THE INFLUENCE OF THE NANO-FILLER FILLING AMOUNT ON CREEP PROPERTIES

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This article deals with the issue of the amount of clay type nano-fillers used for the improvement of mechanical properties of the basic material HDPE. These fillers already showed their positive influence on various mechanical properties. This article is primarily concentrated on the percentage of filling, which has the significant influence on these properties and also on the final product price in which is the price of used fillers included. It is desirable to find a suitable concentration of filling of the basic material for the improvement of creep properties. As a percentage of filling the lower concentrations were used which are in the practice more common in connection with the nano-fillers which have a high ratio of shape dimensions.

Polyethylene, creep, nano-material, tensile – creep modulus, concentration

1 INTRODUCTION

The nano-fillers belongs to new composite materials, which show much higher improvement of physical properties in comparison to common composite materials and there is no need to use the high concentration. After addition of the nano-fillers the improvement of hardness, toughness and simultaneously lowering of the weight occur. These materials show also the better resistance against high temperatures and thanks to their structure they block the penetration of the gas and the liquids. Nano-fillers are materials, which contain two or more various components from which at least one is in the form of particles and has a size in units to ten nanometers. Nano-fillers are divided according their dimensions in nanometers. If in nanometers is only one particle, it is in the shape of plates and bullets. If there are two dimension in nanometers, it is carbon nanotubes. Izo-dimensional particles have to be all three particles in nanometers. On the base of layers arrangement of nano-fillers in polymers, there are three types of dispergation of layered silicate in the polymeric matrix. [Bagheri 2018], [Dobransky 2013]

- **Phase-separable silicate** – Layered silicate retains the structure.
- **Intercalated composite –** Between individual layers of the silicate the polymer gets, but the structure is still retained.
- **Exfoliated composite –** The individual parts of silicates are dispersed into whole polymeric matrix and the layered structure disappears.

As indicated in one article [Mofokeng 2018], there is a demonstrable influence of addition of nano-fillers on the original matrix properties. This influence was also demonstrated by [Bagheri 2018] in his article, where concentrated on material testing in the tensile test and the protection against its break. [Behalek 2013], [Kelnar 2015]

2 METHODS

To verify the most suitable concentration of the proposed nano-filler, a system of measurement of creep properties was chosen for the device, which allows measurements on small test bodies according to ISO 527-2 1BA. An injection moulding machine from Arburg was used to produce these test bodies, the basic parameters of which are given in Table 1 and can be seen in Figure 1. [Maghsoud 2018], [Senkerik 2016]

Manufacturer	ARBURG
Model	Allrouder 170U
Clamping force	150 kN
Maximal size of mould	170x170x200 mm
Screw diameter	22 mm
Maximal injection volume	34 cm^3

Table: 1 Machine parameters

Figure 1: ARBURG Allrouder 170U

High-density polyethylene (HDPE) was used as a matrix and was chosen as a suitable for this type of test, particularly from the point of view of creep properties. To the original material in the form of granulate, a filler material was gradually added in the form of a powder with a resulting mass concentration of 1%, 3% and 5%. The thus-prepared material was mixed in a drum mixer which allowed a uniform distribution of the filler throughout the matrix volume.

Parameter	HDPE
Injection temperature	200 °C
Barrel temperatures	195 °C, 190 °C, 180 °C
Mould temperature	40 °C
Injection velocity	40 mm/s
Injection pressure	60 MPa
Cooling time	45 s

Table 2: Process conditions

The prepared granulate and powder mixture was placed in the hopper of the injection moulding machine where the moulding of test bodies was carried out under the injection conditions shown in Table 2.

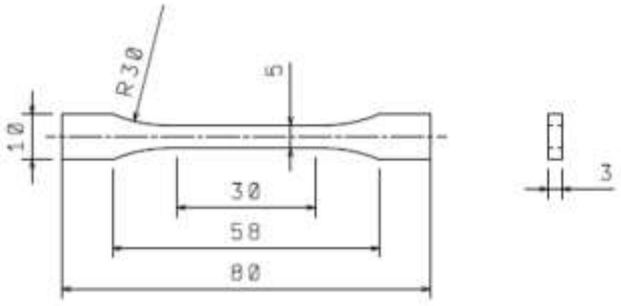

Figure 2: Sample of measurement

The final shape of test bodies shown in Figure 2 was used to clamp into shaped jaws to prevent slippage during the test. The test was then carried out on equipment of its own production under constant conditions. Basic test conditions are displayed in Table 3 below.

Parameter	HDPE
Initial Stress	3.6 MPa
Preload	2 N
Time	24 hours
Temperature	80±0.5 °C

Table 3: Test parameters

In order to maintain the repeatability between the individual measurements and thus to eliminate the measurement error, uniform procedures for the clamping and starting of the test were followed. To determine the load force, it was necessary to perform a series of measurements on the Zwick tearing machine, where the load value for the proportionality was deduced, on the basis of which the load value for the creep test was determined. Due to the different properties of the filled and non-filled material, this value has to be lowered so that there is no overload during the test. This problem occurred primarily at a concentration of 5%.

Figure 3: Clamping of sample

After adjusting the initial voltage, respectively load forces and measurements at the same loading force, the bodies would last for the entire duration of the test and it was therefore possible to determine the total elongation at the end of the test. To assess total sample elongation, the movement of the jaw was recorded vertically using a dial gauge whose values were electronically recorded.

3 RESULTS

The formula 1 below will be used to evaluate and calculate the creep modulus. Using this formula, the value of the creep modulus is calculated based on the relative elongation of the test specimen. In this case, the jaw displacement itself was measured during the test.

$$E_t = \frac{FL_0}{A_0(\Delta L)_t} \quad (1)$$

As can be seen from the initial measured data of the creep curves presented in Figure 4, the effect of the environment is evident, even though the requirement for repeatability of measurement in a high degree was observed during the measurement.

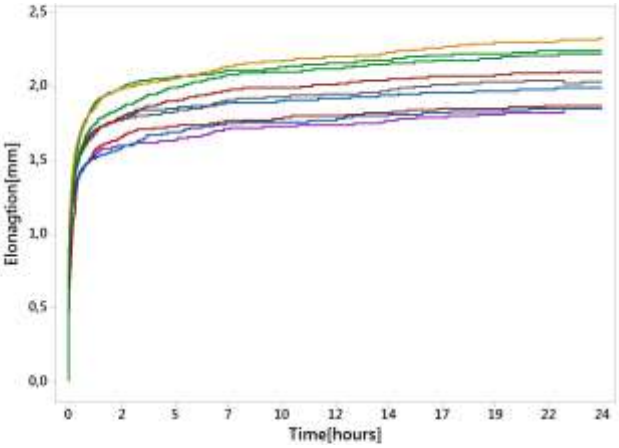

Figure 4: Elongation of non-filled HDPE

The two measurements made in this way clearly indicate the individual flowing areas for non-filled HDPE. The primary part of the creep curve can be seen at a time of 0-1 hour where a sudden stretching of the sample occurs. In the secondary region of the creep curve, which follows the primary region and lasts until the end of the observed time period, creep occurs. If the measurement continues for a longer time, the area of tertiary creep with subsequent tearing of the test body would also ccur. In Figure 5, it is possible to see measurement results for individual specimens of test specimens that were filled with 3% by weight of nanofibers.

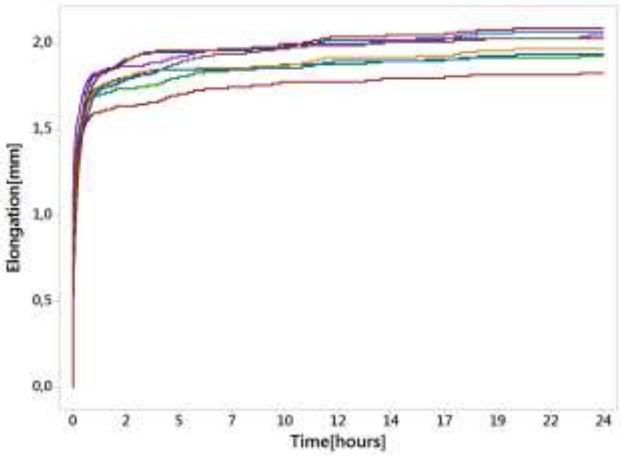

Figure 5: Results of individual measurements for 3% of filling

Compared to the measurement data for pure HDPE, we can see a smaller span over the entire test time by adding the filler to the matrix and positively affecting the creep stability during the test.

In the same manner as for 3% filling, other concentrations of material have been prepared and controlled to demonstrate the same trend of creep stabilization and scaling for individual time slots.

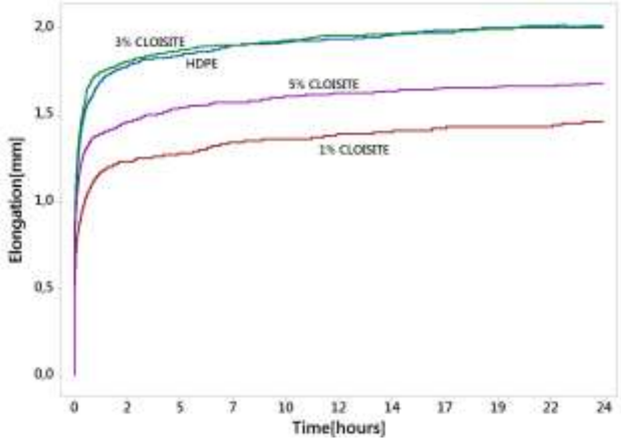

Figure 6: Elongation results for the individual concentration of the fillers

In Figure 6, we can see a comparison of the elongation of the individual percentages of filling. Displayed curves represent always the mean value of the measured data in the form of the median. From the overall view of individual curves, we can see only slight differences in the character of the curves. The differences are then only caused by the actual displacement of the entire Y-axis curve, which is particularly evident in the samples filled with 1% and 5% by weight.

4 DISCUSSION

Due to the methodology of measurement and evaluation of the entire test, which took place on a larger number of samples, a gross error was excluded. Excluding this error and all others that could be caused by the measurement method, it is obvious that the displacement of the individual curves in the vertical direction is due only to the effect of the matrix filling by the applied nano-filler.

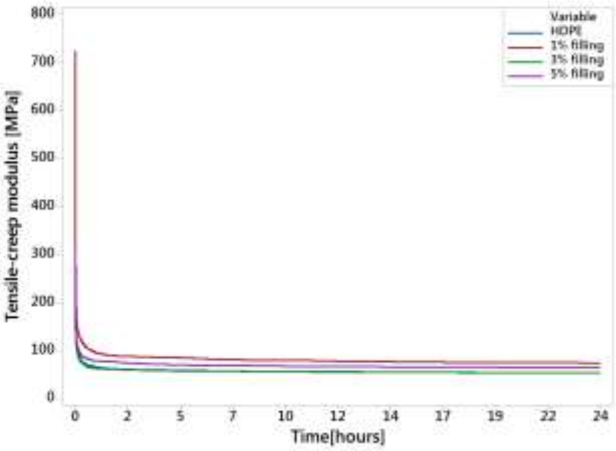

Figure 7: The creep modulus in whole time

The initial curves thus obtained were then recalculated according to Formula 1 to calculate the time-dependent creep modulus. From the simple conversion shown in Figure 7, the first phase of the creep test is evident, where it drops from 700MPa to about 80MPa in a few minutes. Although this drop is particularly interesting from the point of view of the initial load of the sample, but if we want to understand deeply the creep behaviour over a longer period of time, it is not very appropriate. The reason for inappropriate use of the data thus obtained is, in particular, the distortion of the effect of the filling on the creep modulus, the markedly impaired resolution in the final stage of the crunch test.

However, this undesirable effect can be easily eliminated by simply trimming the phases of the cure test phase. Removing this phase, which does not have a significant impact on the overall evaluation of the creep test, will make a significant contribution to the better readability of the other data in the chart, especially the mutual shift of the creep modulus curves.

A sample of this modified graph can be seen in Figure 8. Here, the initial phase of the creep was cut at 0-1 hour. After this treatment, the most significant effect on the creep modulus is at 1% filling. The mean effect of filling can be seen in 5% of the filling, whose impact is roughly half as much as one percent of the filling. The most striking effect on creep properties is a dose of 3%, which is almost identical to the pure matrix and therefore does not have any significant effect in its use.

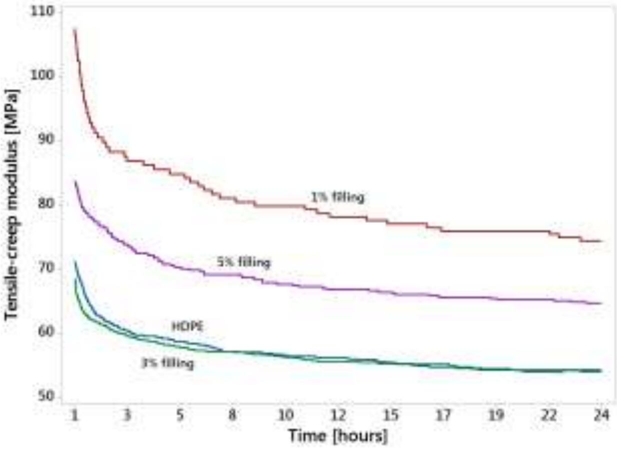

Figure 8: The creep modulus in time 1 – 24 hours

For a more detailed examination of the results listed in Table 4, this effect can be clearly quantified in 18% improvement in 5% filling and 37% improvement in 1% filling. For samples that were filled with 3%, the effect of this filler on the creep properties was not impaired.

	E_t[MPa]	*Improvement [%]*
HDPE	54	-
1% filling	74	+ 37
3% filling	54	0
5% filling	64	+ 18

Table 4: Test parameters

X-ray diffraction analysis (XRD) was also performed. The instrument diffractometric URD 6 was used. [Marinska 2014] Measurements were done in the reflection mode in the 2θ range of 2– 8° at a voltage of 40 kV and current 30 mA with a step size of 0.0263°.

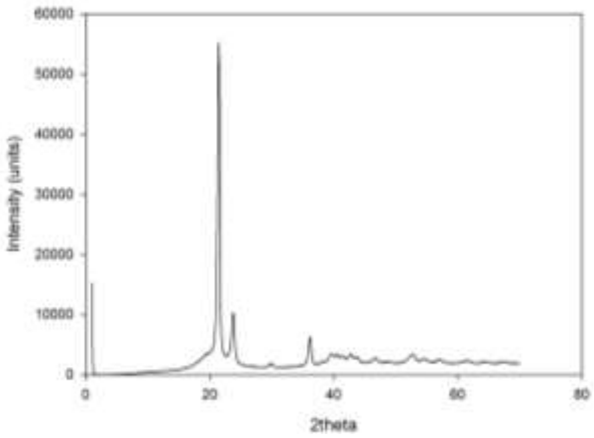

Figure 9: RTG for clear HDPE

In Figure 9, the diffractogram of non-treated HDPE is shown. At the beginning, in the area about 5 value of 2Θ, it is possible to recognize almost direct part of the curve. The next part belongs to the crystal structure of HDPE. For our assessment, the area at the beginning is important, because in this area diffractograms of clay nano-fillers have their peaks.

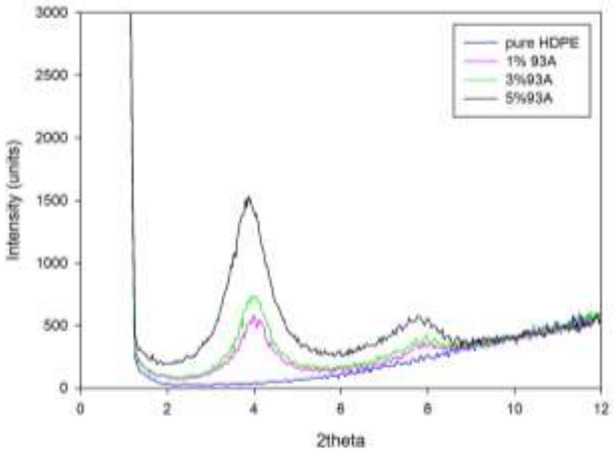

Figure 10: Peaks nano-fillers

This is possible to see in the Figure 10 where in the area of 2 it is possible to see a steep increase of the peak belonging to the rest on non-exfoliated MMT particles. The amount of this is the highest for the filling of 5% wt. The connection of this observation will be discussed later.

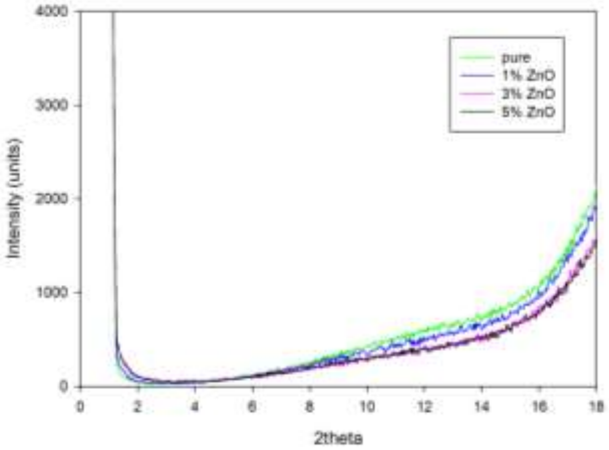

Figure 11: Difractoram of ZnO particles

For the diffractogram of ZnO particles (Figure 11) it is possible to notice that the structure of this type of nano-filler is different, there is no regular layer arrangement thus in difractogam observing the same area as in the previous graph the XRD measurement did not recognize any peaks regardless of which nano-filler concentration has been measured.

5 CONCLUSION

This article was measured to investigate the effect of adding nano-fillers to the matrix of polymeric material made of HDPE. This study builds on earlier publications where this influence has been demonstrated and extends it to study the effect of the amount of nano-fillers thus added. The nature of the nano-fillers, especially their size and area, compared to other fillers, played a significant role here, as shown in individual graphs and tables. The very low concentration of fillers in the order of percentages leads to a marked improvement in the investigated creep properties. At one percent by weight, a significant improvement in the material creep resistance was achieved, by 37% compared to the non-filled material.

When examining the results in more detail, it can also be concluded that increasing cessation of dosing increases even in the creep modulus. Here, the maximum use value for the already mentioned 1% load is confirmed, where the costs associated with adding fillers to the material are effectively utilized.

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