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A comparative study of polyethylene oxide/nanoclay composite preparation via supercritical carbon dioxide and melt processing

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Summary

The efficacy of supercritical carbon dioxide ($ScCO_2$) treatment compared with conventional melt processing methods in preparing nanoclay composites from poly(ethylene oxide) (PEO) of varying molecular weight (400-10,000) and a fluorinated ethoxide (EO) was studied. At low polymer loadings (~ 20 wt% PEO), the results obtained using either method were broadly consistent for each molecular weight of PEO studied, although $ScCO_2$ processing yielded more homogenous samples. The $ScCO_2$ technique was found to be most effective when used with PEO of higher molecular weight (10,000) or fluorinated EO, which is otherwise difficult to process using conventional techniques.

1. Introduction

Polymer/nanoclay composites are currently enjoying a renaissance in interest as they promise superior material properties over conventional polymer composites at low filler content, typically < 5wt%, such that the physical properties of the polymer matrix are not lost [1]. However, widespread adoption of nanoclay fillers has been hampered by difficulties in rendering these hydrophilic clays compatible with non-polar polymers, and in the processing of polymer/nanoclay composites.

Preparation of poly(ethylene oxide)/nanoclay composites in solution has been widely reported since interest in these systems first emerged during the 1950s, as the PEO/nanoclay system serves as a model for polymer composites. To prepare the composite in solution, typically, a slurry of nanoclay in a large excess of water is prepared, then the polymer is added and the whole stirred with heating for several hours until the polymer enters the interlamellar galleries of the swollen nanoclay. The composite is recovered by filtration followed by successive washings with water and organic solvent. Except at laboratory scale, this process is impractical on account of the large volumes of water and solvent required and the low yield of composite obtained. As an alternative, PEO/nanoclay composites have been prepared by melt intercalation, although it is difficult to obtain homogenous samples when prepared on a small scale [2-5].

The present work aims to compare the efficacy of supercritical carbon dioxide ($ScCO_2$) treatment with conventional melt processing methods to prepare nanoclay composites from PEO of varying molecular weight and a fluorinated ethoxide (EO). Zhao and Samulski reported the preparation of polymer/nanoclay composites with PEO of molecular weight 10,000 using $ScCO_2$ processing [6]. Their study compared two methods of sample preparation in which the PEO was intercalated into montmorillonite clay via either a small scale (2.5 ml chamber) $ScCO_2$ process or solution modification using water or alcohol as solvent. Rather than acting as solvent for the polymer, the mechanism proposed is that $ScCO_2$ plasticizes the polymer, facilitating its melt-like intercalation into the nanoclay's layered structure.

Early studies [7] demonstrated that the mechanism of PEO adsorption onto montmorillonite in solution is that swelling of the nanoclay occurs first, followed by intercalation and coiling of the polymer chain. Once a bilayer of polymer is present in the gallery (above 17 wt% PEO), the polymer adopts a helical structure. This structure remains unchanged until the PEO loading exceeds 30 wt%. Hence, within the range 17-30 wt%, the exact concentration of PEO present is not expected to alter the configuration of the polymer chain within the clay gallery.

2. Experimental

Bentone MA (cation content 100meq/100g) was supplied by Elementis Specialities, Highstown, New Jersey, USA. Poly(ethylene oxide) (PEO) of average molecular weight 400, 2000 and 10,000 were purchased from Aldrich; fluorinated ethoxide (EO) (Zonyl FSO 100, mol. wt. 164-1423) was obtained from DuPont. All other chemicals used were of reagent grade; all clays and chemicals were used as received.

2.1 Sample Preparation

To prepare samples for melt or $ScCO_2$ processing, 1.00g PEO and 4.00g nanoclay were ground together in a mortar and pestle. In the case of samples prepared using fluorinated EO, 1.00g liquid was warmed to 40ºC, then 4.00g nanoclay was added in portions with stirring to disperse it in the surfactant. Care was required in this step as the EO tended to adsorb quickly onto the clay, making thorough mixing difficult to achieve. For $ScCO_2$ processing, the clay/PEO mixture was transferred to the $ScCO_2$ chamber, then CO_2 gas was introduced via an ISEO syringe pump until the chamber was pressurised to 2800 psi. The chamber was heated to 60ºC via electric heating bands and the sample stirred constantly via a stirring plate and magnetic follower. Each sample remained in the chamber under these conditions for 24 hours. Samples prepared for melt processing were pressed into pellets and annealed in an oven at 70ºC for 6 hours according to the method described by Vaia *et al* [2]. After cooling to room temperature, the sample was ground with a mortar and pestle to pass a 180-micron sieve.

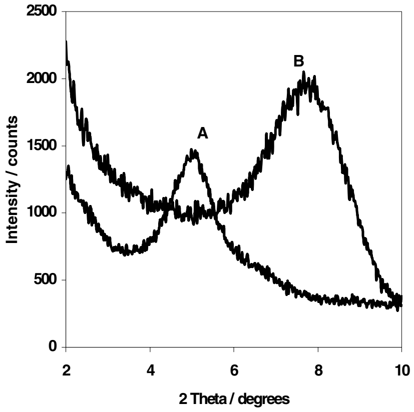
2.2 Characterisation

X-ray powder diffraction (XRD) patterns were collected on a Siemens D500 diffractometer fitted with a Cu Kα radiation source. The powders were passed through a 120-micron sieve and deposited on glass slides thinly coated with vacuum grease. A step size of 0.020º 2θ and collection time of 1sec/step was used for all experiments. Replicate experiments were conducted for each sample; the average gallery spacing observed for each sample is reported here; the measurements were found to be reproducible to ±0.1Å. Thermogravimetric analysis (TGA) was conducted on a Perkin Elmer Pyris 1 TGA at a ramp rate of 10ºC/min in flowing air. Typical sample masses were 10.0mg. Differential scanning calorimetry (DSC) was conducted on a Perkin Elmer Diamond DSC using sealed aluminium sample pans and an atmosphere of flowing nitrogen at heating and cooling rates of 20ºC/min and 200ºC/min respectively. Typical sample masses were 5.0mg. In all cases, the melt transition temperature, T_m is reported as the maximum of the melt endotherm.

3. Results and Discussion

Three principal criteria were used to assess the effectiveness of $ScCO_2$ and melt modification of the PEO/nanoclay composites: 1) the level of intercalation achieved was observed from the increase in gallery spacing of the composite compared to virgin nanoclay, 2) the loading of PEO achieved was determined by TGA and 3) DSC was used to investigate the extent to which this PEO was intercalated in the nanoclay galleries.

In the present study, a low loading of PEO in the composite (4:1 nanoclay/polymer ratio) was preferred because this resulted in the nanoclay being intercalated by the polymer rather than being fully delaminated. Intercalation allowed the use of XRD to follow the process quantitatively, whereas complete delamination can only be verified qualitatively by microscopy. From the XRD patterns, only peaks for virgin nanoclay (11.4Å) and fully intercalated composite (~17Å) were observed. It was concluded that none of the composites prepared were partially intercalated, as partially intercalated samples would have exhibited peaks at both ~17Å and ~11Å in their powder diffraction patterns [2]. Intercalation is a one-step process, hence intermediate peaks are not observed. As shown in Fig. 1, the gallery spacing achieved for each molecular weight PEO are smaller for samples prepared by $ScCO_2$ than for the corresponding melt process; the difference was observed to decrease with increasing PEO molecular weight. Low molecular weight PEO has a lower affinity for the nanoclay's surface than high molecular weight polymer [7], but it diffuses into the



Sample	Gallery spacing (Å)	
	Melt processed	$ScCO_2$ processed
PEO 10,000	18.0	17.7
PEO 2,000	17.9	17.5
PEO 400	17.7	16.8
Fluorinated EO	15.1	15.2
Virgin clay	11.4	

Fig. 1: XRD diffraction patterns for fluorinated EO/nanoclay composite (a) and virgin nanoclay (b) (left), and gallery spacing observed for melt- and $ScCO_2$-processed samples (right).

clay galleries faster. However, the molecular weight of polymer intercalated into the clay gallery does not affect the final structure of the composite [8]. It is proposed that, in the present study, the gallery spacing for composites prepared by $ScCO_2$ were lower than those prepared by melt because PEO does not coil in the same manner when plasticized as in the molten state.

Table 1 shows the results of TGA for the composites. Composites prepared by the $ScCO_2$ method had lower polymer loading than the equivalent sample prepared by melt processing: the corresponding mass loss step is illustrated in Fig. 2. As before, the difference in polymer loading was observed to decrease with increasing PEO molecular weight. Also, it was noted from TGA results that the water of crystallization which is adsorbed onto the virgin nanoclay was displaced during processing, although no significant difference was observed in the water content of melt- and $ScCO_2$–processed samples.

Table 1: Comparison of water of crystallization and PEO content for composites, by mol. wt. of PEO used in preparation, for melt- and $ScCO_2$-processed samples.

Sample	Melt processed		$ScCO_2$ processed	
	Water (wt%)	Polymer (wt%)	Water (wt%)	Polymer (wt%)
PEO 10,000	2.1	21.0	1.9	21.4
PEO 2,000	2.1	21.2	2.3	19.7
PEO 400	1.8	24.7	2.3	17.8
Fluorinated EO	3.0	22.4	2.9	21
Virgin nanoclay	6.6	-	6.6	-

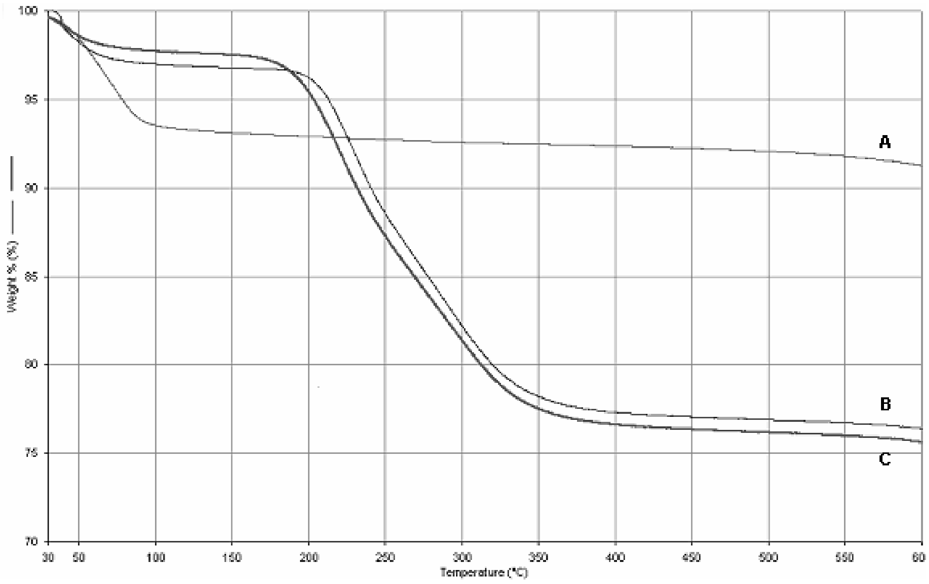


Fig. 2: Comparison of TGA trace for virgin nanoclay (a), $ScCO_2$ processed PEO 2000/nanoclay composite (b) and melt-processed composite (c). Water of crystallization is lost between 30 and 125°C; polymer is lost between 125 and 500°C. The remaining nanoclay undergoes thermal degradation above 500°C.

DSC experiments were conducted to determine whether all the PEO present in the composites was intercalated between the lamellae of the nanoclay (the space between lamellae is also known as the clay's 'gallery'). PEO/nanoclay composites that contain excess polymer over that intercalated in the nanoclay galleries present show a smaller melting transition (T_m) at lower temperature than virgin PEO [2,8]. As intercalation proceeds, the T_m of the excess PEO decreases and the area under the endotherm peak also decreases. Fully intercalated composites show no T_m for PEO as the polymer adopts an amorphous structure in the presence of the clay. Though T_m has been reported by Ogata *et al* [9, 10] to decrease slightly as the polymer/clay ratio decreases in PEO/nanoclay composites, this factor is not considered to play a primary role in the present study as the greatest variation in PEO content was 3.7 wt% between melt-processed samples; Ogata *et al* found that increasing the nanoclay content of the composite by 10 wt% only caused T_m to decrease by 1°C.

For PEO 400, 2000 and 10,000, T_m was only observed in melt-processed samples, indicating that the polymer was not fully intercalated into the clay galleries for these samples. Fig. 3 shows representative DSC traces for composites prepared with PEO of molecular weight 2,000. No T_m was observed for samples prepared by $ScCO_2$ processing. In the case of composites prepared with fluorinated ethoxide, no T_m was observed for melt-and $ScCO_2$-processed samples alike, i.e. the EO was fully intercalated following both processing methods.

The PEO content calculated for each melt-processed composite that exhibited T_m is listed in Table 2.

To calculate percentage crystallinity, $\Delta H_m°$, the standard heat of fusion for 100% crystalline PEO, was taken to be 197J/g [8]. Strawhecker *et al* reported that, for

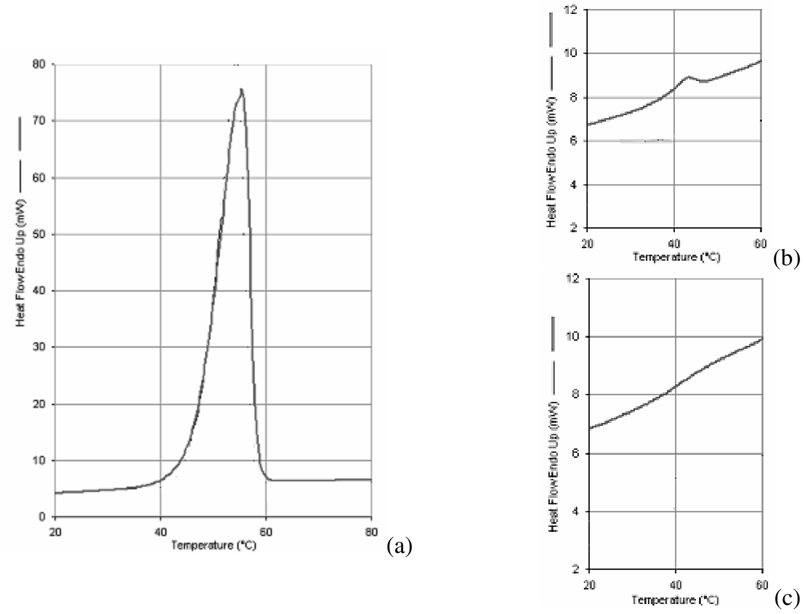


Fig. 3: Comparison of melt transition observed by DSC for virgin PEO of mol. wt 2,000 (a) and composite prepared by melt processing (b). No T_m was observed for the $ScCO_2$ processed composite (c).

PEO/nanoclay composites containing >90 wt% PEO, ΔH_m was not strongly affected by the polymer/clay ratio or the cooling rate used in DSC experiments [11]. It was found that, for PEO/nanoclay composites prepared by melt processing, peak T_m were comparable for composites prepared with PEO of molecular weight 2000 and 10,000. The percentage of non-intercalated PEO present in both these samples and the PEO 400 composite was consistent, indicating that the same extent of intercalation was achieved in all three melt-processed samples. Comparing the TGA results for each molecular weight of PEO used in the study (cf. Table 1), for each mol. wt. the $ScCO_2$ processed samples had lower PEO content that the corresponding melt processed samples. In light of these results, it is proposed that during $ScCO_2$ processing and subsequent venting of the chamber, polymer not intercalated into the nanoclay was removed from the samples, whereas for melt processing the polymer that was not intercalated remained in situ with the modified nanoclay. Therefore, it was concluded that the $ScCO_2$ preparation yielded more homogenous samples as no non-intercalated PEO remained in the composites prepared using $ScCO_2$.

Table 2: Shift in PEO T_m and % non-intercalated (crystalline) PEO content of each melt-processed sample as determined from DSC experiments.

	PEO T_m (°C)	Composite T_m (°C)	Composite ΔH_m (J/g)	% non-intercalated PEO in composite
PEO 10,000	64.5	42.4	0.37	0.19
PEO 2,000	54.4	42.7	0.56	0.28
PEO 400	4-8 [a]	1.3	0.31	0.16

[a] Value taken from Certificate of Analysis

The findings of the DSC analysis is in agreement with those reported by Zhao and Samulski [6] who found that, compared with composites prepared by solution methods, composites prepared via $ScCO_2$ processing had lower T_m and smaller ΔH_m.

Conclusion

This comparative study of $ScCO_2$ and melt processing techniques demonstrated that, at low polymer loadings (~ 20 wt%), the results obtained using either method were broadly consistent for each molecular weight of PEO studied. $ScCO_2$ processing yielded more homogenous samples i.e. more of the polymer was found to be intercalated in the nanoclay's galleries. The samples prepared using $ScCO_2$ were heated to lower temperatures than required for melt processing: this is an advantage if thermally sensitive additives (e.g. drug or cosmetic compounds) are to be incorporated into the composite. The $ScCO_2$ technique was found to be most effective when used with PEO of higher molecular weight (10,000) or fluorinated EO, which is otherwise difficult to process considering its poor solubility in common solvent and the difficulties observed in achieving homogenous mixing of the polymer and nanoclay during melt processing.

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