Polymer–clay nanocomposites via chemical grafting of polyacrylonitrile onto cloisite 20A

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Abstract. The synthesis and characterization of polyacrylonitrile (PAN) nanocomposites through grafting the polymer onto organophilic montmorillonite have been reported. Cloisite 20A reacted with vinyltrichlorosilane to replace the edge hydroxyl groups of the clay with a vinyl moiety. Because the reaction liberates HCl, it was performed in the presence of sodium hydrogen carbonate to prevent the exchange of quaternary alkylammonium cations with H^+ ions. Only the silanol groups on the edge of the clay reacted with vinyltrichlorosilane. The radical polymerization of the product with acrylonitrile (AN) as a vinyl monomer leads to chemical grafting of polyacrylonitrile onto montmorillonite surface. The homopolymer formed during polymerization was separated from the grafted organoclay by Soxhlet extraction. Chemical grafting of the polymer onto Cloisite 20A was confirmed by infrared spectroscopy. The prepared nanocomposite materials and grafted nanoparticles were studied by XRD and TEM. Exfoliated nanocomposites were obtained for 0.5–7 wt% clay content. The nanocomposites were studied by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMTA).

Keywords. Grafting; polyacrylonitrile; nanocomposites; Cloisite 20A; organophilic clay.

1. Introduction

During past decades polymer/layered silicate nanocomposites have attracted great interest, both in industry and in academia, because they often exhibit remarkable improved material properties (Ray and Okamoto 2003). The homogeneous dispersion of organically modified clays in polymer matrices could lead to enhanced thermal stability (Phang *et al* 2005; Zhao and Wang 2006; Jin and Chang 2008; Rubal *et al* 2008), mechanical properties (Gintert *et al* 2007; Jia *et al* 2008; Stefanescu *et al* 2008; Njuguna *et al* 2008; Mansoori *et al* 2010a,b), gas barrier (Yudin *et al* 2007; Huang *et al* 2008), dielectric properties (Gu *et al* 2001) and solvent resistance (Huang *et al* 2001) compared to the virgin polymers or conventional micro- and macro-composites. Montmorillonite is the most commonly used layered silicate due to its high cation-exchange capacity, excellent swelling ability, high aspect ratio and ease of modification, which are important for the preparation of clay/polymer nanocomposites (Zhao *et al* 2009).

PAN is an important thermoplastic from industrial point of view because of its favourable properties. Furthermore, AN can be easily copolymerized with other vinyl monomer and thus the resulting copolymers may be used as plastic resins, fibres or rubbers. It is the most common precursor to create carbon nanofibres (Wang *et al* 2005; Kim *et al* 2008; Zhang

et al 2009; Nataraj *et al* 2009; Karimi *et al* 2011). Heating of PAN over 700°C in a non-oxidative atmosphere leads to production of a polyaromatic structure similar to a graphitic sheet (Beretta 2009).

Several research groups have focused their efforts on studying PAN-based nanocomposites using PbS (Qiao *et al* 1999), carbon nanotube (Wang *et al* 2008), CdS (Feng *et al* 2009) and iron (Zhang *et al* 2010) as nanofiller. The investigations on polymer layered silicate nanocomposites with homopolymer of PAN have recently been noted. Chung and co-workers reported the synthesis of exfoliated PAN/sodium montmorillonite (Na–MMT) nanocomposites via emulsion polymerization. The nanocomposites showed exfoliated morphology up to 20 wt% of Na–MMT. Storage moduli of PAN/Na–MMT nanocomposites were enhanced compared with pristine PAN (Choi *et al* 2002). They have also reported the preparation of exfoliated PAN/Na–MMT nanocomposites using initiators adsorbed on silicate. The initiator adsorbed on silicate commenced the polymerization of AN, delaminating silicate layers in PAN/Na–MMT nanocomposites (Choi and Chung 2004). Yu *et al* (2007) reported the co-incorporation of two different forms of nanomaterials into polymer matrix. They synthesized PAN/Na–MMT/SiO₂ nanocomposites via *in situ* emulsion polymerization. It was found that the PAN/Na–MMT/SiO₂ nanocomposites exhibit considerably enhanced moduli compared with the PAN/Na–MMT and PAN/SiO₂ nanocomposites due to the synergistic reinforcing effect (Yu *et al* 2007). Yang *et al* prepared organically modified Na–MMT with 12-aminododecanoic

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acid as filler to prepare a series of composite polymer electrolytes based on PAN and LiClO_4 . It was found that the organoclay particles were well dispersed in the composite polymer electrolytes and the corresponding cell exhibited excellent electrochemical stability and cyclability (Yang *et al* 2009). Recently, Sun *et al* (2010) reported the preparation and characterization of novel nanocomposites based on PAN/kaolinite by a simple *in situ* emulsion polymerization. The crude kaolinite was firstly modified by dimethylsulfoxide-methanol and potassium acetate-aqueous systems. AN was then intercalated into kaolinite by displacing potassium acetate from KAc-kaolinite. It was observed that the presence of clay results in an increase in molecular weights compared to pure PAN polymer due to the highly crosslinked structure (Sun *et al* 2010).

One of the major problems in preparing nanocomposite materials based on organoclay is the hydrophilicity of the clay that makes the clay less compatible with the organic polymers. Several efforts have been made to modify the inorganic clay with organic polymers for a better compatibility. These methods include incorporation of AIBN-type initiator into the intergalleries of the clay by ion exchange reaction (Fan *et al* 2003a,b), synthesis of ionically bound methacryl type monomer (Mittal 2007), grafting of polymers from clay nanoparticles via high-dose gamma-ray irradiation (Wang *et al* 2007), surface-initiated redox polymerization (Chen *et al* 2010a), and grafting of polymers onto inorganic substrates via surface-initiated atom transfer radical polymerization (Chen *et al* 2010b).

Nevertheless, clay remains hydrophilic after these modifications. This hydrophilic nature can be attributed to the polar silanol groups located at the edges of layered silicates. To make the organoclay more compatible with polymers, the edge silanol groups can be replaced with polymer chains that make the organoclay more compatible with the polymer to be used later (especially if both polymers are the same). Using of mono- and tri-functional organo-alkoxysilane derivatives carrying a terminal reactive methacryloyl group, as reagents for silylation of synthetic Laponite clay platelets, have been reported by Herrera *et al* (2004). Polymer grafting was performed by emulsion polymerization of the silylated clay in the presence of styrene and butyl acrylate at 70°C for up to 24 h (Herrera *et al* 2004). A major drawback of the method is the susceptibility of the Si–O–C linkage, which connects the polymer chain onto inorganic substrate, to hydrolysis in aqueous solutions (Gorgani *et al* 1985). In order to overcome this problem, Agudelo *et al* (2011) reported the synthesis of random copolymers based on poly(styrene-co-triethoxyvinylsilane) and their application as macrosilanes for grafting silica particles with PS chains. We also recently reported the grafting of polyacrylamide, poly(methyl methacrylate) (Mansoori *et al* 2010a,b), and polyvinyl acetate (Mansoori *et al* 2011) onto Cloisite 20A. In these methods, the polymer chain was grafted onto the inorganic substrates via a strong Si–C linkage that was quite stable in acidic and weak alkaline aqueous media (Waddell *et al* 1981).

In the present study, we wish to report the grafting of PAN onto Cloisite 20A nanoparticles. Organophilic clay was vinyl-modified by silylation reaction with vinyltrichlorosilane and then free radically co-polymerized with AN in the presence of benzoylperoxide (BPO) as an initiator. The grafted polymer acts as a compatibilizer between the polymer and the clay phases because both the polymers have the same polarity. Chemical grafting of the polymer onto the surface of Cloisite 20A was clearly confirmed by FTIR spectroscopy after Soxhlet extraction and separation of homopolymer. The prepared nanocomposites and grafted nanoparticles were studied by XRD and TEM. The properties of the nanocomposites were investigated by conventional TGA and DMTA techniques.

2. Experimental

2.1 Materials

The commercial nanoclay Cloisite 20A was purchased from Southern Clay Products (Gonzales, TX) and dried under vacuum at 60°C for 24 h before silylation. Vinyltrichlorosilane and AN were obtained from Fluka Co. and Merck Co., respectively. BPO was obtained from Merck Co. and recrystallized from ether prior to use. All other chemicals were of reagent grade and were used without further purification.

2.2 Measurements

FTIR (KBr) spectra were recorded on a Perkin Elmer RXI spectrophotometer (2 w/w% in KBr, resolution, 4 cm^{-1} , number of scans, 6). TGA and DMTA curves of the powdered samples were obtained on Linseis STA PT 1000 and Triton Tritec 2000 DMN instruments, respectively. Wide angle X-ray diffraction (XRD) measurements were performed at room temperature on a Italstructures MPD3000 X-ray diffractometer by using Ni-filtered $\text{Co-K}\alpha$ radiation. The scanning rate was 1°/min over a 2θ range of 2–10°. TEM images of nanocomposite samples were obtained by using a transmission electron microscope (EM 208 S, Philips, The Netherlands) with an acceleration voltage of 100 kV. Prior to TEM experiment, the nanocomposite sample was completely dried under vacuum and then embedded in an epoxy matrix. Subsequently, it was cut into a 70–100 nm thick section with a diamond knife and placed onto a 400 mesh copper grid.

2.3 Preparation of vinyl-modified clay

The preparation of vinyl-modified clay was performed according to the method described earlier (Mansoori *et al* 2010a,b). 10 g portion of Cloisite 20A and NaHCO_3 (42 g, 0.5 mol) were placed in a 500 ml three-neck round bottom flask charged with 300 ml of anhydrous acetone. The system was vigorously stirred under nitrogen for 15 min. Then a 50 ml portion of vinyltrichlorosilane was added drop wise

to the suspension over 3 h. The mixture was gently refluxed for 8 h and the product was filtered, successively washed with acetone, acetone/H₂O (50/50), filtered, dried under vacuum at 40°C, and stored for the subsequent experiments: FTIR (KBr): 3635 (*m*, OH), 3064 (*w*, vinylic CH), 2927 (*m*, surfactant), 2853 (*m*, surfactant), 1041 cm⁻¹ (*s*, Si–O).

2.4 Polymer grafting

In a three-necked round bottomed flask equipped with a magnetic stirrer and a reflux condenser, silylated Cloisite 20A (5 g), AN (1.482 g, 28 mmol) and BPO (0.130 g, 0.54 mmol) were placed in 15 ml of DMF. The flask was purged by dry, oxygen-free argon for 20 min. The system was heated and magnetically stirred at 90–95°C for 8 h. Then the reaction mixture was transferred into a Soxhlet apparatus and extracted with CH₂Cl₂ for 72 h. The grafted powder was then dried at 40°C for 24 h in a vacuum oven. FTIR (KBr): 3632 (*m*, OH), 2927 (*m*, surfactant), 2855 (*m*, surfactant), 2246 (*w*, C≡N), 1040 cm⁻¹ (*s*, Si–O).

2.5 Blank experiment

The blank experiment was performed under same conditions using unmodified Cloisite 20A.

2.6 Typical procedure for preparing PAN clay nanocomposite, 1 wt%

In a three-necked round bottomed flask equipped with a magnetic stirrer and a reflux condenser, silylated Cloisite 20A

(0.040 g) was dispersed in 15 ml of DMF. The suspension was stirred at room temperature for 24 h under argon. AN (4 g, 75.5 mmol) and BPO (0.360 g, 1.49 mmol) were added and the mixture was stirred at room temperature for an additional 24 h under argon. The reaction mixture was heated at 90–95°C for 8 h. The viscous suspension was trickled slowly into 100 ml of MeOH while vigorous stirring, filtered, thoroughly washed with MeOH and then dried at 60°C for 24 h in a vacuum oven.

3. Results and discussion

Organophilic clay, Cloisite 20A, was silylated with vinyl-trichlorosilane. Because the reaction liberates HCl, it is very important that the quaternary alkylammonium cations are not exchanged with H⁺ ions. If the protons are not removed, the silylation reaction can occur on both external and internal surfaces, decreasing the basal spacing. The internal surface silylation is eliminated by capturing the protons with a base such as sodium hydrogen carbonate so that the basal spacing almost was not changed (Zhang *et al* 2006). In the IR spectrum of the silylated Cloisite 20A (figure 1b), absorption bands appeared at 3064 cm⁻¹ and 3029 cm⁻¹ that can be attributed to the stretching of the vinylic C–H bonds. In the next step, vinyl-modified Cloisite 20A was copolymerized with AN by free-radical polymerization reaction in the presence of BPO as an initiator (scheme 1).

To confirm the grafting reaction by conventional analytical methods, the homopolymer must be separated from the

Figure 1. FTIR spectrum (KBr) of (a) Cloisite 20A, (b) silylated Cloisite 20A and (c) polyacrylonitrile-grafted Cloisite 20A.

Scheme 1. Hydrogenated Tallow (HT) is derived from natural product with average 17 number of carbon.

Figure 2. Schematic representation for a PAN-grafted Cloisite 20A.

grafted organoclay particles. For this reason, after completion of polymerization, the product was extracted by using Soxhlet apparatus with CH_2Cl_2 to remove the homopolymer. The complete removal of the homopolymer was confirmed by doing a blank polymerization experiment with the unmodified Cloisite 20A. After 72 h of Soxhlet extraction of the blank experiment product with dichloromethane, FTIR spectrum observed was the same as that for Cloisite 20A, and the absorption bands related to PAN were not observed. In the FTIR spectrum of the separated Cloisite 20A grafted with PAN, the absorption band observed at 2246 cm^{-1} is related to nitrile stretching. The strong, broad band in the region of $1000\text{--}1160\text{ cm}^{-1}$ is likely due to siloxane (Si–O–Si) bond (figures 1a–c).

The radical polymerization of acrylonitrile with different amounts of vinyl-modified organoclay in the presence of BPO in DMF leads to the formation of PAN–clay nanocomposite materials (PCNs) in which some PAN chains are

Figure 3. TGA thermograms (N_2 atmosphere, scan rate of $10\text{ }^\circ\text{C/min}$) of PAN, silylated Cloisite 20A and PAN-grafted Cloisite 20A.

grafted onto the montmorillonite surface. A schematic representation for grafted clay particle is shown in figure 2. Therefore, a wide range of grafted organoclay materials with desired polarities can be prepared by utilizing this approach with vinyl monomers of different polarities.

The amount of grafted polymer can be estimated by TGA measurement (Wheals 1975; Waddell *et al* 1981; Zhang *et al* 2006; Mansoori *et al* 2011). Figure 3 shows TGA curves of silylated Cloisite 20A, PAN-grafted Cloisite 20A and pristine PAN. After prolonged Soxhlet extraction of the PAN-grafted Cloisite 20A it was found to give a significant weight loss

Figure 4. Wide-angle powder X-ray diffraction patterns of (a) Cloisite 20A, (b) silylated Cloisite 20A and (c) PAN-grafted Cloisite 20A.

Figure 5. Wide-angle powder X-ray diffraction patterns of Cloisite 20A and PAN–clay nanocomposites.

Table 1. Diffraction peaks and basal spacing of Cloisite 20A, silylated Cloisite 20A, PAN-grafted Cloisite 20A and nanocomposites.

Product	Diffraction peak and basal spacing	
	Typical diffraction peak (°)	Basal spacing (nm)
Cloisite 20A	3.42	2.6
Silylated Cloisite 20A	3.70	2.4
PAN-grafted Cloisite 20A	5.14	1.7
^a PCN 0.5%	–	–
PCN 1%	–	–
PCN 3%	–	–
PCN 5%	–	–
PCN 7%	–	–

^aPolymer–clay nanocomposites.

after ashing at 600°C. This weight loss starts at 275°C that is higher than that of main step decomposition of pristine PAN ($T_D = 260^\circ\text{C}$). The difference between weight losses of silylated Cloisite 20A and PAN-grafted Cloisite 20A after ashing at 600°C ($\Delta m = 1.76\%$) can be attributed to weight of the grafted polymer. Therefore, amount of grafted polymer (17.6 mg/g of clay) can be calculated from (1).

$$\text{Grafted amount (mg/g)} = \frac{\Delta m}{100} \times 1000. \quad (1)$$

Wide-angle powder X-ray diffraction patterns of Cloisite 20A, silylated Cloisite 20A and PAN grafted Cloisite 20A are shown in figures 4a–c. A strong peak is observed at $2\theta = 3.42^\circ$, corresponding to the (001) plane for Cloisite 20A, indicating that the interlayer d -spacing of the organo-clay is ~ 2.6 nm. This value is comparable to the value (2.4 nm) reported by the supplier (Southern Clay Products, Inc.). The interlayer d -spacing is slightly decreased to 2.4 nm ($2\theta = 3.70^\circ$) after silylation that is in agreement with results reported earlier (Zhang *et al* 2006). This can attributed to partial exchange of ammonium groups by H^+ ions. The interlayer d -spacing reaches 1.7 nm ($2\theta = 5.14^\circ$) after grafting

and complete drying. The diffraction peaks and calculated basal spacings of the products are summarized in table 1.

The wide-angle powder X-ray diffraction patterns of Cloisite 20A and a series of PAN–clay nanocomposite materials are shown in figure 5 and summarized in table 1. No peak is observed at a clay loading of 0.5–7 wt% (PCN 0.5–7%) at $2\theta = 2\text{--}10^\circ$, as opposed to the peak at $2\theta = 3.42^\circ$ (d -spacing = 2.6 nm) for Cloisite 20A. This observation indicates less agglomeration and potentially exfoliated nanocomposites at a clay loading of 0.5–7 wt%.

Generally, the absence of diffracting peak would indicate an exfoliated structure or full disordering. In the case of intercalated nanocomposites, polymer chains are inserted into the clay galleries; however, the clay platelets are still organized into an ordered structure despite swelling of the galleries. The absence of diffraction peaks in WXR patterns should not be used as sole evidence for the formation of an exfoliated structure because factors such as clay dilution and peak broadening can yield false results that show that exfoliation has occurred. Other factors, such as the preferred orientation effect, can lead to false conclusions that exfoliation has not occurred. In this study, insertion of polymer chains into

Figure 6. TEM micrographs of PCN 1% showing formation of exfoliated structures.

Table 2. Thermal and mechanical analysis (DMTA and TGA) results.

Polymer	T_g (°C) ^a	10% Weight		T_{D1} (°C) ^c	T_{D2} (°C) ^d	Char yield ^e	Storage modulus (GPa)				
		loss (°C) ^b					−20 °C	0 °C	40 °C	70 °C	85 °C
Pure PAN	87.6	301.8		259.1	353.3	51.7	7.27	7.09	6.60	5.85	5.06
PCN 0.5% ^f	101.6	333.4		268.1	358.8	63.4	2.79	2.78	2.72	2.59	2.47
PCN 1%	94.1	286.8		269.0	361.9	47.2	2.70	2.65	2.56	2.50	2.36
PCN 3%	90.2	291.1		269.4	363.2	53.3	5.73	5.63	5.33	4.87	4.38
PCN 5%	89.9	292.4		272.3	364.4	52.5	4.50	4.42	4.17	3.88	3.64
PCN 7%	89.7	289.8		275.0	365.3	53.6	6.09	5.99	5.63	5.18	4.46

^aObtained from DMTA measurements based on $\tan \delta$ versus temperature curves; ^bobtained from TGA measurements; ^cinitiation temperature of first stage decomposition; ^dinitiation temperature of second stage decomposition; ^eat 600 °C; ^f measurement was repeated on sample prepared separately.

the clay galleries increased the clay spacing compared to the pristine Cloisite 20A. The formation of either intercalated or exfoliated nanocomposites can be confirmed by TEM. Figure 6 shows representative TEM micrographs of the PCN 1%. These micrographs reveal the formation of exfoliated structure. In this regard, TEM can provide useful information and conclusive evidence concerning the morphology, structure and spatial distribution of dispersed clay platelets in the polymer matrix (Tjong and Ruan 2008). In addition, TEM photographs could allow us to establish the silicate dispersion grade. Thus, in the image of PCN 1%, regions where silicate aggregates are found, indicated as “A”, as well as regions where some intercalated and exfoliated platelets are found, indicated as “I” and “E”, respectively are observed. The clay is homogeneously distributed in the matrix and the clay aggregates are not large.

The results of thermal and mechanical analyses by TGA and DMTA are summarized in table 2. The T_g value increases from 87.6°C for pure PAN to 101.6°C for PCN 0.5%. This observation is tentatively attributed to the interaction of polymer chains with the clay galleries that prevents the segmental motions of the polymer chains (Liu and Guo 2006). However, further addition of organoclay up to 7 wt% leads to a

decrease in T_g . This decrease might be due to the aggregation of organoclay particles that reduces the interfacial interaction between organoclay and PAN matrix (Ray and Okamoto 2003). Additionally, a large amount of intercalating reagents in the organophilic clay may act as a plasticizer or as a lubricant; the glass transition temperature is lower than that with a low amount of clay (Liqiang *et al* 2008). DMTA curves of PAN and nanocomposites with 0.5–7 wt% clay loadings are shown in figure 7.

Variation of storage modulus with temperature for PAN and its nanocomposites has been shown in figure 8. A considerable decrease in storage modulus is observed for PCN 0.5% and PCN 1% with respect to virgin polymer especially below glass transition temperature. This may be due to the difference in the polarity of the polymer matrix and the surfactant used in the modification of the organoclay. PAN is a quite polar polymer while in the Cloisite 20A the clay particles are lipophilized with a quaternary alkyl ammonium salt having long alkyl chain that is non-polar. This factor destroys the crystallinity of PAN matrix especially at low clay loadings. For PCN 1–7% the storage modulus is influenced by the amount of grafted clay and increases with increasing organoclay content.

Figure 7. DMTA curves of PAN and PAN–clay nanocomposite materials (PCNs).

Figure 8. Temperature dependence of storage modulus of PAN and PAN–clay nanocomposite materials (PCNs).

The dynamic properties of PAN and its nanocomposites at various temperatures are summarized in table 2. It is observed that in the PCN materials the drop in the storage moduli below glass transition temperature occurs slower than that for pure PAN. For example, storage moduli of pure PAN and PCN 0.5% change from 7.27 and 2.79 GPa at -20°C to 5.85 and 2.59 GPa at 70°C , respectively. This can be attributed to the fact that, for pure PAN, the polymer crystallinity can be destroyed only by heating near the glass transition temperature. While, as mentioned above, in the cases of PCN materials the crystalline structure of the polar polymer matrix was partly destroyed by PAN-grafted organoclay and cannot be further influenced by heating near glass transition temperature.

TGA curves of PAN and nanocomposites with 0.5–7 wt% clay loadings are shown in figure 9. Pure PAN and its nanocomposites are observed to degrade through two steps in N_2 atmosphere. In the first step, the cyclization of CN groups in a polyconjugated structure, happens at about $259\text{--}275^{\circ}\text{C}$, immediately followed by the aromatization step with loss of hydrogen molecules and the formation of a ladder aromatic

Figure 9. TGA thermograms (N_2 atmosphere, scan rate of $10^{\circ}\text{C}/\text{min}$) of PAN, PCN 1%, PCN 3%, PCN 5% and PCN 7%.

structure. In the second step, heating at temperatures above 350°C results in lateral condensation of ladder structures, with loss of hydrogen (Hay 1968; Grassie and Macguchan 1970; Beretta 2009). As seen from the data collected in table 2, temperature of 10% weight loss and char yield at 600°C are significantly increased in PCN 0.5% with respect to virgin polymer. Similar results were obtained for the sample prepared separately. This may be due to better miscibility and high interaction between the polymer and the clay for PCN 0.5%. The initiation temperatures for the first and second stages (T_{D1} and T_{D2}) are also increased with increasing clay loading for PCNs 0.5–7%. The improvement of thermal stability can be attributed to the barrier effect of organoclay. Cloisite 20A is a layered structure and small molecules generated during thermal decomposition process cannot permeate, and thus have to bypass Cloisite 20A layers (Santiago *et al* 2007).

4. Conclusions

PAN was chemically grafted onto Cloisite 20A after silylation of the edge silanol groups of the clay by vinyltrichlorosilane. To demonstrate successful grafting, the homopolymer formed during polymerization was separated from grafted Cloisite 20A by Soxhlet extraction. Chemical grafting of the polymer onto the Cloisite 20A surface was confirmed by FTIR spectroscopy. The interlayer d -spacing of the grafted organophilic clay was investigated by WXR. Polymer–clay nanocomposites with different clay contents were prepared by free radical copolymerization of vinyl-silylated Cloisite 20A and AN monomer in DMF. The interlayer d -spacing and surface changes in the prepared nanocomposite materials were studied by WXR and TEM. Exfoliated nanocomposites were obtained for PCN 1%. The thermal and mechanical properties of the nanocomposites were also studied by TGA and DMTA. Based on these measurements, it is observed that

the glass transition temperature (T_g) and thermal stability are improved in PCN 0-5% with respect to pristine polymer. This observation is tentatively attributed to the better miscibility and effective interaction between polymer and exfoliated organoclay at low clay loading.

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