THE EFFECT OF POST PROCESSING ON HDPE/CLAY NANOCOMPOSITES PERFORMANCE

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ABSTRACT

In this study, HDPE/HDPE-g-MA and HDPE/HDPE-g-MA/clay nanocomposites were melt compounded using twin-screw extruder followed by compression moulding, then part of the compression moulded sheets were biaxially stretched. We have also studied different compatibiliser/clay ratios (α) in order to determine if interactions exist between processing route and polymer-clay compatibility. HDPE/ HDPE-g-MA (95/5) and HDPE/HDPE-g-MA/Clay with α value of 1 to 4 were examined. The structure was examined using XRD and TEM. Tensile properties and oxygen barrier properties were also determined. For the compression moulded sheets, no significant effect of compatibiliser/clay ratio on d-spacing was found, while for biaxially stretched sheets the enhancement is better at a ratio of 4.0. It was found that biaxially stretched sheets produced better enhancement in properties than the compression moulded sheets. The best enhancement in tensile modulus was found to be 100% for a biaxially stretched nanocomposite with α=4.0, which also showed the best enhancement in oxygen barrier (40%). The Halpin-Tsai model was employed to predict relative modulus values. For the best level of compatibilization which was found in biaxially stretched sheets at α = 4.0, the experimental relative modulus is greater than the predicted value, which may indicate the existence of a 'nano' effect at the polymer-clay interface.

INTRODUCTION

High density polyethylene (HDPE) has many applications, including plastic bags, chemical resistance piping systems, bottles, and different containers for water, milk and detergents. Such products are made via different processes such as thermoforming, stretch blow moulding, blown film extrusion and injection moulding. Nanofillers at extremely low contents (up to 5wt %) such as nanoclays have the ability to enhance the mechanical and barrier properties of many polymers. Nanocomposites are normally made by melt compounding the polymer, compatibiliser (if the clay and polymer are not naturally compatible) and clay. In order to make a final product, a second operation to shape the polymer takes place. The polymer-clay compound thus experiences a range of deformational and thermal regimes which can be expected to influence degree of clay exfoliation, dispersion and orientation of the final product. Melt compounding of HDPE/Clay nanocomposites has been studied in the literature; melt compounding using a twin screw extruder (1-3), and melt compounding using a twin screw extruder followed by either compression moulding (4-5), blown film extrusion (4, 6-9) or by injection moulding (10-12). Some studies focused on effect of compatibiliser of the structure and properties of the systems (1-2, 11,13). Others looked at the clay type and content (1,7). In this study we focused on the effect of post processing on the structure and properties of the nanocomposites. HDPE, compatibiliser and clay were melt compounded using a twin screw extruder followed by compression moulding, and then part of the compression moulded material was biaxially stretched. Biaxial stretching forms the basis of both stretch blow moulding and thermoforming processes which are considered an important post processing that are used for production of bottles and containers. In addition, different compatibiliser: clay ratio (α) was used in order to determine if interactions exist between processing and polymer-clay compatibility.

MATERIALS

The HDPE used in this study was SABIC® HDPE F00952EQ with MFI of 0.05 g/10min (at 190 °C and 2.16 kg). DuPont™ Bynel® 4033 was used as the compatibiliser with MFI of 2 g/10min (at 190 °C and 2.16 kg). The clay used was Cloisite 20A, which is a montmorillonite modified by dimethyl, dehydrogenated tallow, quaternary ammonium.

METHODS

Compounding and Processing

[HDPE - (HDPE-g-MA) - clay] with formulations (wt%) of (95-5-0, 90-5-5, 85-10-5, 80-15-5, 75-20-5) were compounded. All batches contained 5wt% clay content, which was chosen because we found during our previous studies that higher clay contents may cause clay to agglomerate inside polymer matrix causing properties to decline. Compatibiliser to clay ratio was chosen to be from 1.0 to 4.0 to check the ratio that provide good compatibility degree without affecting properties of polymer matrix which may start to decline due to higher MFI of compatibiliser compared to HDPE (lower molecular weight). All batches were melt compounded into pellets using a Dr. Collin twin screw extruder ZK 25 at temperature range from 185˚C to 200˚C from zone 1 to 6. Produced pellets were compression moulded using Dr Collin P200P platen press at temperature of 170˚C and pressure of 107 Pa. Sheets of 1 x 76 x76 mm3 were produced. Part of compression moulded sheets was biaxially stretched at temperature of 120°C, strain rate of 16s-1, and a stretching ratio of 3.5. Biaxial stretching was performed using QUB biaxial machine which was developed in order to duplicate the deformation behavior of polymeric materials in thermoforming and stretch-blow moulding under controllable conditions (deformation temperature, deformation rate and deformation mode). Deformation during biaxial stretching occurs at the semi-solid state. First the specimens are clamped using 24 nitrogen-driven pneumatic clamps, 7 along each side of the sample, then heat is applied by two hot-air blowers which are mounted vertically just above and below the sample. The machine is capable of stretching speed up to 1200mm/s, and is capable of producing constant width, simultaneous equal biaxial and sequential stretching. The maximum elongation distance that the machine can extend to is 266mm, which is equivalent to a stretching ratio of 4.5 for a sample of 76 mm width. The stretching results in term of time, x-axis displacement and its force, and y-axis displacement and its force are recorded in an excel file by LABVIEW data-logging package, which can be transformed into stress-strain data.

Characterization

XRD

A PW3040 Console was used to check the d-spacing in the original clay and in the clay introduced into the polymer matrix in the nanocomposites. The X-ray beam was Cu Kα1 (λ= 1.5418 A°). Data were collected from 1 to 40º. Samples of 2 cm diameter were tested.

TEM

Philips TEM microscope at magnification of x39K was used.

Tensile test

An Instron 5564 Universal tester with extensometer at a crosshead speed of 1mm/min was used to measure the sample modulus, (BS EN ISO 527: 1996) (14). Test was repeated on 5 samples.

Oxygen barrier

A Mocon machine - OX-TRAN® Model 2/21 was used to measure the permeability of oxygen transmission rate. The testing area was 1 cm^2 using an aluminum mask. Each test was repeated on 3 samples, and average values were computed.

Modeling

The Halpin-Tsai model for both randomly orientation and oriented systems was used to predict tensile modulus in compression moulded and biaxially stretched sheets.

RESULTS AND DISCUSSION

TEM and XRD

XRD results are shown in figure 1 and table 1, which show that there is an enhancement in d-spacing of the clay when it is introduced into the polymer matrix**.** This can be concluded from the change of the peak height position (moving to the left) using Bragg's law. Table 1 show that at α of 1.0, 2.0 and 3.0 the d-spacing had increased moderately in compression moulded sheets and biaxially stretched sheets compared to d-spacing in the original clay, while at α = 4.0, the enhancement is moderate in the compression moulded sheets, and is great in the biaxially stretched sheets**.**

Table 1 – XRD results - d-spacing values

Sample		d-spacing (A˚)
Cloisite 20A		23.73
Compression Moulded sheets (CM)	α 1	29.52
	α 2	28.91
	α 3	30.25
	α 4	29.19
Biaxially Stretched sheets (BS)	α 1	28.24
	α 2	28.28
	α 3	27.24
	α 4	39.06

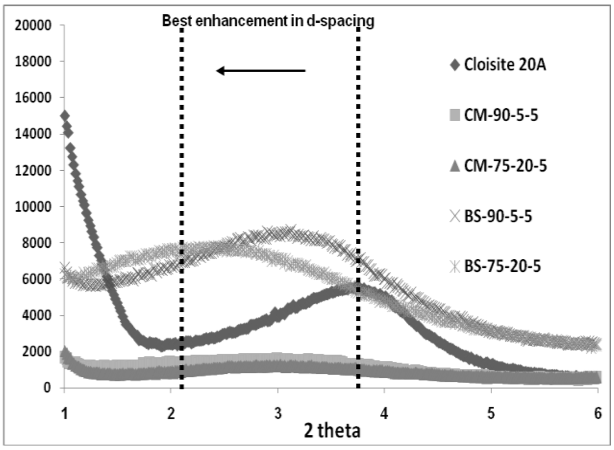


Figure 1 - XRD traces for Cloisite 20A, Compression moulded sheets (CM) and biaxially stretched sheets (BS) for nanocomposites at α = 1 and α = 4.

Enhancement in d-spacing indicates that there is some degree of intercalation of polymer molecules into the spacing between the clay layers. d-spacing results also show that there is no effect of α in compression moulded sheets, while it's very clear that it has big effect in biaxially stretched sheets This may be because during extrusion the large clay stacks are broken into smaller ones, so the role of compatibiliser is not important, as seen in the compression moulded sheets. However, during the second processing (stretching- elongation) the clay layers are peeled off the stacks, and the role of compatibiliser becomes more important for peeling off because the higher the compatibiliser content the better the bond between clay and polymer and the easier the peeling off (15). Another point to mention here is the peak height of XRD traces (Fig.1). It can be noticed that the peaks are higher in case of BS compared to CM, which is due to orientation effect, the higher the orientation, the higher the peak. TEM results confirm the conclusions of XRD. Figures 2 and 3 show images for CM and BS sheets at α of 1 and 4. Figures 4 and 5 show thickness analysis made on TEM images. Thickness was chosen to be shown here as one of representative parameters for degree of intercalation/exfoliation. As seen in figure 4, thickness analysis of clay tactoids show that tactoid thickness in BS sheets is lower in general, due to higher degree of intercalation/exfoliation, in addition to higher percentage of individual layers (1 nm) in BS compared to CM sheets especially at α=4. Figure 5 show the average tactoid thickness. It confirms that α has no or little effect on the degree of intercalation in CM sheets, while it has an effect on BS sheets' degree of intercalation.

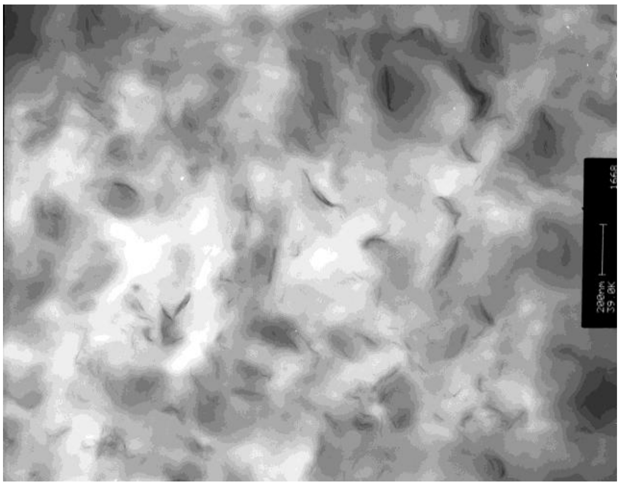


Figure 2-a – TEM image of CM sheet – α=1, scale bar = 200 nm (15)

Figure 2-b – TEM image of CM sheet – α=4, scale bar = 200 nm (15)

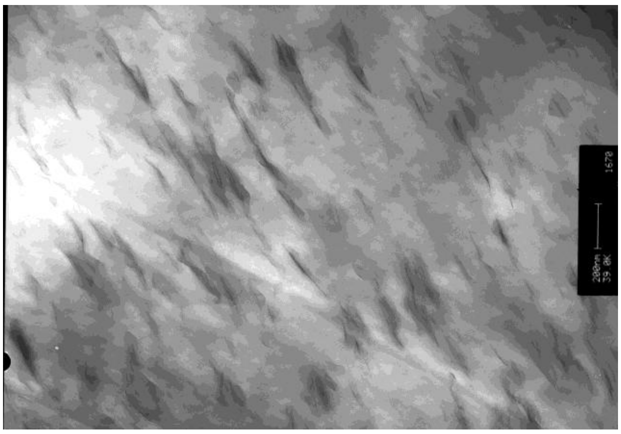
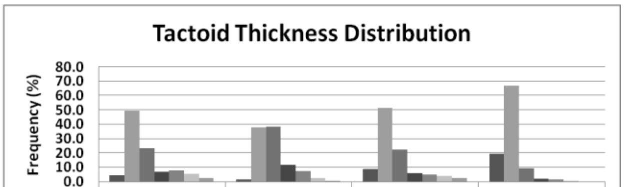


Figure 3-a – TEM image of BS sheet – α=1, scale bar = 200 nm (15)

Figure 3-b – TEM image of BS sheet – α=4, scale bar = 200 nm (15)



	CM90-5-5	CM75-20-5	BS90-5-5	BS75-20-5
1 nm	4.4	1.7	8.8	19.3
2-3 nm	49.6	37.8	51.6	67.0
3-4 nm	23.3	38.4	22.5	9.3
4-5 nm	6.9	11.9	6.0	2.1
5-7 nm	7.9	7.3	4.9	1.4
7-10 nm	5.2	2.4	3.6	0.6
> 10 nm	2.8	0.5	2.6	0.3

Figure 4- Tactoid thickness analysis- TEM results.

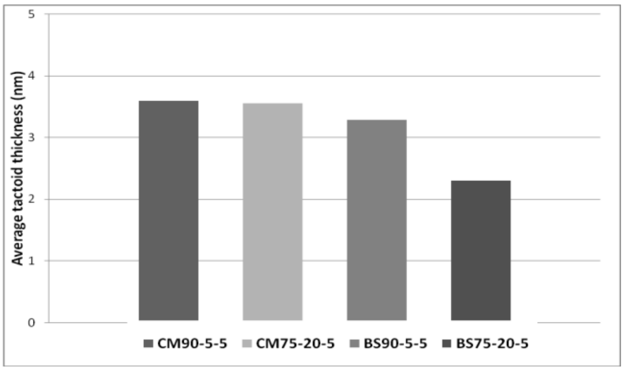


Figure 5- Average tactoid thickness – TEM results

Tensile tests

Figures 6 and 7 show the tensile modulus values for compression moulded sheets and biaxially stretched sheets respectively. As seen the enhancement in BS sheets is much higher than that in the CM sheets. This reflects the structural results obtained from XRD and TEM which shows that the degree of exfoliation is better in BS, especially at high α.

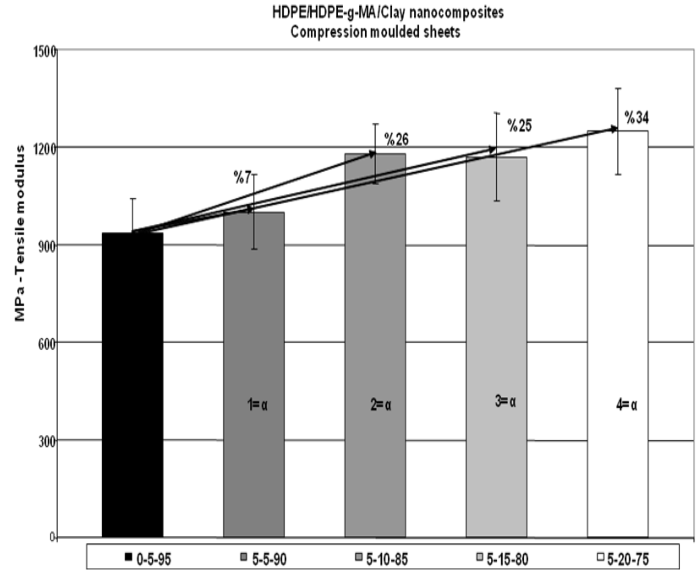


Figure 6- Tensile modulus- Compression moulded sheets (15)

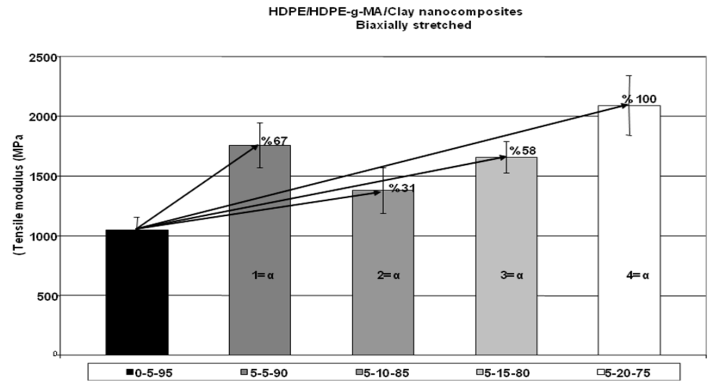


Figure 7- Tensile modulus- Biaxially stretched sheets (15)

Oxygen Barrier tests

As seen in figure 8, biaxially stretched sheets have better barrier properties, which is due to higher molecular and clay orientation and higher clay aspect ratio. In the biaxially stretched sheets, the higher the compatibiliser: clay ratio (α), the better the barrier properties, which is due to better degree of exfoliation, and consequently longer tortuous path.

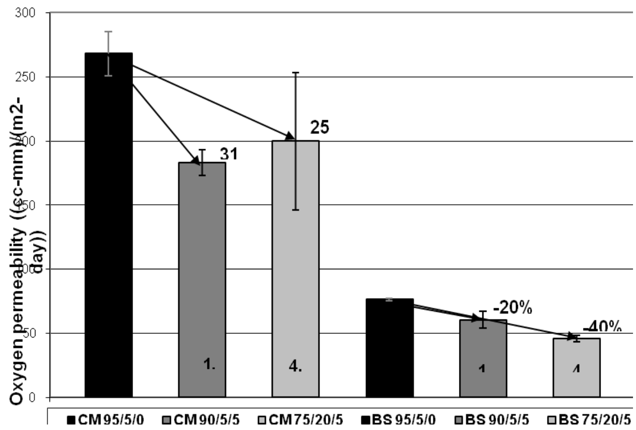


Figure 8- O_2 Barrier tests results

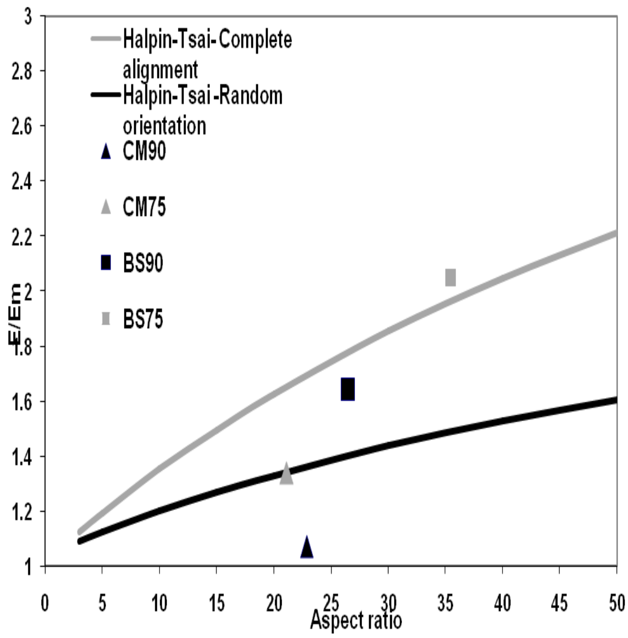


Figure 9 – Experimental realtive moduli versus predicted relative moduli

Modeling

Figure 9 shows the experimental vs. the predicted relative modulus values using the Halpin-Tsai (H-S) model. The top solid line represents predictions for a composite in which particles are fully aligned in the deformation direction. The biaxially stretched samples are highly aligned (although not perfectly) so experimental data will be compared with this line. The bottom solid line represents a composite in which the particles are randomly aligned. The compression moulded samples most closely approach a random alignment so the experimental data for compression moulded samples should be compared with this line. It is clear from Figure 9 that the relative modulus for compression moulded sample at α=1 is significantly lower than the predicted value. This is to be expected because these samples do not have good compatibility between clay and polymer. When the compatibility is improved by increasing α to 4.0 the experimental value coincides with the predicted H-S value. For the biaxially stretched samples at α=1.0 the experimental value is just below the fully aligned H-S while for α=4.0 value the experimental value exceeds the H-S line for completely aligned. This provides some evidence of a 'nano' effect for the well compatibilized samples (15).

CONCLUSIONS

The importance of this study was mainly to show the effect of post processing on the structure and the properties of HDPE/clay nanocomposites. It showed that property enhancement as a result of biaxial stretching is very significant. In addition it showed that there is an interaction between polymer/clay compatibility and the processing route of the polymer/clay nanocomposites. Best enhancement in structure and thus in properties was found in the nanocomposite with best compatibility between HDPE and the clay which was found at compatibiliser: clay ratio of 4.0 of the biaxially stretched sheets. Best enhancement in tensile modulus was 100%, and best enhancement in O_2 barrier properties was 40% in this nanocomposite. Another important finding in this study was the evidence of a 'nano' effect of the well compatibilized samples which was found when experimental relative modulus exceeded the predicted one.

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