tests like universal tensile machine (UTM), differential scanning calorimetery (DSC), thermo gravimetric analysis (TGA), scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR).

3. RESULTS AND DISCUSSIONS

3.1 Physical Appearance

Pebax 3533 was observed to have very good film formation property and they were peeled off easily from Teflon trays. Films prepared have thickness around 200 µm and are observed to have pale appearance and smooth surface. SiO_2nano particles were added in various weight percentages of 3%, 5% and 7%. With addition of nanoparticles, films are getting tougher and white in color.

3.2 Universal Testing Machine

The graphs provide us with a plot between extensions versus force which indicates the variation of mechanical strength of the various samples. A significant increase in elasticity modulus was observed on addition of SiO_2nano-particles with the highest value at 5% of nano-particles indicating composite becoming more rigid and stiff. A similar observation was found for tensile strength as well, indicating maximum ability to withstand stress before breaking. Increase in modulus is also an indication of good matrix filler adhesion and thus a presence of physical interaction. Modulus for 7% filler concentration is found to decrease due to increase in yield points in the curve indicating de-wetting effect between matrix and fillers. The graphs obtained are as follows:

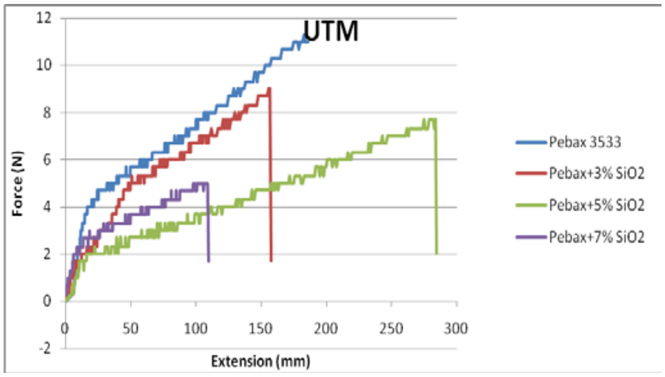


Fig. 2: UTM graph for Pebax and Pebax + SiO2 nanoparticles

Table 2: UTM tabulated results

	Pebax 3533	Pebax+3% SiO_2	Pebax+ 5% SiO_2	Pebax+ 7% SiO_2
Tensile (MPa)	13.45	15	27.5	8.33
Max force (N)	11.3	9	7.7	5
Stress at break (MPa)	131	28.33	7.14	28.33
Force at break (N)	11	1.7	2	1.7
Elongation (%)	744	632	1139	439.5
Stress at 30% (MPa)	15.48	28.33	35.71	33.33

3.3 Differential Scanning Calorimetery (DSC)

The graph indicates the first cooling cycle from 200 ˚C to -130 ˚C and second heating cycle from -130 ˚C to 200 ˚C. [2, 15]During cooling cycle, the samples show two dominant exothermic crystallization peaks, one due to the semi-crystalline segment, PA block at higher temperature and the other peak due to the amorphous segment, PTMO block at lower temperature. The amount of crystallinity is reflected in their corresponding ΔH_C. The second heating scan indicates the melting of these crystalline segments. The amorphous PTMO segment melts at a lower temperature of -15.47˚C and the semi-crystalline PA segment at a higher temperature of 80.6 ˚C.

DSC curve for Pebax 3533 containing 5% SiO_2 nanoparticles is shown in Fig. . Melting temperature of PA block was found to increase from 80.6 ˚C to 86.27 ˚C which indicate increase in crystallinity due to addition of nano particles [2, 15]. This is proved from the UTM results indicated by an increase in modulus value. ΔH_m for PA segment decreases on addition of nano filler which may be due to partial cross linking of PA block with nano particles.

Table 3: DSC tabulated results

	Pebax 3533	Pebax 3533+5%SiO_2
Tm PTMO (°C)	-15.47	-16.03
Tm PA (°C)	80.6	86.27
Tc PTMO (°C)	10.11	9.74
Tc PA (°C)	147.33	146.56
ΔH_m (J/g) PTMO	18.53	17.21
ΔH_m (J/g) PA	10.94	7.714
ΔH_c (J/g) PTMO	20.74	19.43
ΔH_c (J/g) PA	10.30	7.693

Tc–crystallization temperature; Tm–melting temperature; ΔHc - enthalpy of crystallisation; ΔHm–enthalpy of melting; PTMO–ether block ; PA–amide block

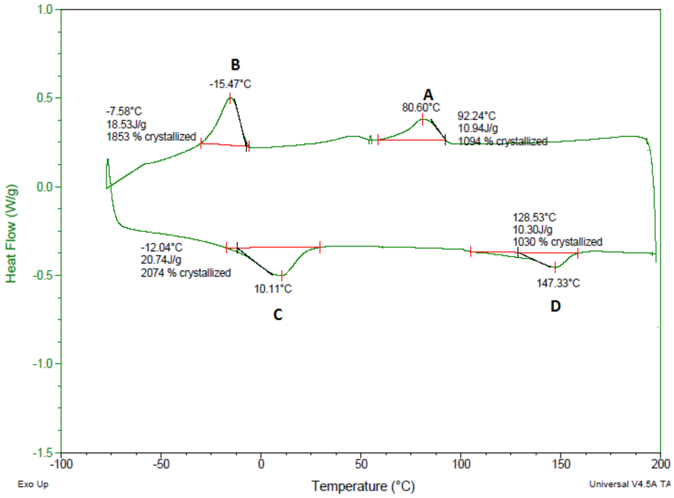


Fig. 3: DSC curve for Pebax 3533

3.4 Thermo Gravimetric Analysis (TGA)

TGA (Thermogravimetric analysis) for the samples containing 0%,3%,5% and 7% nanosilica was conducted in the instrument *Q50*.During thermal analyses the weight loss of the materials are measured as a function of increasing temperature or time. The samples were heated from 30 ˚C to 700 ˚C using a temperature ramp of 10˚C/min in TA Q50 TGA instrument. Graph is plotted between weight percentages an temperature in ˚C.

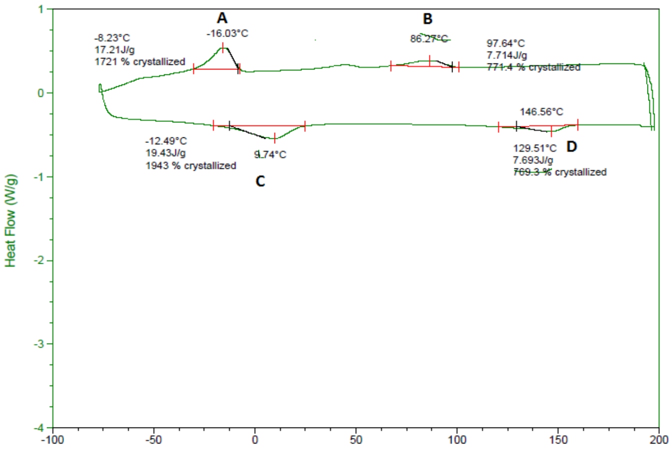


Fig. 4: DSC curve for Pebax 3533 + 5% SiO2

Table 4: TGA tabulated results

	Pebax 3533	Pebax 3533+5% SiO_2
Onset temperature(°C)	358.85	374.22
Residual mass (%)	0.033	4.526
Temperature at 50% mass	405.1	411.82

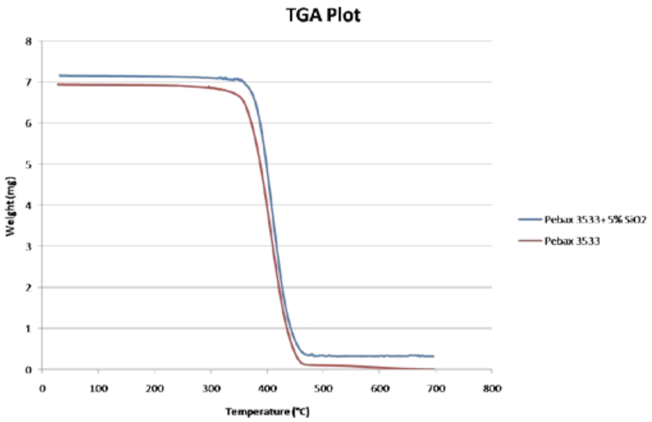


Fig. 5: TGA graph

In the results, a single onset temperature (temperature at which a material starts to degrade) is observed for the polymer, which indicates that both ether and amide block degrades at the same temperature. Increase in onset temperature for nano composite from 358.85°C to 374.22°C indicates improved thermal resistance. Significant increase in the residual mass from 0.033% to 4.526% further indicates char formation. The stabilization effect is evident where the nano particles improve the thermo-oxidative stability of Pebax matrix.

It can be concluded that addition of nano particles into polymer matrix has enhanced its thermal stability by acting as a heat barrier. During thermal degradation, char formation is enhanced by the restricted chain mobility [10].

3.5 Scanning Electron Microscopy (SEM)

Fig. s 6 and 7 show the morphologies observed by the scanning electron microscopy for pure Pebax 3533 and the nano composites. For the nano composites, independent of the composition range investigated here, no phase separation was found. The inorganic phase was found to be uniformly distributed in the organic polymer matrix in these systems. Particles can be visualized which were of equal shape and size. For samples containing 7% SiO_2 nanoparticles, dendritic or fibrillar structure was observed which is a characteristic of crystalline polymers [8]. Domains of SiO_2 were found to some extent which may be due to the agglomeration of particles.

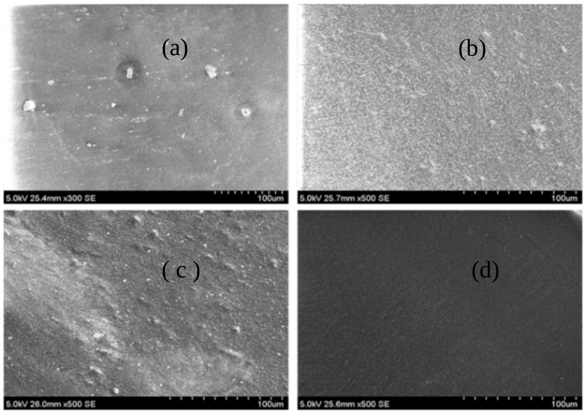


Fig. 6: SEM images of samples (a) Pebax 3533 (b) Pebax 3533 + 3% SiO2 (c)Pebax 3533 + 5% SiO2 (d) Pebax 3533 + 7% SiO2

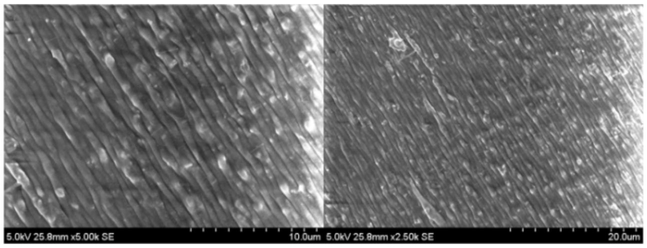


Fig. 7: SEM image of Pebax 3533 + 7% SiO2 showing rod like structure

3.6 X-ray diffraction (XRD)

The XRD (X-ray diffraction) analysis was done for all samples, namely for 0%, 3%, 5% and 7% in the instrument. It was found that there is a peak at $2\theta = 20°$ for pure polymer. The peak is observed to decrease for membranes with 5% and 7% nanosilica. It shows that the *d*-spacing between adjacent chains is increased. According to Bragg's law, the *d*-spacing for pure membrane is equal to 0.479 nm and that for membranes with 7% nanosilica increases to 0.509 nm. The analysis also shows that the intensity of samples with addition of nanosilica is more than that of the pure case. This issue indicates the free volume has more regularity at impure cases.

It shows the cavity size distribution of samples with 7% nanosilica is more suitable than that in pure and 5% cases.

It can be considered that the second peak appears in the nanosilica loading membrane which is caused by silica phase. It is clear from the graphs that the addition of SiO_2 increases the crystalline nature of Pebax-3533.This is seen from the increase in the number of small and sharp peaks from the addition of 3% to 7% SiO_2 nanoparticles.

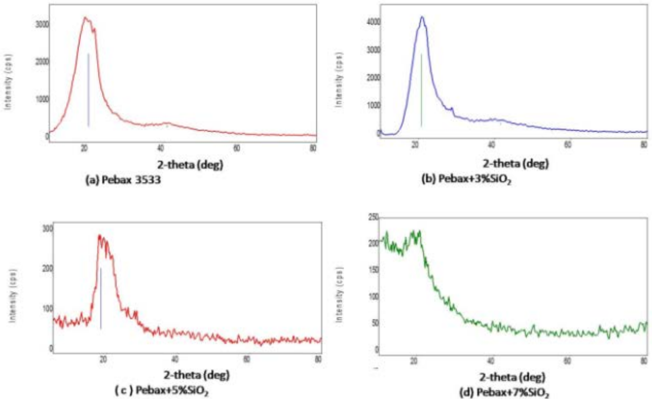


Fig. 8: XRD images

3.7 Fourier Transform Infrared Spectroscopy (FTIR)

Pebax/SiO_2 membranes with 0 wt.% SiO_2 and 5 wt % SiO_2 loading was prepared for FTIR analyses. The infrared spectra of neat Pebax and Pebax/SiO_2 membranes in the region 400 cm^{-1} to 4000 cm−1 is shown in Fig. s. The two absorption bands in Pebax, the H–N–C O near 1640 cm^{-1} and the –C–O– at 1000 cm^{-1} are particularly sensitive to the hydrogen bonding [7,16]. Nylon 12 generated a peak at 3200 cm^{-1} which denotes the imide N-H bond [9].

Analysing the results for nanocomposite, the new peaks formed at 1567 cm^{-1} indicates the carboxylate groups of 1, 3, 5- benzene tri-carboxylate ligands for the asymmetric vibration. Similarly the peaks at 723 cm^{-1} indicates O-Si(Al)-O symmetrical bending and that at 469 cm^{-1} indicates Si-O-Si bending vibration. The NH stretching vibrations shown at 3501 cm^{-1} has found to disappear at that of the composite's results.Hence the appearance and disappearance of certain peaks denotes interaction between nano-filler and Pebax 3533.

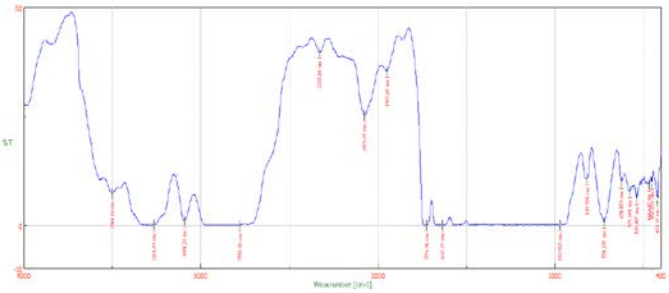


Fig. 9: FTIR result for Pebax 3533

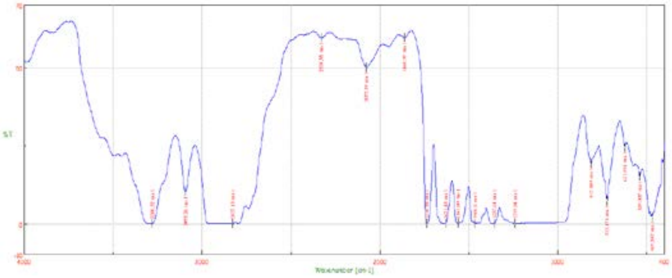


Fig. 10: FTIR result for Pebax 3533 + 5% SiO2

4. CONCLUSION

Pebax 3533 is observed to have very good film formation property and they can be easily peeled off from the substrate.Films prepared have thickness around 200 µm and are observed to have pale appearance and smooth surface.SiO_2 nanoparticles were added in various weight percentages of 3%, 5% and 7%. With addition of nanoparticles, films are getting tougher and white in colour.

From UTM results, significant increase in elasticity modulus was observed on addition of SiO_2 nanoparticles with the highest value at 5% of nanoparticles indicating composite becoming more rigid and stiff. The tensile strength also shows a similar behaviour. Thus from the UTM results, 5% was concluded to be the optimum nano filler concentration. The TGA analysis showed that there was a considerable increase in the onset temperature with the addition of 5% nanoparticles, which shows a higher thermal resistance. This is further supplemented by the increase in residual mass.

The melting point of both PA and PE blocks was found to increase in the 5% nano composite from the DSC results which indicates increase in crystallinity due to addition of nanoparticles. It was found that both ether and amide blocks were affected by the nano particles, indicated by the shift in peaks as well as enthalpy associated with them. XRD results shows that there is a progressive increase in the crystalline character with the addition of nanoparticles. The decrease in peak from 2θ =20 for nano composites shows that the *d*-spacing between adjacent chains is increased. From the SEM images, no phase separation was found for the nano composites, irrespective of the composition range investigated. For samples containing 7% SiO_2 nanoparticles, dendritic or fibrillar structure was observed which a characteristic of crystalline polymers. From the characterization tests, 5% is concluded to be the optimum nano filler concentration with the best properties. It has applications in gas transportation. The improved mechanical strength, which is proved by the UTM results, makes it capable of withstanding high gas flow rates. The better thermal properties, indicated by the DSC and TGA results, make the film suitable for higher temperature applications. Thus, the nano composite is better suited or industrial applications than the pure polymer.

5. ACKNOWLEDGEMENT

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