ANALYSIS OF MECHANICAL PROPERTY DEGRADATION IN POLYMER NANOCLAY COMPOSITES

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ABSTRACT

Polymers are used in various industrial applications due to their ease of production, light weight and ductility. Fillers such as nanoclays are added to polymers to improve a range of factors such as material processing, thermal properties, fire retardance and cost. However, adding nanoclays may negatively impact the mechanical performance, affecting the strength, stiffness and impact resistance of the composite.

There are two important ways to mitigate this degradation in mechanical properties. The first is to improve the chemical adhesion between the polymer and the filler by adding an appropriate compatibiliser, and the second is to control the amount of nanoclay added. There have been several studies in literature that investigated both options to understand the interaction between the polymer matrix, nanoclay and compatibiliser and the resulting influence on the mechanical performance. These studies generally aim to find a composition ratio which results in improved properties (processing, thermal, chemical, fire resistance, low weight, etc.) and a good enough mechanical performance for a desired application. When designing such a composite without severely impacting the mechanical performance, an understanding of the mechanical property degradation due to increased weight loading of nanoclay is beneficial.

This study aims to define the problem of determining an upper limit for nanoclay inclusions. Commercial nanoclay particles are compounded with high density polyethylene (HDPE) at weight loadings of 2.5%, 5%, 7.5%, 10%, 15% and 20%. The effect of inclusion fraction on strength, stiffness and elongation to failure are investigated.

KEYWORDS: Polymer nanoclay composites, mechanical properties, degradation

1. INTRODUCTION

Polymer nanoclay composites have received considerable attention in recent years, both in research and industry, as they allow for the manipulation of the base polymer material to improve on the thermo-mechanical properties by adding small nano-sized clay fillers (platelets, fibers or particles) [1-5]. By adding these clay fillers the final composite material may have improved material, thermal and electrical properties, as well as a high strength to weight ratio at lower costs, all desirable traits for various industrial applications [1-7]. However, even when clay is added with the intention of improving a certain set of properties for a specific application area, we still need to understand the effect on the mechanical properties.

Much research has focussed on finding the clay loading that will yield the optimum thermo-mechanical properties for a desired application. The desired improvement of the mechanical properties is most often obtained at a relatively low clay loading of below 5wt% [1-3]. As such, most experimental studies normally only investigate low clay loadings of, for example, 3wt% [4], 5wt% [8-10] and 7wt% [11]. Heydari-Meybodi et al. [11] concluded in their study that the Young’s modulus decreased with an increase in clay loading from 5wt% to 7wt%. Romo-Uribe [4] mentioned that a clay loading of 10wt% or more only results in small improvements of some of the mechanical properties. Zabihi et al. [6] also mentioned that when the clay loading is increased beyond the threshold limit value, the Young’s modulus will level off. They attribute this to a change in the clay-polymer interaction. Thermo-mechanical properties are dependent on the interactions between the clay particles and the polymer matrix which include the type of clay, compatibilizer or surface treatment used as well as its dispersion in the matrix [6].

It has been observed that while including clay fillers may increase the Young's modulus and tensile strength of the nanocomposite, other important mechanical properties such as elongation to failure and impact fracture toughness often decrease [8,9]. This degradation in mechanical performance is an important variable to understand in designing a composite material system [17,18]. Nevertheless, there are few reports from literature on the threshold clay loading beyond which the mechanical properties start to degrade.

The aim of this study is to investigate the effect of clay loading on the mechanical properties of a polymer nanoclay composite. Two stages of experimental investigation are presented: the first investigation aims to find the optimum clay loading to enhance mechanical properties;

the second aims to identify the point at which mechanical properties begin to degrade. As a result of these experiments we are able to propose a direction for future investigations.

2. MATERIALS AND METHODS

For this study a B7550 grade high density polyethylene (HDPE) was chosen as the polymer and a commercial coated DHT4-A as the clay. The manufacturing and testing were performed by undergraduate students over two years and documented by Ellis [12] and Heymans [13].

2.1. Manufacturing

To manufacture the testing samples the HDPE is pulverised into a fine powder and mixed with the desired clay loading in a bag for 45min to ensure proper dispersion. The polymer-clay mixture is then extruded into a long wire by means of a twin screw extruder after which the wire is fed through a chipper to obtain pellets. This process was repeated a second time as a previous study indicated that the clay particles tended to agglomerate due to bad dispersion with only one extrusion and found two extrusions to provide better dispersion [14].

To create the tensile testing samples the polymer nanocomposite pellets were stacked into specimen moulds which were developed by Parschau [14] based on the ASTM D638-02 Type I [15] dimensions. The specimens were then compressed using a vertex hot press at a fixed temperature of 180° and a pressure of 15 MPa applied in increments. Finally specimens were cured at room temperature before removing them from the moulds and finishing the surfaces to remove any excess material or impurities due to the pressing procedure that could influence the tensile testing results.

2.2. Tensile Testing

Before any experimental tests are conducted the sample length, width and thickness is recorded. On average the sample width was 13mm and the thickness 3mm. A minimum of 5 samples per batch are required to obtain statistical significance according to ASTM D638-02 [15]. To adhere to this requirement, 5 samples were manufactured per batch for each of the clay loading cases considered. For the neat HDPE 5 batches were manufactured of which there were 5 defective samples leaving a total of 20 usable samples. For the first set of experiments (clay loading of 2.5wt%, 5wt% and 7.5wt%) 2 batches of each case were manufactured, where there were 2 defective samples for the 5wt% and 7.5wt% cases leaving a total of 10 (2.5wt%) and 8 (5wt% and 7.5wt%) usable samples. For the second set of experiments (clay loading of 0wt%, 15wt% and 20wt%) only 1 batch of each case was manufactured with no defective samples which resulted in 5 usable samples for each case.

To obtain the desired mechanical properties a tensile test was conducted using a 5kN Tensile Machine with a displacement rate of 5mm/min as recommended by ASTM D638-02 [16]. Ellis [12] noted that the 5kN Tensile Machine is adequate to determine the ultimate tensile strength, but does not provide the 0.2% offset Yield Strength and Elastic Modulus. A clip gauge was therefore used to measure the specimen displacement for the first set of experiments to obtain a more accurate representation of the composite strain. During the second set of experiments the clip gauge continued slipping and was therefore not used [13].

3. FIRST EXPERIMENT: LOOKING FOR AN OPTIMUM

When we started this research project the main question we wanted to answer was:

What is the optimum clay loading which improves the composite material and the mechanical properties?

As literature had indicated an improvement in mechanical properties can be achieved at low levels of clay loading [1-7] the initial tests were conducted considering 2.5wt%, 5wt% and 7.5wt% of the DHT4-A loading in an HDPE B7550 matrix along with the neat HDPE B7550 for comparison. The samples were manufactured, tested and processed as described in Section 2 and the resulting stress-strain curves for all these cases are shown in Figure 1.

To answer the posed question the first thing is to determine the elastic modulus and ultimate tensile strength from these curves as both these are desirable properties to enhance. A schematic of how to calculate these properties is shown in Figure 2 using a sample curve. The elastic modulus (E) is the gradient of the linear elastic region of the stres-strain curve and the ultimate tensile strength (UTS) is the maximum stress value on the curve.

The elastic modulus and ultimate tensile strength for each data set and each considered case is shown in the scatterplot in Figure 3, and averages and standard deviations are tabulated in Table 1.

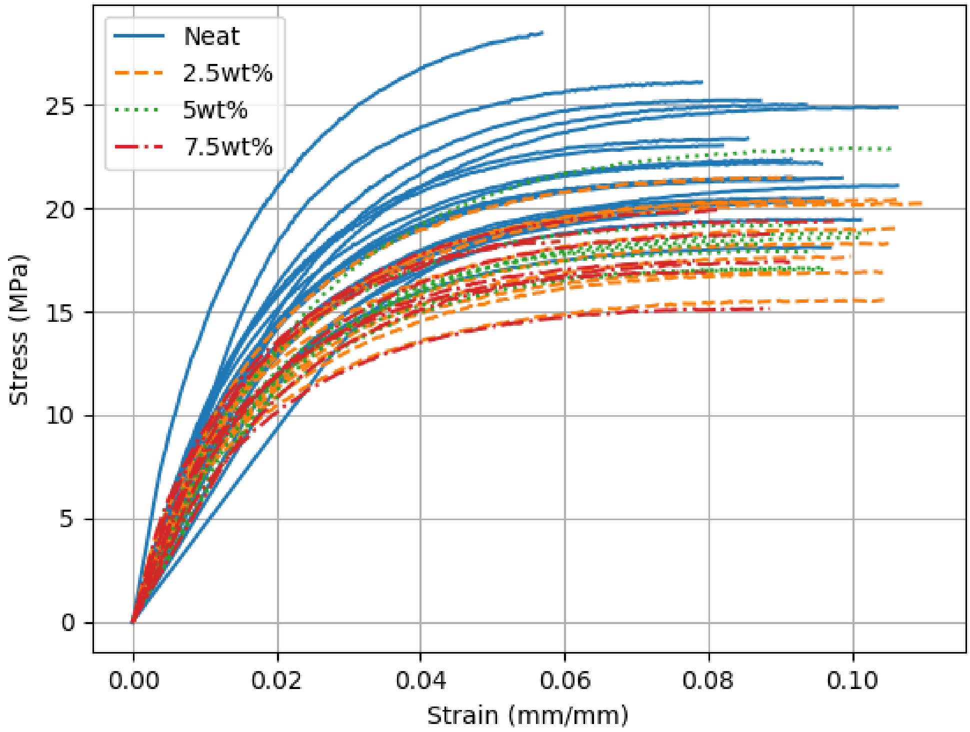


Figure 1: Corrected stress-strain curves from the tensile tests for the first experiment considering a neat HDPE, HDPE-2.5wt% DHT4A, HDPE-5wt% DHT4A and 7.5wt% DHT4A.

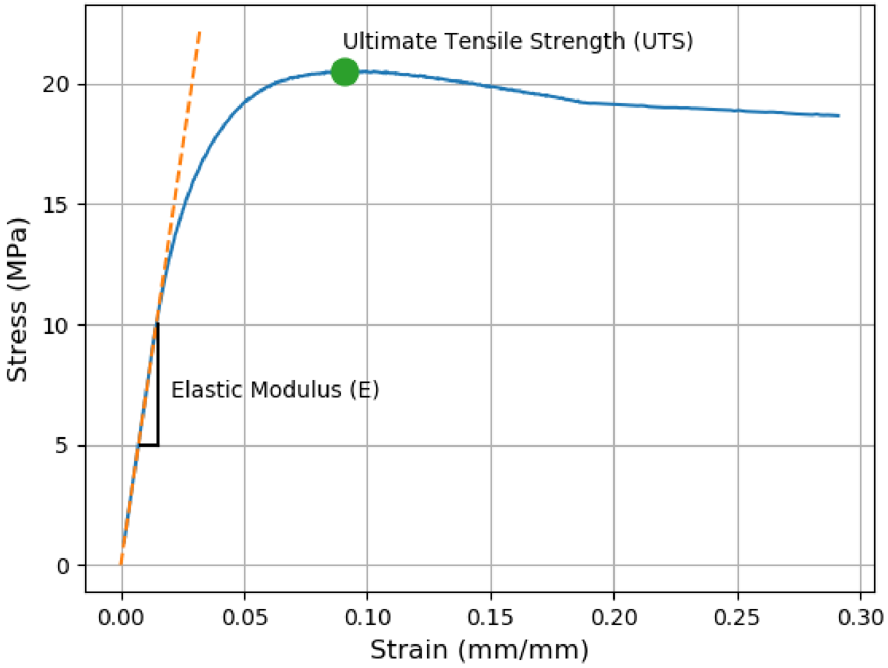
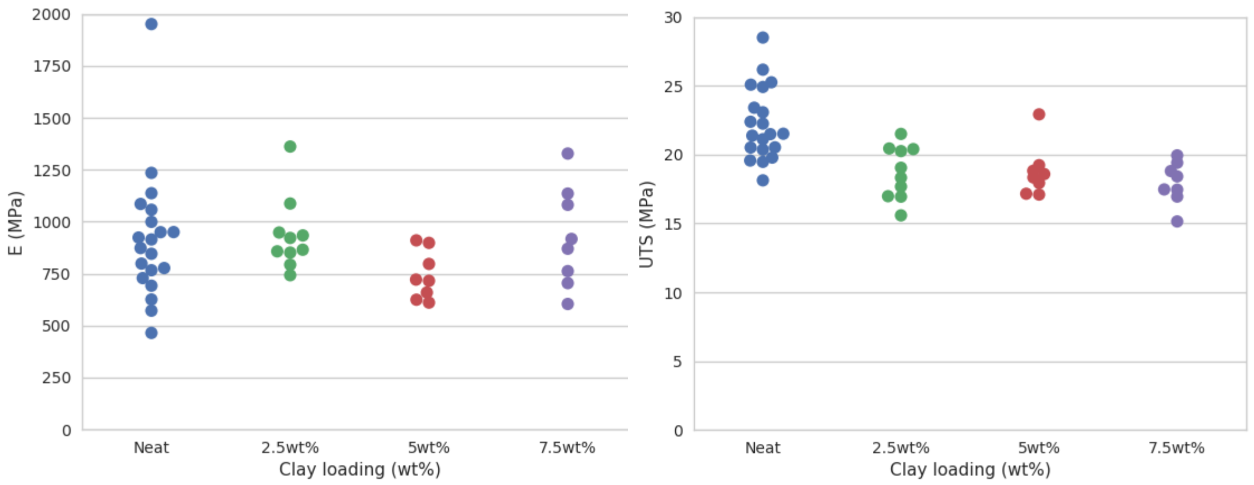


Figure 2: Schematic of a stress-strain curve used to determine the elastic modulus and ultimate tensile strength.



(a) (b)

Figure 3: Scatter plot for the (a) elastic modulus and (b) ultimate tensile strength for the neat HDPE, HDPE-2.5wt% DHT4A, HDPE-5wt% DHT4A and 7.5wt% DHT4A.

Table 1: Mean and standard deviation (SD) for the first experiment. The error between the mean and clay loading is indicated in brackets.

	Neat HDPE	**2.5wt%**	**5wt%**	**7.5wt%**
Elastic Modulus (MPa)				
Mean	917.38	936.25 (+2.06%)	742.18 (-19.1%)	925.27 (+0.86%)
SD	±302.68	±167.44	±108.73	±226.91
Ultimate Tensile Strength (MPa)				
Mean	22.24	18.71 (-15.86%)	18.76 (-15.65%)	17.95 (-19.31%)
SD	±2.56	±1.83	±1.72	±1.43

The elastic modulus ranges, on average, from 500 to 1250 MPa (with the exception of a few outliers). As seen in Figure 3(a) there is no significant change between the neat HDPE and the nanoclay composite. The slight variations between different clay loading cases are not larger than the statistical variations within each case.

The ultimate tensile strength ranges from 25 to 30 MPa. There is a noticeable decrease from the neat HDPE with an introduction of clay. However, there is no substantial difference between the different clay loading cases.

These results do not suggest the existence of an optimum clay loading for this polymer/clay combination.

4. SECOND EXPERIMENT: LOOKING FOR A LIMIT

After the first experiment yielded no optimum result, a change in approach was needed. Instead of searching for the optimum, we decided to rather ask the question:

What is the clay loading limit we can achieve before degradation of the mechanical properties?

To investigate this, an additional set of tests were conducted, this time considering an increased clay loading of 10wt%, 15wt% and 20wt% of DHT4A in the HDPE matrix. The samples were manufactured, tested and processed as described in Section 2 and the resulting stress-strain curves for all the cases considered are shown in Figure 4 (note this includes some of the data shown in Figure 1). The x-axis is plotted to a strain of 0.3, although a few tests were run beyond this level.

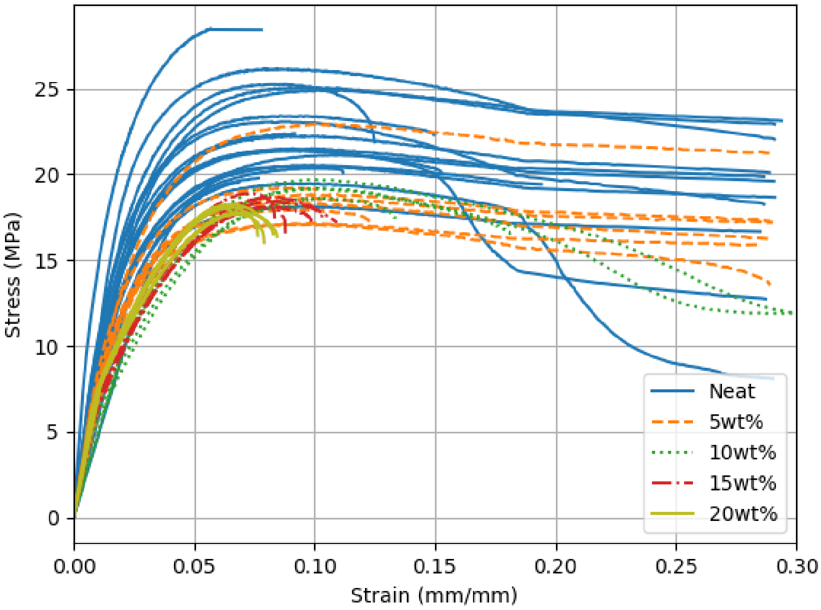
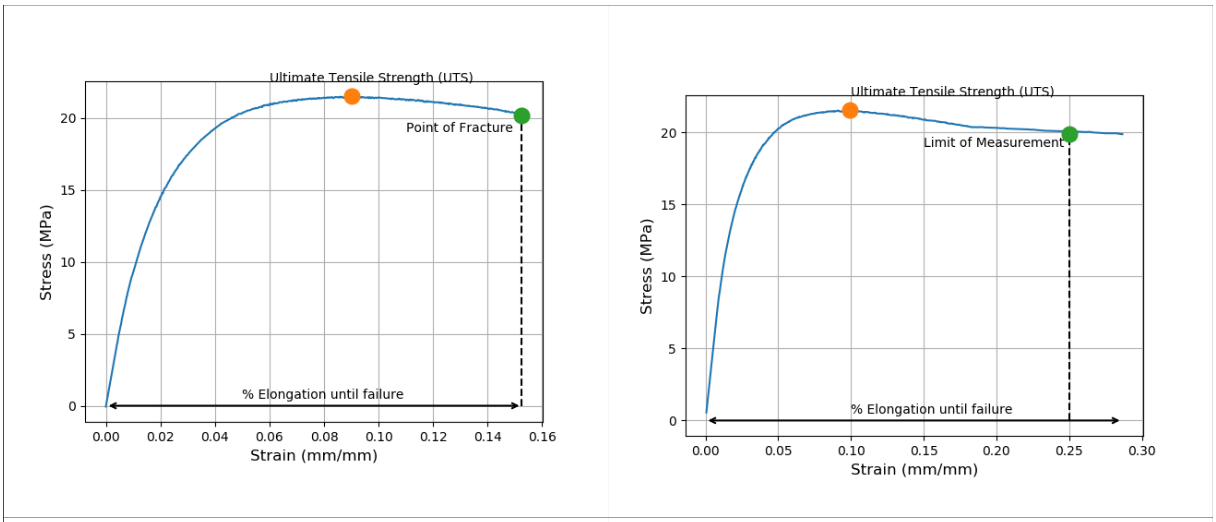


Figure 4: Corrected stress-strain curves from the tensile tests for the second experiment considering HDPE-10wt% DHT4A, HDPE-15wt% DHT4A and 20wt% DHT4A in addition to those for the first experiment.

In evaluating degradation of mechanical properties we want to take note of a transition between ductile behaviour and brittle failure. The percentage elongation to failure characterises this transition. A schematic to determine the ultimate tensile strength and percentage elongation to failure is shown in Figure 5.

In this paper we classify the failure as brittle if the percentage elongation to failure is below 25%. As shown in Figure 5(b), for cases where the percentage elongation to failure is greater than 25%, or where failure had not occured before the tensile test was stopped, the percentage elongation was set to a limit of 25%. These specimens are classified as ductile.

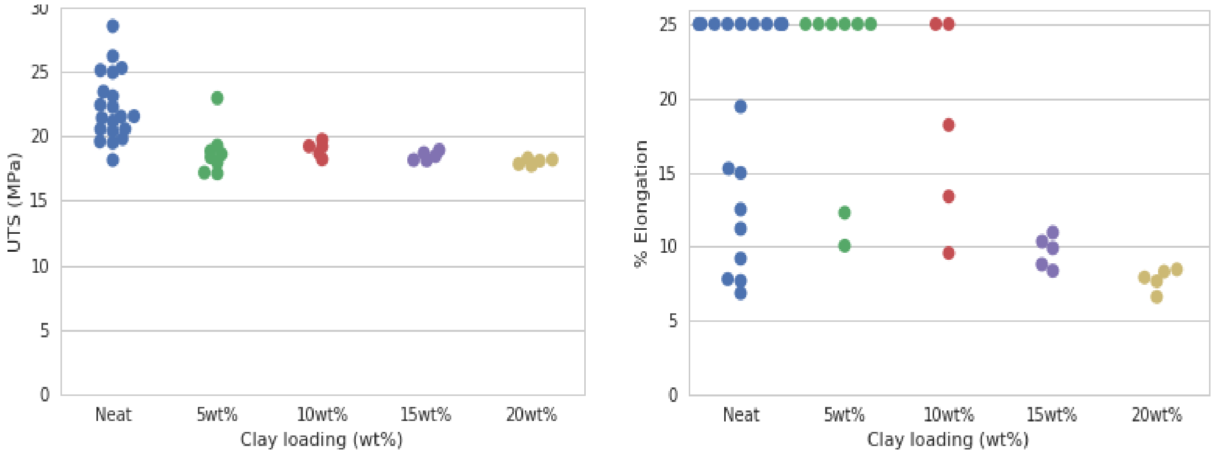
The elastic modulus could not be compared between the two sets of experiments. The first set of experiments measured the displacement using a clip gauge. In the second set the machine displacement was used and a stiffness correction was implemented to approximate the specimen displacement. This approximation significantly impacts the accuracy with which the stiffness of the linear region can be computed. However, it does not have a large impact on larger displacement measurements.



(a) (b)

Figure 5: Schematic of a stress-strain curve used to determine the ultimate tensile strength and %elongation to failure. In (a) the %elongation to failure is calculated at the point of fracture. This is considered a *brittle* failure. In (b) failure has not occurred before the test ends and the %elongation is set to a limit of 25%. This is considered *ductile* behaviour.

The ultimate tensile strength and %elongation are shown in the scatterplots in Figure 6. The additional ultimate tensile strength means and standard deviations are summarised in Table 2. The percentage of all failures which were brittle is presented in Table 3.



(a) (b)

Figure 6: Scatter plot for the (a) elastic modulus and (b) ultimate tensile strength and (c) % elongation for all the clay loading cases considered.

Table 2: Mean and standard deviation (SD) for the second experiment. The error between the mean and clay loading is indicated in brackets.

	Neat HDPE	**10wt%**	**15wt%**	**20wt%**
Ultimate Tensile Strength (MPa)				
Mean	22.24	18.98 (-14.67%)	18.45 (-17.06%)	18.00 (-19.07%)
SD	±2.56	±0.52	±0.31	±0.21

Table 3: Percentage of brittle failures.

Neat HDPE	**5wt%**	**10wt%**	**15wt%**	**20wt%**
45%	25%	60%	100%	100%

As in the first experiment the introduction of any clay into the polymer is observed to slightly reduce the ulitmate tensile strength. However, the amount of clay in the composite appears to have no effect on the strength. It is clear that the strength does not degrade even for significant clay weight loadings.

When we look at the percentage elongation to failure, however, we can see there is substantial degradation for clay weight loadings above 10wt%. While only 45% of the neat HDPE specimens failed in a brittle manner, all of the specimens for the 15wt% and 20wt% had brittle failure very close to UTS.

5. CONCLUSION

This research started with aim of finding the optimum clay loading at which the mechanical properties improved. The elastic modulus and ultimate tensile strength were determined as these properties are indicative of mechanical improvements. However, it was observed that low clay loadings (2.5wt%, 5wt% and 7.5wt%) don’t provide any conclusive results to determine an optimum clay loading. This observation is contrary to literature [1-3] which has indicated that improvements can be obtained with clay loadings of below 5wt%.

This led to a new question in which the aim was to determine the limits of an increase in clay loading, that is, when will this increase start to degrade the mechanical properties. In addition to the ultimate tensile strength, the percentage elongation was determined, as it is a measure of the material ductility and therefore an indicator of material property degradation. UTS for higher clay loadings (10wt%, 15wt% and 20wt%) provided no further insights. However, the percentage elongation at failure showed clearly the onset of material property degradation for clay loadings above 10wt%. This initial observation should be supplemented with other measurements such as toughness and impact resistance in future studies.

These results have highlighted the need for a better approach to designing the experimental studies required to better understand the influence of increased clay loading on mechanical properties. One such approach was developed by Fechter [17] and Fechter et al. [18] where they developed an optimisation approach to determine the ratio of ingredients required to develop a poly(vinyl chloride) compound with a set of desired thermomechanical properties. This approach included an extensive statistical design of experiments to determine the minimum number of experimental studies to be conducted, the data of which was used to develop and validate a predictive model which was used in the optimisation solution. Fechter [17] and Fechter et al. [18] showed the benefits in using a numerical modelling approach to improve the experimental design and can be used as an alternative to the one-factor-at-a-time experimental approach.

In future work, we propose that such an approach is used to determine the kind of experimental studies required to fully characterise and understand the mechanical properties of the HDPE-DHT4A nanocomposite.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the final year undergraduate mechanical engineering students, Chris Parschau (2016), Brian Ellis (2017) and Dane Heymans (2018) who developed and refined the manufacturing and testing methodologies as part of their respective research projects, and for supplying the data used in this study.

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