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Qualitative Assessment on the Surfactant Traces from the Organically Modified Nanoclay Containing Polymer Nanocomposite

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Abstract. Traces of quaternary ammonium salt from dispersed nanoclay in PA6/6.6 polymer nanocomposite may have some potential toxicological effects that could pose a risk to human health. Modified nanocomposite system was produced by masterbatch melt extrusion process while water-assisted nanocomposite was prepared via direct melt extrusion process. Investigations were conducted by hyphenated thermogravimetric analysis coupled with Fourier transform infrared spectroscopy (TGA-FTIR). Small traces of surfactant alkyl ammonium ions in the nanocomposite can be found in the masterbatch and nanocomposite.

Key Words— Thermal degradation, Melt extrusion, Process temperature

INTRODUCTION

Polymer nanotechnology is now mature and has attracted both academic and industrial areas with interest on various industrial applications such as food packaging, automotive and aeronautical **[1, 2].** However, the use of polymer nanocomposites on food packaging remains a human health concern as mixture of surfactants (alkyl dimethyl benzyl ammonium chloride and didecyl dimethyl ammonium chloride) revealed some health impacts on mice by reducing their reproductive performance **[3].** Additionally, an organoclay (Cloisites93A) modified with methyl, dihydrogenated tallow ammonium surfactant induced cytotoxicity during the in-vitro study on HepG2 cells **[4].** As such, migration of surfactant (used to modify nanoclay) from the polymer nanocomposites into the foods during packaging could pose a risk to human health. It is then the aim of this study to investigate the remains of surfactant alkyl ammonium ions in the food packaging comprised of polymer nanocomposite material after multiple melt extrusion processes. Investigations were conducted by hyphenated thermogravimetric analyser coupled with Fourier transform infrared spectroscopy (TGA-FTIR).

EXPERIMENTAL

Materials

Pristine nanoclay was supplied by Ecca Holdings, South Africa. The nanoclay, Betsopa™OM (*BET*), is a South African natural bentonite modified with dimethyl dihydrogenated tallow quaternary ammonium surfactant *(2M2HT).*

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According to the supplier (Akzo Nobel), *2M2HT* consists of two methyl substituents and two hydrogenated tallow tails. *BET* has cation exchange capacity (CEC) of 65 meq/100g with 3.25nm *d-spacing* (d_{001}); and it was supplied by CSIR Pretoria, South Africa. Polyamide resins C40L used in this study is a copolymer of *(PA6/6.6)* from BASF, Europe.

Nanocomposite preparations

Modified polymer nanocomposite was prepared by producing a masterbatch using a melt extrusion process; followed by dilution with neat *PA6/6.6* to produce polymer nanocomposite containing 7 wt% silicates. The samples were designated as *Masterbatch* and *PAPNC-BET*, respectively. Another system of pristine nanoclay-based nanocomposite was prepared using water-assisted extrusion and it was denoted as *PAPNC-WA*. In both systems, pulverized *PA6/6.6* and nanoclay were premixed in the solid phase prior to the melt extrusion. In the case of modified nanocomposite system, all materials were dried overnight under vacuum at 60 ^{0}C before extrusion. Melt extrusion process was conducted in a TE-30 co-rotating twin screw extruder (Nanjing Only Extrusion Machinery Co. Ltd., China) at extrusion speed of 156 rpm and feed rate of 4.4 kg/h. The diameter of the screw (D) was 30 mm; and the length (L) to diameter ratio, L/D was 40:1. The diameter of the die was 3 mm and the temperature profile of 120| 180| 200 260| 260| 250| 245| 240 ^{0}C was used. Neat polymer was also extruded using the same processing conditions and used as a control. Extrudates were pelletized and then dried overnight under vacuum at 60 ^{0}C prior to characterisation.

Hyphenated thermogravimetric analysis coupled with Fourier transform infrared spectroscopy (TGA–FTIR)

Thermal degradation of the neat materials and nanocomposites were investigated using thermogravimetric analysis (TGA, PerkinElmer, Pyris 1) coupled with Fourier transform infrared spectroscopy (FTIR, PerkinElmer, FrontierNIR). The gas molecules evolved during TGA (programmed from 30 to 900 ^{0}C) were transferred to the FTIR cell via a TG−IR interface (TL 9000) at 10 ^{0}C /min in a nitrogen environment. To prevent condensation of decomposition products, transfer line and gas cell were kept at 250 ^{0}C. The sample masses were kept in a range of 17 to 18 mg.

RESULTS AND DISCUSSION

Prior to investigating the remains of surfactant alkyl ammonium salt in the modified nanocomposite system, it is important to understand the extent of thermal degradation of the constituents of the polymer nanocomposite. The temperature of 260 ^{0}C will be referred as processing temperature throughout the study. Part (a) and (b) of Fig.1 exhibit the thermal degradation behavior and the residual masses of the samples examined. A degradation peak below 100 ^{0}C is free water between montmorillonite crystalline structure and a peak around 150 ^{0}C is related to strongly bond water attached to the cationic head group within the ionic region of the lamellar surfactant salt structure **[5, 6].** Decomposition region between 100 to 300 ^{0}C is attributed to interlayer water residing between aluminosilicate layers. Region between 200 to 500 ^{0}C is attributed to the degradation of organic surfactant and the stage between 500 to 700 ^{0}C is dehydroxylation of the aluminosilicate **[5, 6].** As evident from the Fig. 1a, *Pristine nanoclay* exhibits a higher onset degradation temperature ($T_{0.05}$) at 456 ^{0}C; while the organic surfactant (*2M2HT*) exhibits a lower onset degradation temperature at 165 ^{0}C. Furthermore, *BET* and *PA6*/6.6 exhibit the onset degradation temperature at 269 ^{0}C and 400 ^{0}C, respectively. On the other hand, a *Masterbatch* and *PAPNC-BET* exhibit the onset degradation temperature at 361 ^{0}C and 385 ^{0}C, respectively; while the onset degradation temperature of *PAPNC-WA* is observed at 398 ^{0}C. The onset degradation temperature of *PAPNC-WA* is quite similar to that of neat PA. Reduction in the onset degradation temperature is indicating that *PA6/6.6* has degraded during processing of masterbatch. The degradation of *PA 6/6.6* was due to the peptide chain scission following attack by water that is released from the polymer and nanoclay itself **[7]**. Furthermore, the *Masterbatch* exhibits a lower onset degradation temperature, probably due to the effect of higher nanoclay loading and degradation of organic surfactant molecular chains.

Fig. 2b shows that the degradation of *2M2HT* occurred in three stages in a temperature range of 200 to 400 ^{0}C. The first peak at 220 ^{0}C and second peak at 246 ^{0}C are assigned to smaller and higher organic chains; while a third peak at 342 ^{0}C is assigned to carbonaceous residual organics **[8].** It can be observed that there is no degradation peak observed around 220 ^{0}C on *BET* that could be related with unbound surfactant chains; indicating that the *BET* was rigorously washed for excess ammonium ions **[5, 9].** Moreover, *BET* adopted a similar degradation pattern of pure *2M2HT* with first minor peak at 264 ^{0}C; second major peaks at 318 ^{0}C; while a third peak was at 429 ^{0}C, respectively. These peaks are not consistent with the degradation peaks of *2M2HT*, indicating the heat barrier effect of nanoclay platelets on the intercalated *2M2HT*; and that an interaction between quaternary ammonium ions and oxygen on the nancoclay surface had occurred**.** These peaks can be attributed to the degradation of eluted smaller and higher surfactant organic chains, respectively; while a third maximum degradation peak observed at 429 ^{0}C is related to thermal cracking of ionic organics mainly by decarboxylation from reaction of positive amino groups with pristine nanoclay surface **[10].** The degradation peak at 638 ^{0}C is assigned to dehydroxylation of the structural water from *pristine nanoclay*. On the other hand, *PA6/6.6* and the nanocomposites exhibit one degradation peak in a range of 370-550 ^{0}C. At processing temperature, approximately 29% degradation of *2M2HT* and 3% degradation of the intercalated *2M2HT* in *BET* indicates the hindering effect of the nanoclay platelets. Meanwhile, both the *PA6/6.6* and the nanocomposites are quite stable during melt extrusion. However, *PAPNC-WA* exhibits more volatile loss than modified nanocomposite systems, due to moisture and interlayer water released from unexchanged sodium cations. On average, it can be concluded that approximately 2wt% volatile loss has been released on both *PA6/6.6* and nanocomposites. These results indicate that the volatiles could not be removed during drying at 60 ^{0}C. Similarly, R. D Davis et.al reported PA6 degradation at 300 ^{0}C from injection moulded PA6/clay nanocomposite; regardless of drying at higher temperature of 180 ^{0}C. The author identified volatiles as water; and small fractions of acid and amine end-group. As a result, it is not clear as to how much of *2M2HT* has degraded from the polymer nanocomposites during processing. It is evident from the degradation peak at 429 ^{0}C that is not seen on the modified nanocomposite system probably due to low amount of *2M2HT* in the *BET* (35 wt%). Nevertheless, the residual masses recorded at 800 ^{0}C, indicate that *BET* was modified with 35 wt% of *2M2HT;* while the amount of nanoclay silicates contained in the *Masterbatch; PAPNC-BET* and *PAPNC-WA* was 23 wt%, 7 wt% and 5 wt%, respectively.

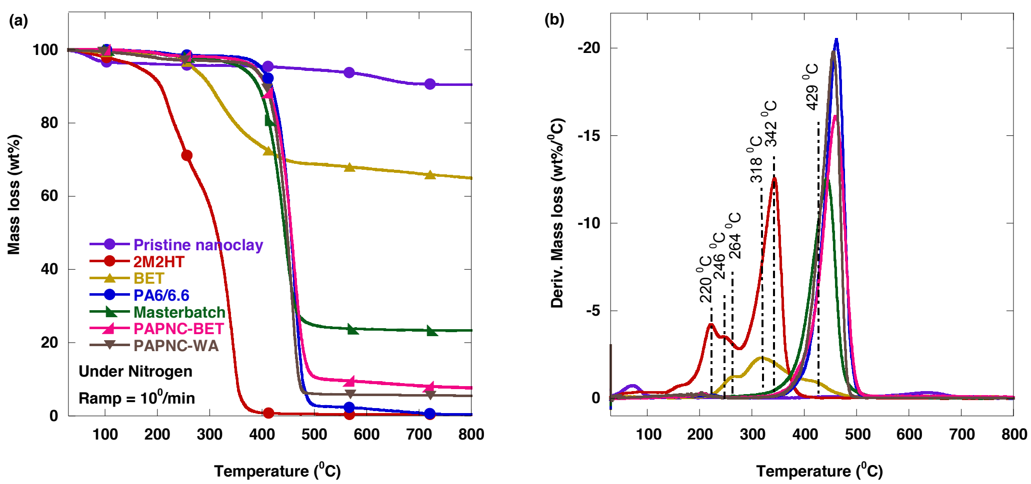

FIGURE 1. (a) TG and (b) DTG of the neat materials and polymer nanocomposites.

The evolved gas molecules from TGA are further analyzed by FTIR to trace the fingerprints of *2M2HT* in the modified nanocomposite. FTIR spectra are collected at 260 ^{0}C and 342 ^{0}C (Fig. 2 and 3, respectively). The temperature of 342 ^{0}C is chosen as it is a maximum degradation temperature of *2M2HT* and can be used to confirm presence of the remains of *2M2HT* in the modified nanocomposite after multiple melt processing. Absorption bands at 2936 cm^{-1}, 2869 cm^{-1} and 1470 cm^{-1} are attributed to methyl and methylene groups of both *2M2HT* and *PA6/6.6*, respectively **[5, 6 & 11]**. Additional bands at 1634 cm^{-1} and 1535 cm^{-1} are attributed to the carbonyl groups of *PA6/6.6*. Absorption bands at 2936 cm^{-1}, 2869 cm^{-1} and 1470 cm^{-1} are also seen on *BET* and are attributed to methyl and methylene groups of *2M2HT*. However, these peaks are absent in the *Masterbatch and PAPNC-BET* suggesting that smaller organic chains have degraded during the *Masterbatch* preparation; TGA results also support this observation. Furthermore, an additional peak at 1388 cm^{-1} can be related to CH_3 C-H asymmetric bending in N^+-CH_3

of *2M2HT*. These results indicate that smaller chains of alkyl ammonium organics degraded into a mixture of alkanes & alkenes; and amines during processing **[5, 6 & 11]**.

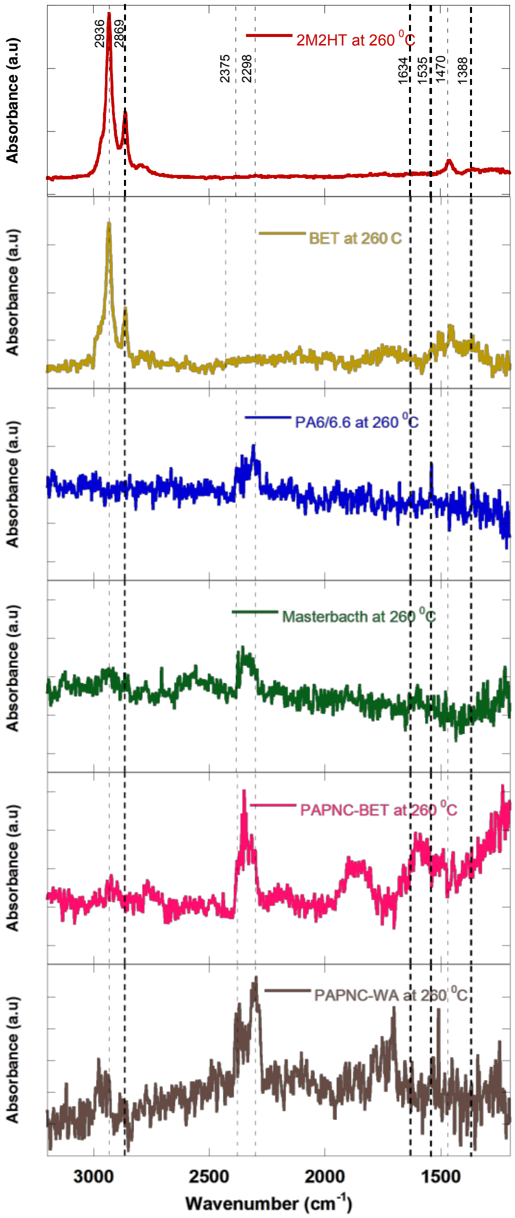

FIGURE 2. FTIR spectra at 260 ^{0}C.

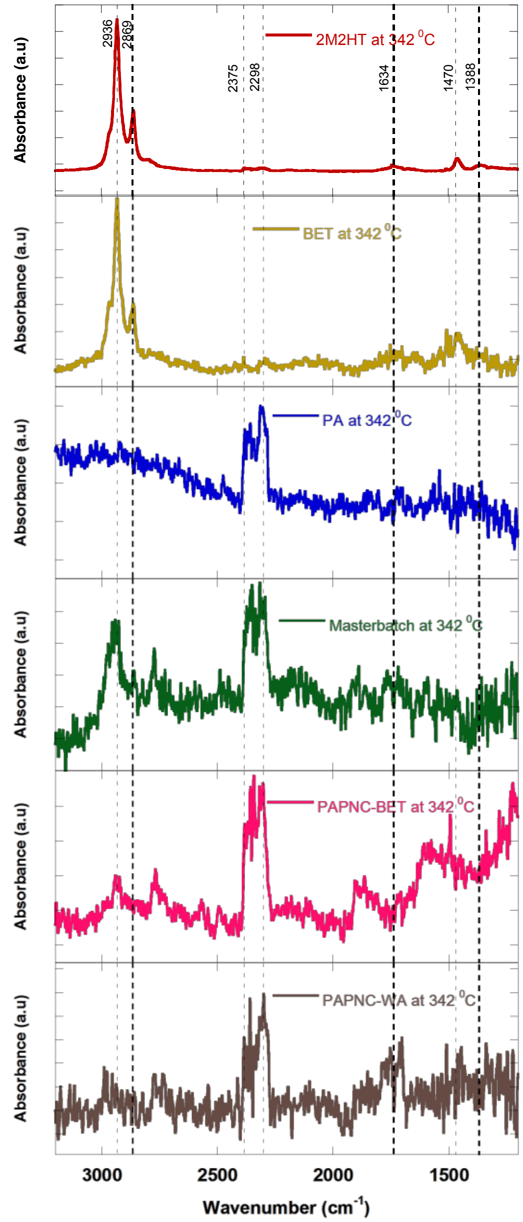

FIGURE 3. FTIR spectra at 342 ^{0}C.

On the other hand, small amount of evolved CO_2 gas is detected on *PA6/6.6* at 2375 cm^{-1} and 2298 cm^{-1}. A significant increase of CO_2 gas releases from *PAPNC-WA* and *PAPNC-BET* when compared with the *Masterbatch* as they contain more *PA6/6.6* matrix than the *Masterbatch*. These results support the TGA mass loss seen on nanocomposites at processing temperature. Similarly, a considerable amount of evolving CO_2 gas is observed by M. Herrera et.al on thermal degradation study of PA66, under nitrogen **[12]**. Fig. 3 permits for the confirmation of the remains of alkyl ammonium ions in the *PAPNC-BET* at 342 ^{0}C. A sudden increase in absorption bands at 2936 cm^{-1}, 2869 cm^{-1} and 1470 cm^{-1} observed in *2M2HT* indicates the maximum degradation of alkyl surfactant ions as seen on Fig. 1(b). However, these peaks could not be clearly distinguished in the *Masterbatch and PAPNC-BET*; due to lower amount of *2M2HT* (35 wt%). Furthermore, these peaks are absent in the *PAPNC-WA* as it contains no surfactant. Moreover, additional peaks at 2375 cm^{-1}, 2298 cm^{-1}, 1739 cm^{-1} and 1388 cm^{-1} indicate the decomposition products from *2M2HT* and are identified as CO_2 gas; aldehydes and carboxylic acids and amines, respectively. These results are in agreement with a well presented thermal degradation mechanism of *2M2HT* via Hoffmann elimination reaction by R. Scaffaro et.al **[13]**. On the other hand, *PA6/6.6* was gradually degrading while releasing more CO_2 gas. It can be observed that similar decomposition products from *2M2HT* are detected on *PA6/6.6*. As such, these results complicate the interpretation of the analysis and it was uncertain to distinguish the decomposition products of *2M2HT* in the *PAPNC-BET*. As a result, the absorption bands at 2936 cm^{-1} and 2869 cm^{-1} on *BET* can be used as trace markers for the remains of alkyl ammonium ions in the *PAPNC-BET* as they are absent in the *PA6/6.6* and *PAPNC-WA* at 342 ^{0}C. As such, presence of higher intensity of vibration band at 2936 cm^{-1} in the *Masterbatch* than *PAPNC-BET* at higher temperature than the processing temperature can be an indication of the remains of alkyl ammonium ions in the *PAPNC-BET*.

CONCLUSION

Investigations into the remains of alkyl ammonium ions in the *PAPNC-BET* after multiple melt extrusion have been conducted by TGA-FTIR. According to TGA-FTIR, small amount of surfactant organic molecules can be detected in the *Masterbatch* and *PAPNC-BET*. Presence of surfactant can have potential health concern especially when the polymer nanocomposite is intended for food packaging applications. Research is going on the possibility of migration of the traces of surfactant from the nanocomposite based packaging into the food materials.

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