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Polyurethane / Carbonaceous Nanofillers based Nanocomposite Films through Thermo-Chemical route for Gas Barrier Property

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Abstract

The carbonaceous nanofillers like acid functionalized multiwall carbon nanotube (f-MWCNT as 1D), edge functionalized hydroxylated few layers graphene (f-FLG as 2D) and f-MWCNT embedded into the graphene flakes as 3D were incorporated into thermoplastic polyurethane by thermo-responsive gelation method for the preparation of cellular structures. The concentration of nanofillers was varied as 0.1, 1 and 5 wt%. The prepared cellular structures were characterized using SEM, XRD and FTIR. The cellular structured polyurethane was then compounded by twin-screw extrusion. The compounded material was used to prepare the films by compression moulding technique. The functionalized carbonaceous nanofillers were also incorporated into the polyurethane by compounding directly in a twin-screw extruder. The dispersion of the nanofillers was studied by scanning electron microscopy (SEM). SEM studies showed very good dispersion of nanofillers in the compounded materials made through cellular structure route. The developed films were studied for the gas barrier properties by measuring the helium gas permeability. The addition of 1 weight percentage of tailor made hierarchical carbonaceous nanomaterials in TPU by thermo-responsive gelation route followed by melt mixing resulted reduced helium gas permeability from 1287 to 548 $cm^3/m^2/day$.

Keywords: MWCNT; Graphene; carbonaceous nanofillers; Polyurethane; Nanocomposites

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1. Introduction

The polyurethane foams (PUFs) are mainly used as an insulating and core materials for furniture, shipbuilding, for cooling in building, freezing systems, etc. The use of the rigid foams is popular due to their low coefficient of heat conduction, low density, relatively better mechanical strength and low water absorption [1].

Because of the combination of good mechanical properties and low density, the rigid polymer foams are suitable materials for the structural applications. However, optimization is necessary to understand the relationship between mechanical properties and microstructure[2].The cellular structure of the PUFs are widely utilised for various applications and dominated the market in comparison with other similar competitive materials [3]. Some technological disadvantages are there with PUF despite its outstanding properties viz. thermal aging, degradation, dimensional stability, etc. The nanocomposites based PUFs have been developed with the tailor made properties by reinforcing carbon based nanofillers to attribute a large number of benefits for specific applications [4].The primary objective to take up this work is to develop flexible polymeric films based on polyurethane with enhanced operational hours for gas barrier properties. For this the main challenge is the dispersion of carbonaceous nano-fillers viz. carbon nanotube (CNT) and graphene or graphite nano-flakes into the polymer matrix. To enhance the dispersion of carbonaceous nano-fillers, one of the most important issues is that they need to be functionalized. Though the functionalization of nano-filler helps to enhance the dispersion still it can be improved further by adopting a novel concept by adapting a thermo-chemical technique with the combination of (i) preparation of cellular structure by thermo-responsive gel formation technique and (ii) compounding by melt mixing twin screw extrusion. The enhancement in dispersion leads to the increase of the length of tortuous path which plays the main role to improve the operational hours by reducing the permeability.

2. Materials and Method

A commercial aliphatic polyether-based TPU (Texin SUN-3006, extrusion grade, Hardness 90: shore A, specific gravity 1.08 g/cm^3, Mn = ~79000, Mw = ~211000 and MFI: 5.1 g/10 min at 200°C with load 2.16 kg) was procured from Covestro, India for this work. The various carbonaceous nanofillers like acid functionalized multiwall carbon nanotube (f-MWCNT as 1D), edge functionalized hydroxylated few layer graphene (f-FLG as 2D) and f-MWCNT embedded into the graphene flakes as 3D were incorporated into thermoplastic polyurethane by thermo-responsive gelation method [5] for the preparation of cellular structures. The concentration of nano-fillers was varied as 0.1, 1and 5wt%. The cellular structured polyurethane was then compounded by twin-screw extrusion. The compounded material was used to prepare the films by compression moulding technique. The functionalized carbonaceous nanofillers were also incorporated into the polyurethane by compounding directly in a twin-screw extruder. The scanning electron microscopic (SEM) images were recorded on a SUPRA 40 VP, Gemini, Carl Zeiss scanning electron microscope for morphological studies. The acceleration voltage was 10 kV. The samples were coated with vacuum gold sputtering prior to SEM studies. Helium gas permeability of the films was measured in a N500 Gas Permeation Analyzer, GBPI Packaging Instruments Co. Ltd. (ASTM D-1434-82). The test was carried out at an average temperature of 25°C. Attenuated Total Reflection Fourier

Transform IR (ATR-FTIR) spectra were recorded in a high Resolution ATR-FTR (from Perkin Elmer, spectrum 100 series) in the range of 4000-600 cm^{-1} with a resolution of 4 cm^{-1}and 8 scans. The ATR element used was zinc selenide (ZnSe) crystal. The X-ray diffraction (powder diffraction XRD patterns) of neat PU and the cellular structure of PU nanocomposite were recorded on the Bruker AXS diffractometer, Germany (D8 Advanced). The X-ray was produced in a sealed tube and wavelength of the X-ray was 0.154 nm (Cu K-alpha).

3. Results and Discussion

The SEM images of carbonaceous nanofillers and 3D hybrid nanofillers incorporated polyurethane cellular structures are shown in the Figure 1. Figures 1(A-C) are showing the (A) f-MWCNT as 1D, (B) f-FLG as 2D,(C) f-MWCNT embedded into f-FLG as 3D hybrid nanofillers, respectively.

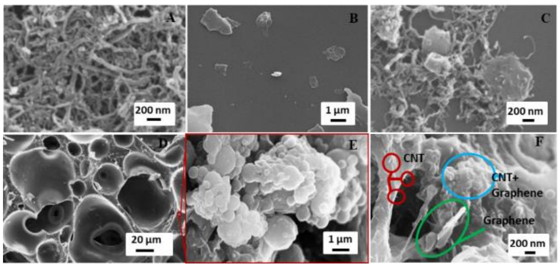


Figure 1: *SEM images of (A) f-MWCNT, (B) f-FLG,(C) f-MWCNT embedded into f-FLG, (D&E)cellular structure of 1wt% 3D hybrid carbonaceous nanofiller incorporated TPU, and (F) cellular structure showing the presence of nanofillers in its morphology.[Scale bars (A&C) 200 nm, (B&E) 1µm,(D) 20µm, and (F) 300 nm]*

Figures 1(D-E) are showing the cellular structures of 1wt% 3D hybrid carbonaceous nano-filler incorporated TPU at different magnification (specified in the figure caption of Figure 1). The presence of nanofillers viz. f-MWCNT and f-FLG in the morphology of cellular structure is shown in the Figure 1F. No agglomerations were found in the SEM images. The cellular structures were prepared by dissolving the polymer into the solvent at the temperature of 90^{o}C. At this stage when all the polymer chains were fully free, the nano-fillers were added and allowed to form gel like structure. The gel like structure forms when the entanglement of the polymer chains occur but remains filled with solvent. The temperature is then allowed to drop upto 60^{o}C when the carbon nanofillers get embedded within the polymer chains by strengthening the wall of the cell like structure. After this the solvent is replaced with medium boiling point, medium density and higher polarity to increase the kinetic of diffusion. Finally the solvent is replaced with the low boiling point, low density and higher polarity at low pressure. The cellular structures in which the walls of the cell are reinforced with dispersed nano-fillers were allowed to dry at room temperature at very slow rate to ensure that the cell remains intact without collapsing. The SEM image (Figure 1E) showed the intact cell structure when the solvent was dried and very good dispersion of nano-fillers (Figure 1F).

The XRD spectra of neat thermoplastic polyurethane (NPU, red color), cellular structure of neat TPU (NCS, black color), 0.1wt% 3D nano-fillers reinforced PU (CS 0.1, blue color, 1wt% 3D nano-fillers reinforced PU (CS 1.0, pink color) and 5 wt% 3D nanofillers reinforced PU (CS 5.0, green color) is shown in Figure 2. The XRD spectra are clearly illustrating the reconstruction of TPU microstructures. The 2θ peaks found at 20^0 and 22.5^0 for amorphous halo because of the soft domains, the short range regularly ordered hard segments of PU and the crystallization of hard segments of PU, respectively [7,8].

The presence of the low dimensional functional carbonaceous nanofillers (LDCN) remarkably influenced the crystallinity of the micro-structure due to the hard segments. The intensity reduction of peak at 22.5^0 due to the incorporation of nanofillers illustrated that the functional nano-fillers considerably decreased the hard segments by penetrating into the microstructural phases.

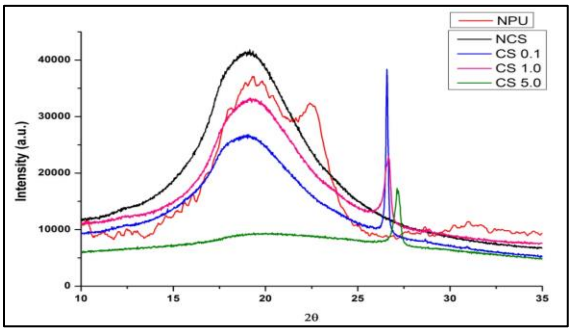
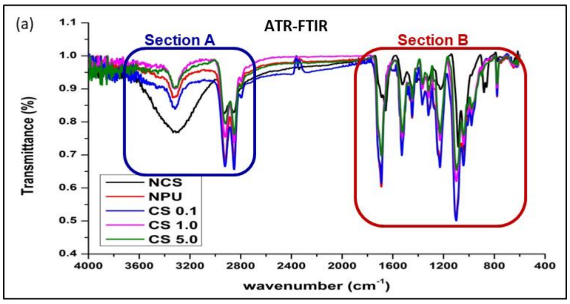


Figure 2: *XRD results of pristine thermoplastic polyurethane (NPU, red color), cellular structure of neat TPU (NCS, black color), 0.1 wt% 3D nano-fillers reinforced PU (CS 0.1, blue color, 1wt% 3D nanofillers reinforced PU (CS 1.0, pink color) and 5 wt% 3D nano-fillers reinforced PU (CS 5.0, green color)*

The width of amorphous halo found to increase in 3D hybrid nanofillers incorporated microstructure indicates that the kinetics of both soft and hard segments of PU matrix was significantly disordered due to the presence of interpenetrating network of hybrid 3D nanofillers in PU matrix. The intensity reduction of the peak at 22.5° hard segments was also reported earlier in waterborne PU nanocomposite reinforced with functionalized graphene sheets [9]. The presence of nanofillers of graphene flakes, CNTs and CNTs embedded into graphene flakes were also found to indicate by the 2θ peaks at around 26° (Figure 2).

ATR-FTIR spectra of neat thermoplastic polyurethane (NPU, red color), cellular structure of neat TPU (NCS, black color), 0.1 wt% 3D nanofillers reinforced PU (CS 0.1, blue color, 1wt% 3D nanofillers reinforced PU (CS 1.0, pink color) and 5 wt% 3D nanofillers reinforced PU (CS 5.0, green color) are shown in Figure 3 in the range (a) 4000-600 cm^{-1}, (b) 3600-2600 cm^{-1} and (c) 1800-600 cm^{-1}. The ATR-FTIR spectra is marked into two different sections and named as Section A and Section B. Figure 3(b) is selected in the range of 3600-2600 cm^{-1} whereas the Figure 3(c) is marked in the range of 1800-600 cm^{-1}.



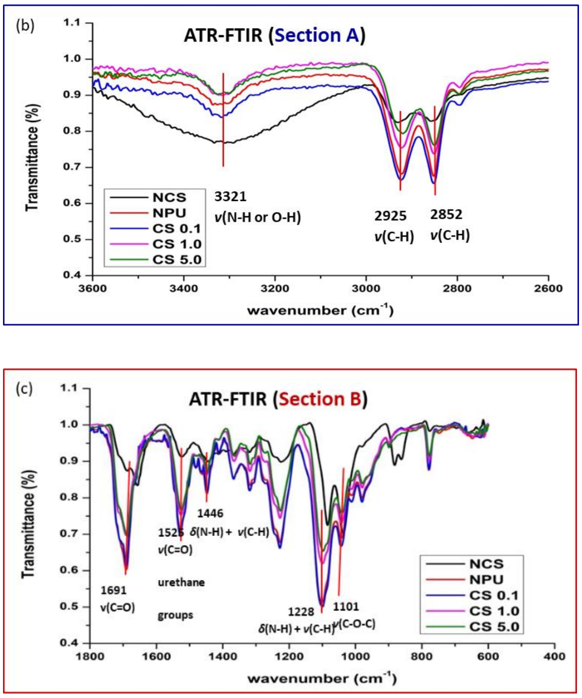


Figure 3: *ATR-FTIR spectra of neat thermoplastic polyurethane (NPU, red color), cellular structure of neat TPU (NCS, black color), 0.1wt% 3D nano-fillers reinforced PU (CS 0.1, blue color, 1wt% 3D nano-fillers reinforced PU (CS 1.0, pink color) and 5 wt% 3D nano-fillers reinforced PU (CS 5.0, green color) in the range (a) 4000-600 cm^{-1}, (b) 3600-2600 cm^{-1} and* (c) *1800-600 cm^{-1}.*

The peak present at 3321 cm^{-1} in the Figure 3, corresponds to the hydrogen bonding of –O-H group with >N-H of urethane group of TPU and the stretching vibrations of -O-H group. There are four different characteristic peaks of vibrational absorption of hydrocarbon chains found at 795 cm^{-1} (out of plane bending, -CH group), 2852 (symmetric C-H stretching), 2925 (asymmetric >C-H stretching) and 1446 (scissoring vibration, >CH$_2$ group) [10]. The stretching vibrations of hydrogen bonded -NH group are shown in the broad peak around 3321 cm^{-1} for the neat polyurethane (NPU in Figure) and cellular structures of polyurethane based nanocomposites (NCS and CS 0.1, CS 1.0 and CS 5.0). The broadening of peak for NCS i.e. cellular structure of neat polyurethane is due to porous structure at 3321 cm^{-1}. The porous cellular structure (NCS) exhibited the higher vibrations than the compact structure of the neat polyurethane (NPU). The peak broadening gradually reduced at 0.1 wt% (CS 0.1) and 1 wt% (CS 1.0) of 3D nanofillers reinforced polyurethane due restriction in vibrations due to the interactions of nanofillers and functional groups in polymer chains. The -NH groups of the urethane linkages are expected to engage in formation of H-bonding with either the carbonyl groups (>C=O) of hard segments or with ether linkages (-O-) of the soft segments. The peak present at 1691 cm^{-1} corresponds to the stretching vibration of hydrogen bonding with the carbonyl group (>C=O) of NPU, NCS and CS 0.1, CS 1.0 and CS 5.0.

The cellular structure was then compounded in a twin screw structure and compression moulded to prepare the films with approximate thickness of 140 µm. The developed films were studied for the gas barrier properties by measuring the helium gas permeability. It was found that the permeability of 1 wt% 3D hybrid carbon nano-filler reinforced polyurethane nanocomposites based film (CS 1.0) showed (Figure 4) very good gas barrier property with the reduction of helium gas permeability to 548 cm^3/m^2/day from 1287

cm^3/m^2/day of neat polyurethane film at 1wt% loading of hybrid 3D nanofiller.

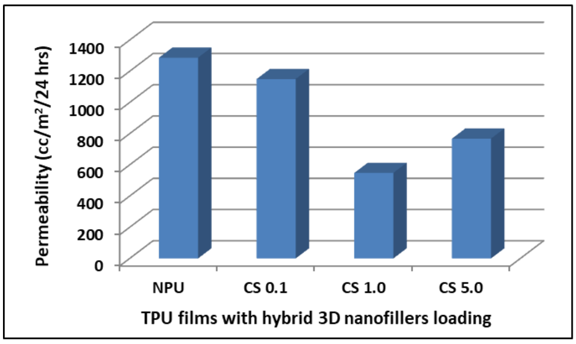


Figure 4: *Permeability of TPU nanocomposite films*

However, the helium gas permeability of 0.1 wt% nanofillers incorporated film was very close to the neat PU as the reinforcement was not enough to increase the tortuosity of the gas molecule. At 5 wt % loading, the permeability was not only found to decrease in comparison with the neat PU but also found to increase in comparison with the 1wt% nanofillers incorporated PU film. This happened because of the agglomeration at higher loading. At higher loading, the surface area of the nanofillers is so large that the polymer chains are not able to accommodate all the nanofillers in its dispersed condition. As a result the nano-fillers get agglomerated. When the agglomeration occurs, the decrease in tortuosity also happens by increasing the permeability in comparison with the dispersed condition where tortuosity is higher. As a result the permeability increases at higher loading of 5 wt%.

Conclusions

SEM studies showed very good dispersion of nanofillers in the compounded materials made through cellular structure route. The XRD spectra showed the reformation of microstructure of polyurethane in cellular structure by reducing the cluster size of hard segment and dispersing the same into the soft segment of polyurethane in presence of carbonaceous nanofillers. The FTIR exhibited the hydrogen bonding between urethane and ester groups of polyurethane and the hydroxyl groups present in the nanofillers. The developed films were studied for the gas barrier properties by measuring the helium gas permeability. The addition of 1 weight percentage of tailor made hierarchical carbonaceous nanomaterials in TPU by thermo-responsive gelation route followed by melt mixing resulted in reduced helium gas permeability from 1287 to 548 cm^3/m^2/day. The reduction in permeability of the developed material makes it highly suitable for aerostat applications with higher flying cycle.

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