

Characterization of Processing Effects in HIPS-CNF Composites Using Thermogravimetric Analysis

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To completely establish the processing–structure–property relationships of polymer composites such as Carbon Nanofibers (CNFs) in high-impact polystyrene, it is necessary to understand the effects of different processes and processing conditions on the properties of the composites. In this work, using thermogravimetric analysis, the effects of solvent processing and twin-screw extrusion on the weight loss rates and the corresponding temperatures were studied. While there were only marginal effects of the CNF concentration, the type of processing significantly affected the thermo-oxidative behavior. Extrusion resulted in composites that had better thermal stability compared to the solvent processed ones. Furthermore, higher shear rates in extrusion also led to composites with higher thermal stability. This has important implications in choosing the appropriate process and processing conditions for producing polymer-CNF composites. It was also demonstrated that thermogravimetric analysis can provide a means of characterizing the degree of dispersion resulting from the processing of the composites that complements conventional microscopy techniques. POLYM. ENG. SCI., 48:1120–1125, 2008. © 2008 Society of Plastics Engineers

INTRODUCTION

Two specific nanoscale fillers, carbon nanotubes (CNTs) and carbon nanofibers (CNFs), have been identified by materials scientists as having the greatest potential to revolutionize the technological landscape of the century ahead. There is now a great deal of research on creating polymer composites using CNTs and CNFs. While the diameter of CNTs ranges from a few nanometers to a few tens of nanometers, the diameter of CNFs is on the order of hundreds of nanometers. Furthermore, while CNTs contain one or more concentric graphene cylinders, CNFs contain

graphene layers arranged as stacked cones, cups or plates instead of perfect cylinders. In spite of their differences, because of their size scale and structure, it is necessary to understand the effects different processes will have on the structure and properties of their composites with polymer. Over the past several years, researchers have adopted a wide variety of methods to produce composites of polymers with CNTs or CNFs and addressed critical issues such as deagglomeration of filler bundles and ropes, dispersion and alignment of the individual filler particles, and interfacial adhesion between the polymer matrix and the filler that directly affect the composite properties [1–3].

Traditionally, researchers have used thermogravimetric analysis (TGA) not only to study the composition of the composite systems [4, 5], but also to identify the purity of nanoscale fillers, and the thermal decomposition behavior of the composite [6]. Chiang et al. [7] compared the thermal decomposition characteristics of single walled carbon nanotubes (SWCNT) produced by different processes and presented them as a measure of detecting the purity of the SWCNTs. Mahfuz et al. [8] reported that the thermal decomposition temperature of composites of Nylon with very low-mass fraction of multiwalled carbon nanotubes (MWCNTs) is significantly higher than the neat Nylon. Furthermore, they also reported similar behavior in various other nanoparticle reinforced polymers [9, 10]. Xu et al. [11] conducted a thorough work on the thermo-oxidative behavior of polystyrene-CNF composites and concluded that temperature at peak weight loss rate (TPWLR) increases more significantly at lower concentrations than higher concentrations of CNFs when compared with the neat polystyrene. They also reported that the CNFs in the nanocomposites decompose at a lower temperature compared to the pristine CNFs. Chatterjee and Deopura [12] studied the thermal and thermo-oxidative behavior of polypropylene-CNF composites in nitrogen and air, respectively. They reported that the degree of enhancement in thermal stability of the composites compared to the neat polypropylene (PP) is more prominent in the presence of air, possibly due to the formation of a char layer that acts as a physical barrier between the

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uncombusted polymer and combustion zone. Similar observations about the increase in the thermal stability of the PP-CNF [13, 14] and polyol-CNF composites were reported in literature and they were attributed to the restriction in the mobility of the macromolecules imposed by the CNFs. In contrast, a few reports on epoxy-CNF composites in literature indicate either no influence [15] on or a slight decrease [16] in the thermal stability with increasing CNF concentration.

Although there has been significant work in identifying the thermal behavior of the polymer composites as a function of the filler concentration, to the best of our knowledge there is no literature identifying the effect of the type of process or processing conditions on the thermo-oxidative behavior of the polymer composites. In this article, using TGA, we compare the composites prepared via solvent and twin-screw extrusion (TSE) processing for their weight loss rate (WLR) and TPWLR. Furthermore, we also present the effect of shear rate in extrusion on the TPWLR of the composites.

EXPERIMENTAL

Materials and Processing

High-impact polystyrene (HIPS, molecular weight $\sim 150,000$; polydispersity index ~ 2.73 ; density ~ 1.04 g/cc), a copolymer of styrene and butadiene, obtained from Nova Chemicals (Calgary, Alberta) was used in this work

because it is well-suited for both solvent processing and TSE. The PR-19 grade CNFs (diameter ~ 100 – 200 nm, length ~ 10 – 30 μm , density ~ 1.95 g/cc) obtained from Applied Sciences (Cedarville, Ohio) were used because they were more affordable than the SWCNTs and MWCNTs. The solvent, dimethylformamide (DMF), was obtained from Fisher Scientific to prepare the composites by a solvent extraction method.

To prepare the HIPS-CNF composites by solvent processing, a suspension of 5 wt% CNFs in DMF was sonicated in an ultrasonic bath (VWR 75D) with occasional stirring. The suspension of CNFs was added to a HIPS solution in the same solvent. The mixture was stirred and sonicated in a closed beaker alternately every 30 min for at least 6 h to obtain a stable suspension. While few agglomerates were visible before stirring and sonication, no visible agglomerates could be found at the end of the stirring and sonication. The composite precipitate was obtained via solvent extraction by using water as the non-solvent. The precipitate was dried for 12–24 h in a vacuum oven at 90°C to remove residual solvent.

To prepare HIPS-CNF composites by TSE, the HIPS pellets and the as-received CNFs were fed into a Werner and Pfleiderer twin-screw extruder (28 mm screw diameter, co-rotating, intermeshing, 30:1 L:D) at a screw speed of 200 rpm. The operating temperatures were 210°C for all the barrel zones and 165°C for the die zone. The feed rate of HIPS was 2 lb/h and the feed rate of CNFs was varied to obtain the desired composition. Figure 1 shows

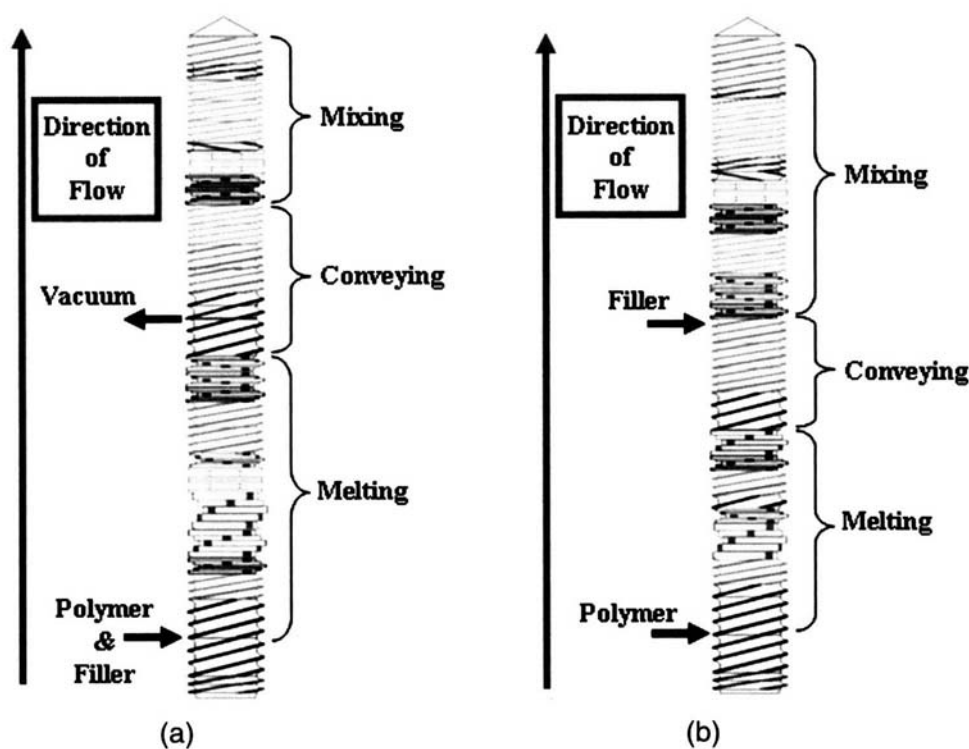


FIG. 1. (a) High shear screw configuration, and (b) low shear screw configuration. Porosity was controlled in the high shear screw configuration by devolatilization at different vacuum pressures.

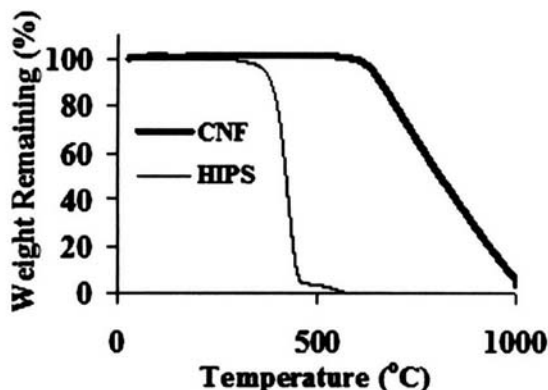


FIG. 2. The weight percent loss profiles of neat CNFs, and neat HIPS subjected to a thermal ramp up to 1000°C.

the two different screw configurations, higher shear and lower shear, used in this work. While the polymer and filler were fed together in the higher shear screw configuration, the filler was fed downstream to a flow of molten polymer in the lower shear screw configuration. Furthermore, the composites extruded using the higher shear screw configuration were processed at two different levels of porosity, referred to as low and high, by devolatilization at vacuum pressures of 30 and 5 torr, respectively. The volume fraction of low- and high-porosity was estimated to be 10 and 17.3%, respectively, from the density of the composite relative to the theoretical maximum density obtained using the density of the filler, the density of the polymer, and the weight fraction of the filler.

HIPS-CNF composites were produced via solvent processing and TSE at 1, 3, 5, and 7 wt% of CNFs to investigate the influence of processing on the thermo-oxidative

behavior. In addition, composites with 10 wt% of CNFs were produced via TSE at varying screw speeds, ranging from 30 to 200 rpm, in order to investigate the influence of screw speed on the thermo-oxidative behavior.

TGA Procedure

A Cahn TG 2131 thermogravimetric analyzer was used to determine the composition and study the thermo-oxidative behavior (i.e., thermal degradation in the presence of oxygen) of the HIPS-CNF composites. In all the TGA tests conducted, the initial weight of the sample was consistently maintained to be around 100 mg. Figure 2 shows the thermogravimetric response of the neat materials i.e., neat HIPS and neat CNFs, in the temperature range of 25–1000°C at a temperature ramp of 10°C/min in an atmosphere of air flowing through the reactor tube. Similar to earlier works [11, 12], the temperature ramp is chosen such that the weight losses corresponding to HIPS and CNFs can be clearly distinguished. It is evident from Fig. 2 that the HIPS shows two distinctly different weight losses and decomposes completely by 550°C. While the former weight loss corresponds to the styrene-rich phase, the latter corresponds to the butadiene-rich phase. The two-stage combustion of HIPS in an air atmosphere is in agreement with an earlier work by Castaldi and Kwon [5]. The neat CNFs start to decompose around 600°C and are nearly completely consumed by 1000°C. Consequently, the TGA of the HIPS-CNF composites was conducted in an air atmosphere using the following temperature profile—ramp at 10°C/min up to 600°C and hold isothermal for 30 min at 600°C. Figure 3 shows the representative weight percent and WLR profiles obtained when

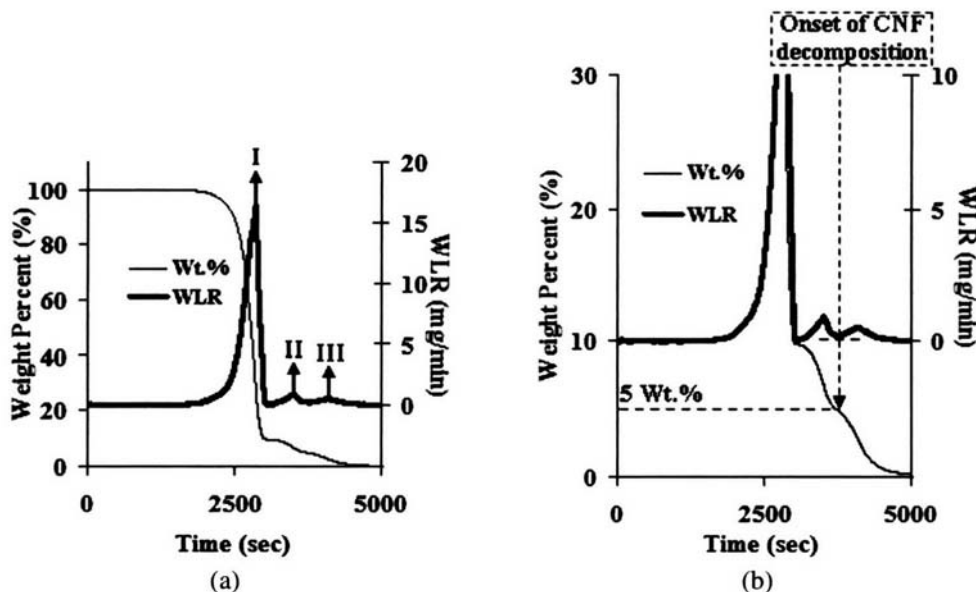


FIG. 3. (a) Representative wt% and WLR profiles for HIPS-CNF composites. The peaks I, II, and III correspond to the styrene-rich phase, the butadiene-rich phase, and CNFs, respectively. (b) Zoomed in view more clearly indicating the presence of a third peak and the determination of CNF composition.

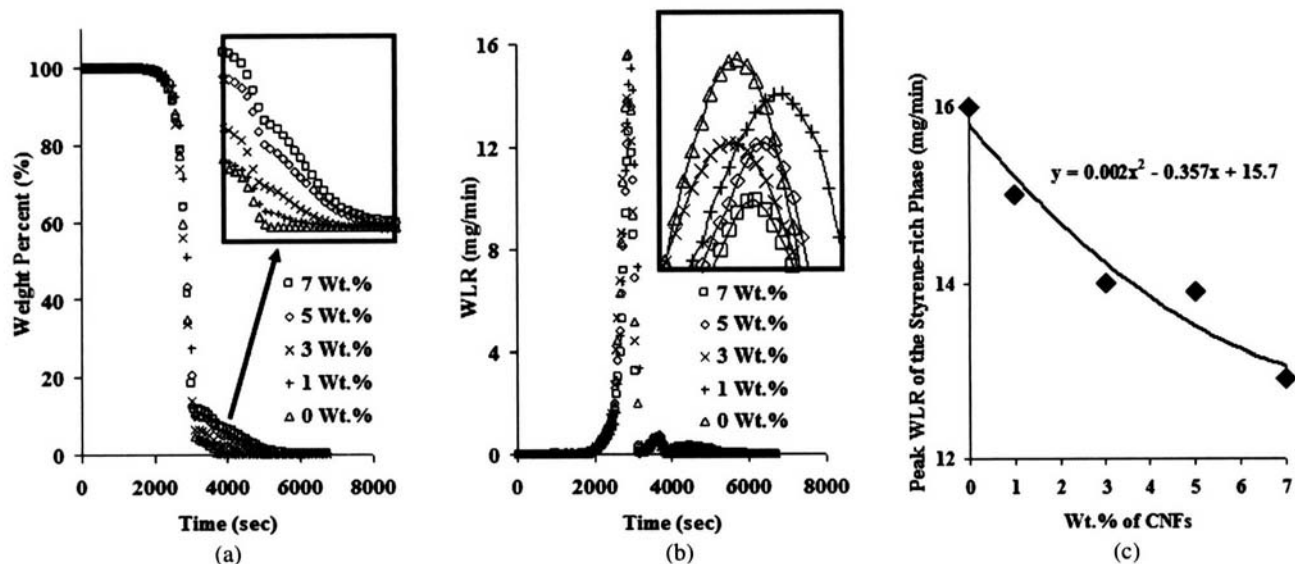


FIG. 4. (a) Weight percent loss profiles of HIPS-CNF composites at various CNF concentrations. The inset more clearly shows the weight percent loss of CNFs. (b) WLR profile of the HIPS-CNF composites at various CNF concentrations. The inset more clearly shows the peak WLR of the styrene-rich phase. (c) The decreasing magnitude of peak WLR of the styrene-rich phase with increasing CNF concentration.

the HIPS-CNF composites were studied using the TGA procedure described earlier. The two distinct weight losses corresponding to HIPS and the third weight loss corresponding to the CNFs are evident. The three corresponding peaks in weight loss rate are also distinct. The composition of CNFs in the composite was determined from the weight percent remaining at the time corresponding to the point of inflection between the second and third peaks of the WLR curve (i.e., when the second derivative of weight percent is zero). From Fig. 3, it is evident that the composite contains 5 wt% of CNFs. This is a rigorous and consistent technique that can be used to characterize materials of unknown composition such as those produced via combinatorial approaches [17].

RESULTS

Influence of CNF Concentration

Figure 4a and b show the weight percent and WLR profiles, respectively, of the low-porosity HIPS-CNF composites extruded using the high shear screw configuration, at various CNF concentrations. The peak WLR of the styrene-rich phase as a function of the CNF concentration can be seen in Fig. 4c. In contrast to the results reported in [11], this work indicates that there is no significant effect of CNF concentration on any of the three TPWLR of the composites processed with either technique. However, the magnitude of the peak WLR corresponding to the styrene-rich phase was found to quadratically decrease with CNF concentration. This is consistent with the quadratic reduction in the weight loss rate that is predicted by simple combustion model [18] for an isotropic solid struc-

ture, such as a sphere or a cube, as its size is reduced (which is analogous to a reduction in the volume fraction of the polymer). Thus, the reduction of the peak WLR of the composite is consistent with increasingly replacing the weight of HIPS with CNFs. The quadratic fit indicates that peak WLR decreases from 15.7 mg/min for neat HIPS to 0 mg/min for neat CNFs.

Influence of Processing

To understand the effect of processing on the thermo-oxidative behavior of the composites, the TPWLR corresponding to the styrene-rich phase, which is an indication of the thermal stability of the material, was compared for the solvent processed and extruded composites of low- and high-porosity. Since there was no significant effect of the concentration of CNFs on the TPWLR, the average of all the TPWLR corresponding to the styrene-rich phase at the concentrations studied was assumed to be a representation of the processing effects. Figure 5 shows the average TPWLR of neat HIPS and the HIPS-CNF composites corresponding to the styrene-rich phase as a function of the processing technique. It is evident that the solvent processed composites exhibit the lowest TPWLR, while the low porosity extruded composites exhibit the highest TPWLR. The neat HIPS results tend to indicate that the solvents contaminate the HIPS, thereby assisting in premature thermal decomposition. This would make TSE a relatively more desirable process for obtaining composites with better thermal stability. In addition, the decrease in TPWLR of HIPS-CNF composites in comparison to neat HIPS indicates that the presence of CNFs, which are thermally more conductive, tends to assist quicker thermal

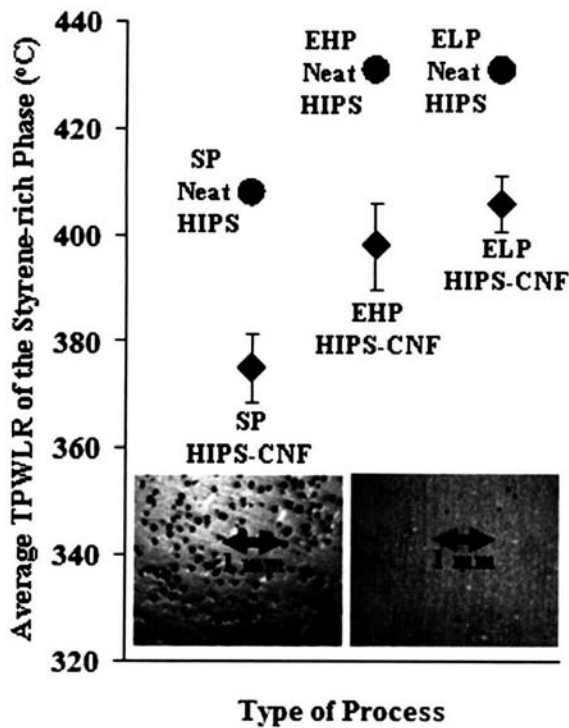


FIG. 5. Average TPWLR of the styrene-rich phase of the HIPS-CNF composites processed via different techniques. SP - solvent processed; EHP - extruded high porosity; ELP - extruded low porosity. The inset shows optical micrographs of surface of the extruded high and low porosity composites.

decomposition by improving the rates of heat transfer. Within the TSE process, the removal of porosity through the use of a vacuum pump tends to marginally improve the thermal stability.

Further insight into the influence of TSE processing conditions on the thermo-oxidative behavior was obtained by studying the TPWLR of the styrene-rich phase as a function of the extruder screw speed, which corresponds to the magnitude of shear rate (see Fig. 6a) in composites with 10 wt% of CNFs. To identify the qualitative trend clearly, the TPWLR of the styrene-rich phase is normalized to vary between 0 and 1. It indicates an approximately linear increase in TPWLR with screw speed. An increase in the agglomerate size at a screw speed of 30 rpm ($\sim 75 \mu\text{m}$) when compared with 200 rpm ($\sim 30 \mu\text{m}$) due to lower shear rates was observed as shown in Fig. 6b and c. Thus, it indicates that increasing the surface area of the agglomerated and dispersed CNFs in the polymer possibly inhibits the initiation of thermal decomposition. This provides additional evidence that the use of solvents is affecting the thermal decomposition of HIPS in a deleterious manner (as shown in Fig. 5) since the dispersion of the CNFs, which is better in solvent-processed PS-CNF composites without agglomerates, should be improving the thermal stability, consistent with prior work [11].

To gain further insight into the effects of the solvent and extrusion processing on the thermal decomposition of the CNFs, the normalized weight loss of CNFs in the

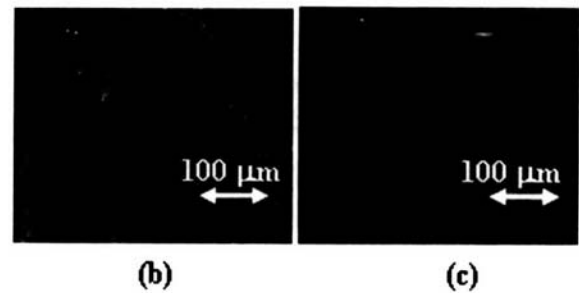
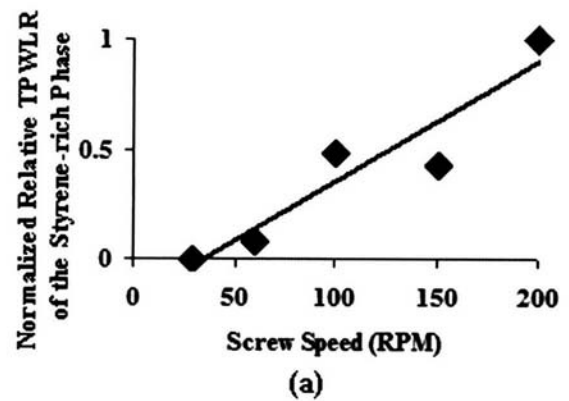


FIG. 6. (a) Normalized relative TPWLR of the styrene-rich phase as a function of the extrusion screw speed. Scanning electron micrographs of the HIPS-CNF composites processed at screw speeds of (b) 30 rpm, and (c) 200 rpm.

composites (i.e., the normalized weight loss after the time corresponding to the point of inflection between the second and third peaks of the WLR curve) was studied as a function of time and compared with unmixed materials (i.e., unprocessed HIPS and CNF). Figure 7 shows that the CNFs in solvent processed composites decompose at a substantially faster rate than the TSE processed ones. It can also be seen that the CNFs in both processes exhibit

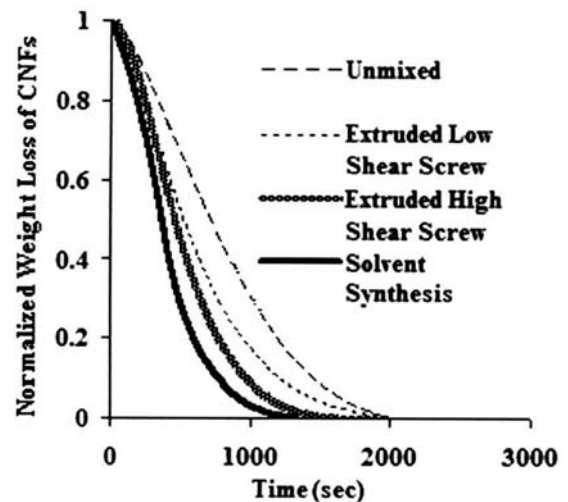


FIG. 7. Normalized weight loss of CNFs as a function of time for the HIPS-CNF composites. Note that the rate of weight loss of CNFs increases with increasing levels of shear mixing.

a faster decomposition rate relative to the unmixed material. Increasing the degree of shear in the TSE process i.e., changing from a low shear to a high shear screw configuration, slightly increases the rate of thermal decomposition. Given that the solvent processing procedure used in this work results in randomly dispersed polymer nanocomposites [19], the thermo-oxidative behavior of the TSE processed material tends to indicate a microstructure in which the CNFs are better dispersed than the unmixed materials, but not dispersed as well as the solvent processed composites. Agglomerations in the extruded composites are clearly evident in the micrographs seen in Fig. 6. Thus, the combination of Figs. 6 and 7 indicate that the TGA measurements can provide insight into the degree of dispersion resulting from the processing of the composites in a manner that is complimentary to conventional microscopy techniques.

CONCLUSIONS

The thermo-oxidative behavior of HIPS-CNF composites produced by solvent processing and TSE has been characterized and compared for the first time. Results indicate that the use of solvents results in lower thermal stability of neat HIPS and the HIPS-CNF composites when compared to TSE. It was also observed that the presence of porosity in the extruded composites has a marginal effect on the thermal stability of the HIPS-CNF composites relative to solvent processing.

Further insight into the effects of TSE processing conditions on the thermo-oxidative behavior of the HIPS-CNF composites was obtained by investigating the TPWLR as a function of extruder screw speed. Using a normalized relative TPWLR, it was observed that increasing the screw speed from 30 to 200 rpm resulted in an approximately linear increase in the thermal stability of the composites. The increased surface area possibly provides additional thermal stability to the HIPS-CNF composites, but the use of solvents appears to offset the benefits in a deleterious manner.

Finally, insight into the effects of solvent processing and extrusion on the thermal decomposition of the CNFs was obtained by studying the normalized weight loss of the CNFs in the composites as a function of time in comparison to the unmixed materials. The use of solvents creates a randomly dispersed microstructure that exhibits a higher thermal decomposition rate in the HIPS-CNF composites than when the materials are unmixed. In contrast, extruded HIPS-CNF composites had decomposition rates that were intermediate between the solvent processed composites and the unmixed materials. The intermediate thermal decomposition rate is attributed to the presence of

agglomerates, and was increased by reducing the agglomerate size via increased degree of shear. Thus, TGA has been shown to provide a means of characterizing the degree of dispersion in HIPS-CNF composites in a manner that is complementary to conventional microscopy techniques.

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