THE INFLUENCE OF THE NETWORK DENSITY ON THE CREEP MODULUS OF RADIATION CROSSLINKED MATERIALS

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This article deals with the creep modulus process comparison of two structurally different materials. These are specific materials HDPE (high density polyethylene) and LDPE (low density polyethylene). These materials were chosen because of their shared monomer from which they were created and differ only in the chain shape. Subsequently these materials were beta radiation crosslinked at six various doses, which changed the inner structure for more complex measurement and the extensive description of the given topic. To obtain data Toledo DMA1 device of the company Metler and earlier data were used for use of knowledge. The results show if the radiation doses efficiency is higher for material with higher or lower density.

KEYWORDS

polyethylene, creep, crosslinked, tensile – creep modulus, modulus, time

1 INTRODUCTION

The present trend of the research and the development of new materials is among one of the most developing area of the science and the technology. The ever greater requirements of product properties make challenging demands on the material, which are produced from. Recent years progress in the area of material engineering enabled development of new devices. Testing devices, which were used in the past, are connected in the one unit with several basic methods or procedures for evaluation of material properties. [Oblak 2016] Testing devices which are used for present research and development dispose of whole range of progressive methods, primarily with a big amount for evaluation of suitability of using material in many applications. These testing methods are mostly know-how of the company, which is protected by the patents. Commercial devices, which are sold as a one unit, represent a significant initial investment in a comparison with devices, which is possible to make them yourself and the data to evaluate relatively cheaply from these measurement. [Kasgoz 2016], [Reznicek 2016]

The material strength is one of the basic quality pointer and the usability under certain conditions. In research practice is possible to mention several different parameters e.g. proportionality limit, elasticity limit, yield point, yield strength, strength at break. All these values have the meaning for the designer. The modulus is the other value which is very often used in the practice. The modulus from ordinary tensile curves significantly affects material properties with one parameter. The practical use of this parameter has delegated use. In other area is possible to see the concept of the creep modulus. [Santilli 2016]

The creep modulus is dependent on the stress and relative elongation. By this easy equation for creep modulus calculation is possible to describe the properties of tested material in time. As has been mentioned, the materials HDPE and LDPE were chosen for the verification of the influence of the chain type. These materials were tested in the pure (non-irradiated) state, which showed the influence of chain construction on the creep modulus. [Manas 2015] These tests were extended with radiation crosslinked samples at doses of 33 kGy, 66 kGy, 99 kGy, 132 kGy, 165 kGy and 198 kGy. These doses were chosen because of practical reasons, these are the most commonly used for modification of these polymer types. From economic point of view it is more interesting method. Irradiated materials have high-tech properties as can be seen in Figure 1.

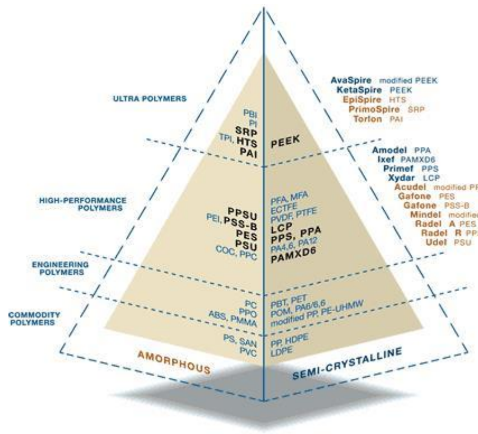

Figure 1. Separation of polymer.

The articles written by Bahramzadeh [Bahramzadeh 2016] and Khonakdar H. [Khonakdar 2003] are also concentrated on the theory of the radiation crosslinking. These scientists studied this influence at different tests in combination with Di-tert butyl cumyl peroxide (BCUP). [Bahramzadeh 2016]

2 METHODS

The aim of this article is to determine the appropriate radiation dose for each material selected so as to allow full use in creep resistance. After the aim determination the hypothesis which says that the higher dose of radiation, the higher degree of crosslinking and thereby the creep resistance, was used.

The crosslinked material was chosen for the measurement of creep properties for the comparison of various options. High density polyethylene from the company DOW (DOW HDPE 25055E) was chosen as the material. Low density polyethylene DOW LDPE 780W was chosen as the second material. Testing samples were made from these materials according to a standard ISO 527-2 1BA for the tensile test.

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 2. ARBURG Allrouder 170U

Process conditions were set according to the manufacturer. During the subsequent quality control of specimens an excessive trough in the stress part of the specimen was detected. This undesirable effect, which could then affect the results of the measurements had to be removed. This removal is performed by changing the moulding process conditions namely by increasing the holding pressure. This pressure was increased by a total of 5 MPa which is reflected in the subsequent quality control of specimens as sufficient.

These samples were moulded by the injection moulding machine ARBURG Allrouder 170U according to the same process conditions.

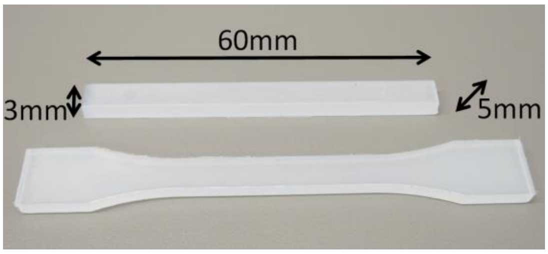

Figure 3. Sample of measurement

The Dynamic mechanical analysis (DMA) is one of the possible methods for measurement of dynamic properties. The samples for this kind of test can be exposed to tension, compression, bending and shear.

The device disposes with the mode TMA, which enables to measure the expansion, creep and relaxation time. The device DMA1 was used for measurement.

Apart from using a standardized sample, it was necessary to use the second part of sample too, because of the reason of restrictions loading forces on one testing device (DMA). As can be seen in Figure 3, this part had the dimensions 5 × 3 × 60 mm. This dimension during clamping proved very useful, mainly because of the need to use special screws for clamping the specimens in the fixed and movable jaws. The length of the test specimen must then be more shortened, so as to allow the use of a closing part of the test chamber.

All these samples were sent to the company B. G. S. to Germany, where the samples were irradiated by doses of 33 kGy, 66 kGy, 99 kGy, 132 kGy, 165 kGy, 198 kGy. The irradiation took place on the Rhodotron electron accelerator, where a radiation dose of 33 kGy was fed at each passage under the radiator. The maximum power of the emitter was 10 MeV. In order to minimize the depth-defect error, all samples were evenly distributed on the belt without stacking. The concurrent measurement followed after irradiation on the device DMA1 from the Company Mettler Toledo.

The most common method of loading sample is cyclic loading. The construction of this device enables to test the samples at various temperatures or in various environments.

Parameter	HDPE	LDPE
Injection temperature	200 °C	190 °C
Barrel temperatures	195 °C, 190 °C, 180 °C	185 °C, 180°C, 170 °C
Mould temperature	40 °C	40 °C
Injection velocity	40 mm/s	40 mm/s
Injection pressure	60 MPa	60 MPa
Cooling time	45 s	40 s

Table 2. Process conditions

The device DMA1 enables the measurement of brittle and though materials, which are suitable for these type of loading, and it enables evaluation in the program STAR. The load modul enables loading from 0.001 to 10 N. The frequency generator enables the variable adjustment of oscillation from 0.001 to 300 Hz.

Parameter	HDPE and LDPE
Voltage Value	7 N
Preload	0.5 N
Time	6 hours
Temperature	22±0.1 °C

Table 3. Test parameters

The total measuring range of deformation (displacement jaws) is ± 1 mm from the middle neutral position sensor. Whole unit can be equipped with an external device for adjusting the test temperature from -190 to 600 °C. Table 3 shows the measurement conditions for HDPE and LDPE.

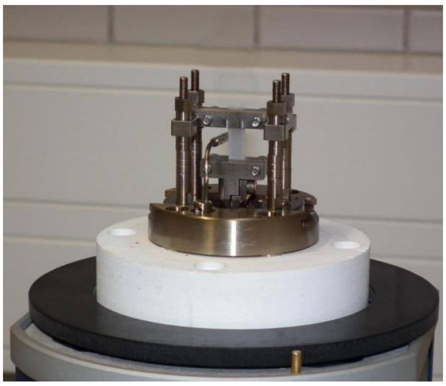

Figure 4. Clamping of sample.

3 RESULTS

Figure 5 shows the values of the minimum and the maximum progress, which have the same trend. The value of the arithmetic average is calculated from all measurements and was used for calculating of creep modulus during the test. This progress is calculated from the equation:

$$E_t = \frac{F L_0}{A_0 (\Delta L)_t} \tag{1}$$

As it is possible to see in equation 1, the creep modulus is calculated from multiplying of force and initial length of tested sample and dividing initial cross-section and current elongation in time t. A simple adjustment of equation leads to result, that the strength values, initial length values and initial cross-section are constants and therefore the dependence of the creep modulus is only inversely proportional to the sample elongation in time. The example of these basic curves of tested sample elongation in time is possible to see in Figure 5. Here are the curves of absolute elongation in µm for pure non-irradiated material HDPE and LDPE.

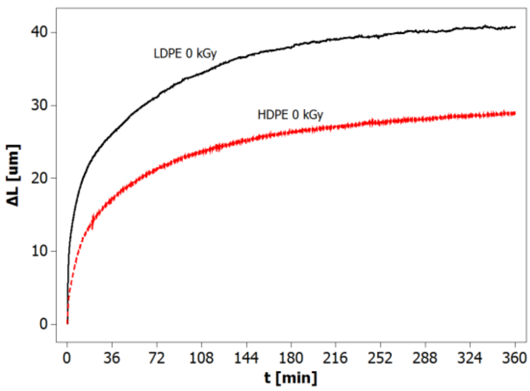

Figure 5. Absolute elongation of HDPE and LDPE

From the measured curves is apparent the dependence of the material structure on creep curves process. For LDPE material is possible to notice a distinctly higher elongation, which is due to the greater distance chains and thus less bond strength between them.

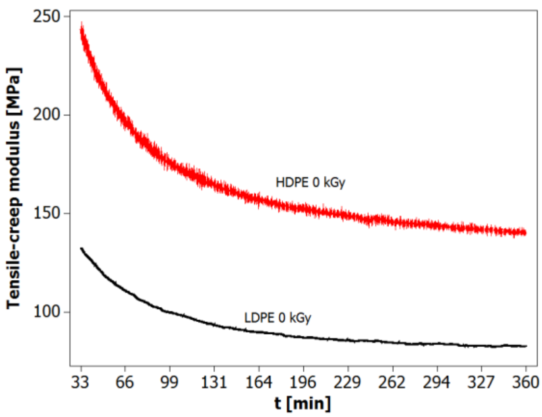

Figure 6. Tensile-creep modulus of HDPE and LDPE

In contrast to this, HDPE has significantly lower elongation when its internal structure is able to resist better to external loads. This dependency corresponds well with other tests e.g. tensile test, which confirms these results.

These results are recalculated according to the equation 1 to tensile-creep modulus, which is possible to see in Figure 6. As has been already mentioned, the creep modulus is the expression inversely proportional in time.

Here is possible to notice a decline in value after the conversion. In the first case shown in Figure 5, values decrease can be seen at time 360 minutes at HDPE by 25 % compared to LDPE. When counting constants results in a recalculation of stress in the tested sample was the difference even higher to the value of 42 % in favor of HDPE.

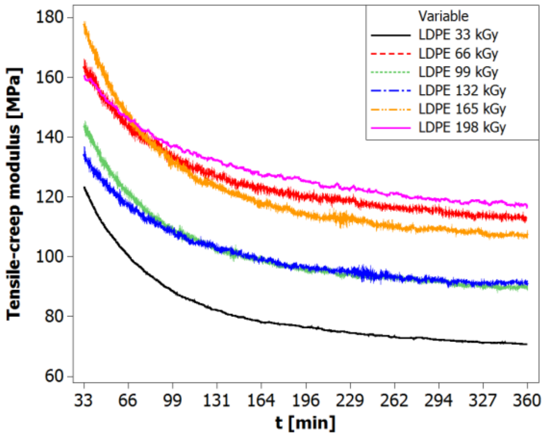

Figure 7. Tensile-creep modulus of irradiated LDPE

Radiation crosslinked materials HDPE and LDPE crosslinked at doses of 33 kGy, 66 kGy, 99 kGy, 132 kGy, 165 kGy and 198 kGy were used for subsequent evaluation the influence of the structure on the creep modulus. LDPE was the first evaluated material, its results of the creep modulus can be seen in Figure 7. From this graph is possible to see the influence of radiation crosslinking on the creep modulus. Contrary to the general assumption that a rising dose should grow creep resistance of the material, this rule is not confirmed. How is visible, the best result of the creep modulus was reached at dose of198 kGy, but the second best result was reached at dose of 66 kGy, which is very interesting primarily from economic point of view.

Similar results can be noted also in HDPE. Here are the benefits mentioned the best dose seems 99 kGy. Although this dose is about half the cost of more expensive than the dose 66 kGy in the material LDPE, wherein, only two passes under the emitter to achieve a desired radiation dose.

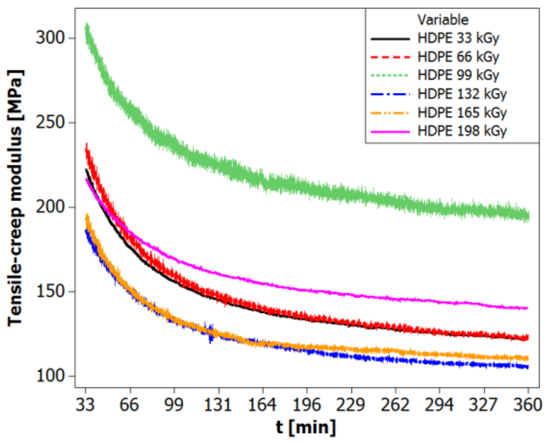

Figure 8. Tensile-creep modulus of irradiated HDPE

From all creep curves is possible to describe the process of these curves. For curves that belong to the material of LDPE can be seen significantly higher rate of elongation in the primary phase, the test and subsequent transition to steady-state flow in the secondary phase. For curves HDPE is the primary extension in the curve with faster slower transition to the secondary part of the curve. While no tests prevent the transition from the secondary part to tertiary. However, for all curve there was a stabilization of elongation, and can thus determine the prospective trend in the future.

4 DISCUSSION

As shown in Manas 2015, the effect of radiation crosslinking on micromechanical properties has been demonstrated as in this article. Also, there has been confirmed the rising resistance to overthrow with a peak in the middle of the range of radiation doses. This effect is due to the process of crosslinking, where the density of the newly created network increases with increasing dose, but at the same time it breaks the original and the newly created network. A certain peak just for HDPE material at a dose of 99kGy. For LDPE, the degradation of the network itself is less, therefore the increase in creep resistance prevails up to 198kGy. Thus, measured data is the most suitable dose of creep radiation for HDPE 99kGy and LDPE of 198kGy. The effect of network growth and degradation can be influenced by the addition of crosslinking agents to facilitate crosslinking, thereby reducing the dose of radiation, which then causes network degradation.

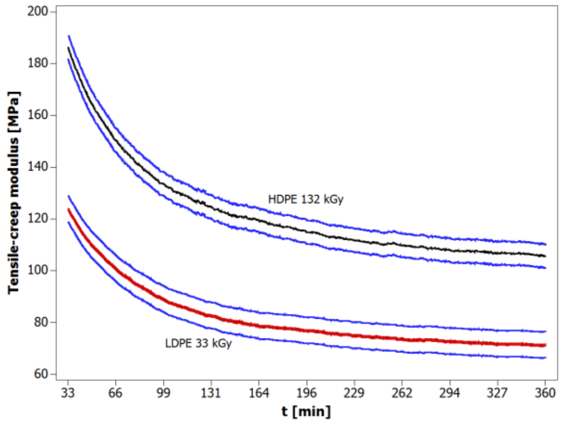

Figure 9. Comparison of the best radiation doses

During comparison of the most suitable radiation doses it is possible to notice the difference not only in the dose itself, which looks as the most suitable, but also the size influence of tensile-ccreep modulus. This difference is mainly caused by the inner structure of each materials and it is possible to see in Figure 9 in time. The difference in the right material and radiation dose selection is possible to deduct up to the value 100 %.

For better interpretation of the results in Figure 9, there is also displayed uncertainty of measurement for the significant dose of radiation. From these borders it is also evident the inconsiderable influence which is caused by the modification using radiation.

Beside this it is possible to notice the smallest influence of radiation doses 33 kGy on material LDPE and the influence of radiation dose 132 kGy on material HDPE. All these differences copy the trend of other measured creep curves. From these reasons and from measured measurements it is possible to state the possibilities of the creep properties improvement in both of materials about approximately the same value and thereby conservation of typical creep characteristics for each material structures.

5 CONCLUSION

This article deals with the influence of network density with radiation crosslinked materials on creep properties. As test materials were chosen HDPE and LDPE, which are based on the same basis. The produced tested samples were then creep tested at room temperature. From the results is possible to find out more pronounced effect for LDPE, the dose of 66 kGy showed a greater influence on the course of creep modulus than a dose of 99 kGy with HDPE. The originally determined hypothesis about proportion of increasing dose and increasing creep resistance was not confirmed and it is possible to recommend only two doses of irradiation in the approximate centre of the spectrum.

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