Interfacial interactions between polyethylene matrix and clay layers in polyethylene/clay nanocomposites

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Abstract: Polyethylene/clay nanocomposites were prepared as blown films using different formulae (clay contents (4 and 6 wt%) and compatibilizer/clay ratio (1/2, 1.0, 2.0)). Structure and mechanical behaviour were tested. It was found that blown film extrusion process decreased the tactoids size and consequently enhanced the exfoliation degree of the clay layers inside the polymer matrix, which is due to the elongational stress during extrusion. Addition of clay had some effects on mechanical behaviour. There was an increase of yield strength (max 32%). Yield strength is related to the interfacial interaction between the polymer and the clay layers in the nanocomposites, which would be enhanced by enhancing the compatibility between polymer and clay layers. Correlation analysis showed good correlation between compatibility and interfacial interaction parameters, and between parameters of interfacial interaction, structure and yield strength.

1.Introduction
Polymer nanocomposites have been studied extensively since the successful production of nylon6/clay nanocomposite by Toyota [1]. However polymer nanocomposites are still not in widespread use in industrial applications and many polymer systems do not achieve the property enhancements reported by Toyota with Nylon 6 nanocomposites. In order to be able to achieve that, relations between processing, structure and performance of nanocomposites were studied.

Regarding the effect of processing on structure, one study on Polypropylene (PP)/organoclay nanocomposites investigated the effect of screw profile in the extruder on the state of clay intercalation/exfoliation [2]. It was found that at low feed rates (long residence time), the screw profiles that are more restricted produced a smaller interlayer distance, however at high feed rates the interlayer distance was not affected by screw profile. The same authors found that neither the screw speed nor the feed rate in the extruder had any significant effect on the degree of intercalation [3]. Jiang et. al. [4] studied the effect of mixing on structuring. They found that chaotic mixing facilitates the dispersion of clay in the PP matrix compared to high shearing/mixing. Kalendova et. al [5] investigated the effect of different types of plasticizer and compounding conditions on the structure of polyvinyl chloride (PVC)/clay nanocomposites. They found that clay modified by plasticizer exhibits fine dispersion of partial to nearly full exfoliated clay. They also concluded that the processing conditions played an important role in nanocomposite production. Abu-Zurayk et. al.[6] investigated the effect of post processing on performance of Polyethylene (PE)/clay nanocomposites. They found that there is an interaction between polymer/clay compatibility and the processing route of the polymer/clay nanocomposites. Regarding the effect of processing and structure on nanocomposite performance, Du et. al. [7] and Shi et. al. [8], have found that the addition of clay up to a certain point enhances the mechanical properties but further increases lead to a reduction in mechanical performance. This was attributed to the formation of clay aggregates, which act as stress concentrators, at high loading [8]. There is
disagreement in the literature regarding the state of exfoliation necessary to maximize composite modulus. Boo et. al [9] found that in a poorly exfoliated system the modulus improved by only 8%, in a well exfoliated system the enhancement was 50%, while in a moderately exfoliated system had the tensile properties lay between the poorly exfoliated and the well exfoliated systems. Bousmina [10] on the other hand published quite different results. He showed that the best enhancement in modulus was achieved in a system with an intermediate level of exfoliation. He attributed this to the fact that the clay particles are flexible that can bend under mechanical stress and that it is better to have the clay layers as 10-20 layers stacks in order to act as rigid fillers. Such stacks would resist the bending much more than the individual layers of a fully exfoliated system. Costantino et. al. [11] investigated the deformation and fracture properties of PP/clay nanocomposites. They concluded that the overall crack propagation energy values varied as a function of the processing conditions. Many questions need to be answered regarding the processing of nanocomposites in order to produce useful products. For example, what is the best structure to have in a plastic sheet that is subsequently to be extruded into a blown film? What are the best processing conditions/formulae to get this structure? What are the interfacial interactions in such system? How would these interactions affect the performance? Not all questions have been answered so far in the literature. This study was performed in order to examine the link between processing and interfacial interactions in HDPE/Clay nanocomposites in a sequence of processing steps that constitute a typical processing route (i.e. compounding of nanocomposite followed by blown film extrusion) and their relations with structure parameters and mechanical performance.

2. Materials
HDPE (HYA 600)-ExxonMobil was used. It has density of 0.954g/cm$^3$ and MFI of 0.35g/10 min (at 190°C and 2.16 kg). Cloisite 20A was supplied by Southern Clay Products. This clay is treated with dimethyl, dehydrogenated tallow, quaternary ammonium ions. Maleated polyethylene DuPontTM Bynel1 4033 was used as the compatibilizer. This has an MFI of 2 g/10 min (at 190°C and 2.16 kg).

3. Methodology
3.1 Nanocomposites preparation
A twin screw Brabender compounder was used for compounding seven batches with different formulae as shown in table 1.

| Batch number | HDPE (wt%) | PE-g-MA (compatibilizer) (wt%) | Clay (wt%) | Compatibilizer/clay ratio |
|--------------|------------|--------------------------------|------------|--------------------------|
| 1            | 100        | 0                              | 0          | NA                       |
| 2            | 94         | 2                              | 4          | 1/2                      |
| 3            | 92         | 4                              | 4          | 1/1                      |
| 4            | 88         | 8                              | 4          | 2/1                      |
| 5            | 91         | 3                              | 6          | 1/2                      |
| 6            | 88         | 6                              | 6          | 1/1                      |
| 7            | 82         | 12                             | 6          | 2/1                      |

The compounded batches were extruded using blown film extrusion at temperature profile from the feeder of the single screw extruder to the die were 185, 195, 200, 205, 210, 210, 215, and 215 °C, and blow up ratio of 5.0 and final thickness of 0.03mm.

3.2 XRD
A 7000 Shimadzu 2 kW model X-ray diffractometer with a nickel-filtered copper X-ray radiation (Cu Ka 1.5418A) was used to carry out XRD on compounded batches and blown films. Data were
collected from 1 to 60°. Samples of 2 cm diameter were tested. Data were used to calculate the d-spacing of the crystal lattice of clay.

3.3 TEM
All samples were ultra-microtomed using a 45° diamond knife. Images of the microtomed sections were taken using TEM microscope. A magnification of 22K was used. Images produced were analyzed for tactoid size (thickness, length) using JMicroVision v1.25 software, which was also used for Aspect ratio (AR), exfoliation number (N) and interparticle distance (IPD). Five images of each sample were taken for analysis.

3.4 Tensile Tests
Tensile test was performed on an Instron 5564 Universal tester according to (ISO 527-3) at a crosshead speed of 200 mm/min in machine direction. Each test was repeated on seven samples for each batch.

4. Results and Discussions
4.1 XRD and TEM
XRD was performed on two systems of nanocomposites, the compounded batches which were introduced into shear stress during compounding, and the blown films batches which were introduced into elongational stress during extrusion. Figures 1 and 2 show XRD diffraction patterns. d-spacing values are shown in table 2.

Figure 1. XRD diffraction patterns of compounded batches
Table 2. XRD parameters

| d-spacing (Å) | 2   | 3   | 4   | 5   | 6   | 7   |
|---------------|-----|-----|-----|-----|-----|-----|
| Compounded nanocomposites | 23.9 | 23.8 | 26.8 | 22.5 | 26.4 | 27.9 |
| Blown films nanocomposites | 24.02 | 25.4 | 26.6 | 25.8 | 22.55 | 26.8 |

It is shown that at 4wt% clay loading, d-spacing was increased with the increase in compatibilizer concentration but this is not clear at all 6wt% clay loading. Based on the peak shifting between different batches as shown in figures 1 and 2, the highest d-spacing was found in batches 4 and 7, which have highest compatibilizer/clay ratio (2.0) for both clay contents (4 wt% and 6wt%). This is expected, because the higher the compatibilizer content the better the bond between clay and polymer which makes it easier for clay layers that are in contact with the polymer to peel off the clay tactoids during shear stress and elongational stress), which would increase the average d-spacing.

TEM analysis was performed to check the detailed information regarding clay tactoids dispersion and degree of exfoliation. Examples of TEM images are shown in figures 3 and 4.
Analyses were performed on TEM images for average tactoids thickness, length, aspect ratio (AR) for all batches, in addition to exfoliation number (N) and interparticle distance (IPD) for blown films. The exfoliation number (N) is defined as the percentage of the total clay interfacial area that is exposed to the polymer matrix. Interparticle distance (IPD) is defined as the mean of all possible straight-line distances in 3D, at arbitrary angles, between arbitrary points on the surfaces of clay particles [12]. Results of analyses are shown in table 3

**Table 3 – TEM analysis parameters**

| Batch | Clay (wt%) | Compatibilizer /clay | Compounded Nanocomposites | Blown films Nanocomposites |
|-------|------------|----------------------|---------------------------|----------------------------|
|       |            |                      | Length (nm) | Thickness (nm) | AR | Length (nm) | Thickness (nm) | AR | N | IPD |
| 2     | 4          | 0.5                  | 339.0        | 34.1           | 9.9 | 267.4        | 30.3           | 8.8 | 6.8 | 1712.9 |
| 3     | 4          | 1.0                  | 237.8        | 12.4           | 19.2 | 202.6        | 19.0           | 10.6 | 12.4 | 1164.8 |
| 4     | 4          | 2.0                  | 241.7        | 14.4           | 16.8 | 189.7        | 12.4           | 15.3 | 18.4 | 818.5  |
| 5     | 6          | 0.5                  | 241.4        | 22.2           | 10.9 | 281.2        | 27.6           | 10.2 | 8.1  | 1076.7 |
| 6     | 6          | 1.0                  | 413.0        | 25.8           | 16.0 | 247.0        | 22.5           | 11.0 | 7.0  | 911.5  |
| 7     | 6          | 2.0                  | 229.0        | 12.2           | 18.8 | 172.6        | 12.6           | 13.7 | 13.2 | 520.5  |
TEM results show that tactoids size in blown films have lower size (length, thickness) compared to compounded batches, which is an indication that blown film extrusion enhances the exfoliation degree of the clay layers inside the polymer matrix regardless of its formula (clay content, compatibilizer/clay ratio). There is a general trend for AR. The higher the compatibilizer/clay ratio, the higher the AR. Same trend is found for N and IPD with compatibilizer/clay ratio. Also, for blown films, at low clay content and high compatibilizer/clay ratio, both AR and N are high, which means that these conditions are best for exfoliation degree based on TEM. Similar results were found on PE/clay nanocomposites systems with different compatibilizer/clay ratios [6], where increasing the compatibility between the polymer and the clay would increase the aspect ratio of the clay layers in the polymer matrix as a result of higher degree of exfoliation. This is expected to affect the mechanical performance

4.2 Tensile test and interfacial interactions

As seen in figure 5, results of tensile tests in machine direction showed enhancement in most nanocomposites yield strength. The strength of nanocomposites relies on the effectiveness of stress transfer between matrix and filler. For well-bonded particles, the applied stress can be efficiently transferred to the particles in the matrix, which clearly improves the strength [13], and this would explain the enhancement of yield strength as result of enhancement of compatibility and bonding between the polymer and the clay.

Figure 5. Yield strength of Blown films nanocomposites

Dependence of yield strength of polymer/clay nanocomposite with homogenous matrices on the interfacial interactions, clay tactoid size, and clay fraction can be modeled using the following equation [14]:

$$\sigma_R = 1 + \phi_f \left(\frac{AR \tau}{\sigma_P} - 1\right)$$

where $\tau$ is the interfacial stress transfer parameter; $\sigma_R$ and $\sigma_P$ are the relative yield strength and the yield strength of the polymer, respectively; $AR$ is the aspect ratio of clay tactoid, and $\phi_f$ is the volume fraction of clay in the nanocomposites.

Applying equation (1) for each batch, using relative AR calculated using TEM analysis and yield strength data, $\tau$ was calculated. In order to check correlations between processing parameters and interfacial interactions and between interfacial interactions and structure and performance, a bootstrapping analysis via MATLAB was performed at confidence interval of 90%. Significant
correlations were found between different parameters, with good correlation coefficients as shown in table 4.

Table 4- Correlation coefficients

| Parameter                  | Processing parameter | Interfacial interaction parameter | Strucutre parameters |
|----------------------------|----------------------|-----------------------------------|----------------------|
|                            | Compatibilizer/clay ratio | τ                  | AR   | N   | IPD |
| Interfacial interaction parameter | -                      | 1.00                | -0.89 | -0.55 |
| Structural parameters       | AR                   | 1.00                | +0.85 | -0.55 |
|                            | N                    | +0.85               | +0.89 | -0.55 |
|                            | IPD                  | -0.79               | -0.80 | 1.00 |
| Mechanical parameters      | Yield Strength       | +0.88               | +0.94 | +0.87 |

As seen in table 4, there is a significant correlation between interfacial interaction parameter and compatibility; the better the compatibility, the stronger the interaction. And this would affect the structure (better exfoliation) and consequently the yield strength of the system. Highest correlations of yield strength were found with interfacial interaction parameter (τ), and aspect ratio of clay tactoids.

5. Conclusions
Blown film extrusion process enhanced the exfoliation degree of the clay layers inside the polymer matrix, due to the elongational stress during extrusion. Regarding effects of clay on mechanical performance of nanocomposites, yield strength was enhanced for different batches of nanocomposites with a maximum enhancement of 32%. Yield strength is related to the interfacial interaction between the polymer and the clay layers in the nanocomposites, which would be enhanced by enhancing the compatibility between polymer and clay layers. This was confirmed by results of correlation analysis which showed good correlation between compatibility and interfacial interaction parameters, and between parameters of interfacial interaction, structure and yield strength.

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7. References
[1] Hussain F, Hojjati M, Okamoto Y and Gorga R 2006 Journal of Composite Material, 40(17) 1511.
[2] Lertwimolnun W and Vergnes B 2007 Polymer Engineering and Science 47 2100.
[3] Lertwimolnun W and Vergnes B. 2006 Polymer Engineering and Science 46 314.
[4] Jiang G and Huang H 2011 Polymer Engineering and Science 51 2345.
[5] Kalendova A, Zykova J, Kovarova L, Slouf M. and Gerard J 2010 AIP Conference Proceeding 1255 181
[6] Abu-Zurayk R and Harkin-Jones E 2012 Polymer Engineering and Science 52 2360.
[7] Du K, He A, Liu X and Han C 2007 Macromolecular Rapid Communication 28 2294.
[8] Shi X and Gan Z 2007 European Polymer Journal 43 4852.
[9] Boo W, Sun L, Liu J, Moghbelli E, Clearfield A, Sue H, Pham H, and Verghese N 2007 Journal of Polymer Science: Part B: Polymer Physics 45 1459.
[10] Bousmina M 2006 Macromolecules 39 4259.
[11] Costantino A, Pettarin V, Viana J, Pontes A, Pouzada A and Frontini P 2013 Journal of Mechanical Engineering 59 697.
[12] Abu-Zurayk R, Harkin-Jones E, McNally T, Menary G, Martin P and Armstrong C 2009 Composites Science and Technology 69 1644.
[13] Tanasa F, Zanoaga M, Darie R 2014 International Conference of Scientific Paper Brasov, 22-24 May 2014.
[14] Durmus A, Kasgoz A and Macosko C W 2008 Journal of Macromolecular Science, Part B: Physics 47 608