EFFECT OF TEMPERATURE, MOISTURE AND STRAIN RATE ON LIMITS OF LINEAR VISCOELASTIC BEHAVIOUR OF POLYAMIDE 66 FILLED WITH TiO$_2$ NANOPARTICLES

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ABSTRACT

Deformational behaviour of neat polyamide 66 and filled with TiO$_2$ nanoparticles was investigated in uniaxial tension tests under different conditions. The elastic and yield characteristics are noticeably higher for the filled polymer, while character of the effects of strain rate, temperature and moisture is similar for both materials. Quantitative estimation of the limits of linear viscoelastic behaviour is performed. The stress limit of the filled polymer is higher than that of the neat one. Their values are as lower as higher temperature and moisture content of samples are, and as lower as lower the strain rate is. A concept of the energy threshold of linear viscoelastic behaviour is used for comprehensive characterisation of the limits in a wide range of test conditions. The energy limit is not influenced by the effect of strain rate, temperature and moisture and its value for the filled polymer is higher than that for the neat one. When plotted in the stress-strain axes, the data obtained for each material at different tension rates, temperatures and moisture contents fall on the common curve described by quasi-linear energy approximation. Decrease of the test rate or growth of temperature or moisture content of samples leads only to a shift along the energy curve to lower stress limits and higher strain limits. The higher is the energy value, the wider is the region of linear viscoelastic behaviour. It is quantitatively shown that the limits of applicability of the theory of linear viscoelasticity were noticeably extended by incorporation of the nanoparticles into the neat polymer.

1. INTRODUCTION

The prediction of long-term properties of polymer materials is a key problem. Many studies have been devoted to this peculiar issue, and the theory of linear viscoelasticity (LVE) has been extensively used as a suitable simple model for characterization of material behaviour [1]. However, most of polymers exhibit nonlinear viscoelastic behaviour under certain service conditions [2 - 7]. Then, validity of the proposed model may be limited to particular materials and/or tests conditions. Quantitative data analysis in the nonlinear region is much more difficult than in the linear region and requires a deeper understanding of the underlying processes controlling the mechanical response. Besides, nonlinear models are complex and their application to a specific material would require a high number of various material parameters from independent experiments [2, 4]. This significantly complicates the task of long-term prediction and reduces its reliability. In order to choose an appropriate model for characterizing the long-term viscoelastic behaviour of polymers, it is important to estimate when transition from linear to nonlinear region takes place [8, 9]. Action of temperature and humid atmosphere accelerates relaxation processes in polymers and promotes development of nonlinear effects in them [10, 11]. As a result, a region of applicability of LVE theory narrows. Although some data have been collected on the qualitative estimation of this subject, data on the detailed quantitative characterisation of the limits of LVE and their changes under environmental conditions are lacking.

Polyamides, and polyamide 66 in particular, are widely used as matrices of nanocomposites with various nanofillers due to their thermal stability and stiffness together with the relatively easy processing and moderate cost [12, 13]. However, potential applications of polyamide matrices and related composites are limited by their poor dimensional stability. The development of nanostructured polymer composites gives one an opportunity to improve

some mechanical properties by incorporating of a very small amount of particles of the nano-size. These systems appear as a new class of materials, when compared to conventional filled polymers. For example, it was shown in [14] that incorporation of already 1vol.% of inorganic TiO_2 nanoparticles into polyamide 66 matrix leads to a restriction of motion of polymer macromolecule chains and, in that way, leads to a significant enhancement of creep resistance. In order to characterize the behavior of nanocomposites comprehensively, it is necessary not only to describe its deformation behavior under certain loading/environmental conditions, but also to reveal features in their performance compared to the neat polymer or conventional filled composites. Although it is used to assume most of thermoplastics for a priori nonlinear materials under common service conditions [4 - 6], evaluation of a region, when their behavior remain linear viscoelastic, is still required for comprehensive characterization, choice of an appropriate model and valid prediction of long-term properties of materials [9]. Moreover, by comparing the limits for neat and nanoreinforced polymers at different environmental conditions it makes possible to estimate the effectiveness of application of a certain material under given service conditions.

Besides, it should be pointed out another reason for selecting the particular thermoplastic polymer for the investigation is that it is a commercial polymer with numerous applications in various industrial and automotive areas. Moreover, because of its low T_g (55-60 ^{o}C) [13, 15] extensive deformations and high sensitiveness both to the changes of temperature and humid atmosphere are expected to happen even in conditions close to room conditions.

The aim of the present study is quantitative estimation of the limits of linear viscoelastic behaviour of neat polyamide 66 and filled with TiO_2 nanoparticles under different strain rates, temperature and moisture conditions.

2. EXPERIMENTS

Materials under investigation are neat polyamide 66 (PA) supplied by DuPont, Zytel 101 and PA filled with TiO_2 particles (PA/TiO_2) supplied by Degussa P25. Diameter of the particles is 21 nm and the volume fraction of the nanoparticles is in a range of 1%. The dog-bone samples for tensile tests were cut from appr. 2 mm thick moulded plates according to the German standard DIN-ISO-527-2 1BA. Parallel part of the samples was 30×5 mm^2.

Uniaxial tensile tests were performed on an universal testing machine Zwick 1485 (max. load 250 kN) using a load cell of 10 kN. The tests were performed at room temperature $T = 22$ ^{o}C at five different constant crosshead speeds: 0.5, 2, 10, 20, and 50 mm/min, which correspond to the constant strain rates $\dot{\varepsilon}$: 0.2, 0.8, 4, 8 and 20·10^{-3} s^{-1}, respectively. Gauge extensometer with a span length of 20 mm was used for strain measuring up to strain level of 10%, whereupon strain was measured by displacement of the crosshead only.

Tests at elevated temperatures were performed using a temperature chamber at a crosshead speed 10 mm/min. Test temperatures -20, 0, 35, and 45 ^{o}C did not exceed the glass transition temperature of the materials [15]. Temperature was measured directly near the sample and its variation was in a range ±2 ^{o}C. After temperature in the chamber was stabilised the samples were preconditioned at a corresponding test temperature for at least 20 min more. Samples with different moisture contents were tested at 10 mm/min at room conditions. Samples preliminary dried in an oven at $T = 65$ ^{o}C for more than 3 days were considered as absolutely dry reference samples. The maximal moisture content was achieved by storing the samples in an atmosphere with relative humidity RH = 98% above the saturated salt solution of K_2SO_4 for more than 3 months up to saturation was achieved. Relative moisture content w [%] was

determined as weight gain per weight unit within accuracy 0.05%. Tests at different strain rates and temperatures were performed on samples stored under room humidity.

The secant elastic modulus, E, was calculated in a strain range of 0.05 – 0.5%. The maximum stress achieved in the tests was considered for the yield stress, σ_y, while corresponding strain value, ε_y, for the yield strain. At least three samples were tested at each condition.

3. LIMITS OF LINEAR VISCOELASTIC BEHAVIOUR

There are two necessary and sufficient conditions required for applicability and validity of LVE theory. The first is stress-strain linearity at any fixed time and the second is satisfiability of the linear superposition principles [1]. To determine limits of LVE a fulfilment of these two conditions has to be checked. Besides theoretical aspects, from physical point of view, transition to nonlinearity takes place gradually and there is no standardized procedure for defining the linear limit. It is commonly determined by an arbitrary way by assumption of a certain allowable percentage deviation related with a magnitude of contribution of nonlinear effects to the viscoelastic deformation. The deviation can be evaluated either by stress or strain or other physical variable depending on a method. Usually the deviation amounts to 1-3% that corresponds to a standard deviation of experimental points in the region of LVE [7, 8].

Commonly, the limit of LVE is defined as a level of stress above which actual behaviour of a material deviates from that predicted on the basis of linearity assumptions. Different methods for determining the stress limits from the data of constant strain rate tests are described in [9]. One of the common ways is use of a concept of the rate independent stress – the reduced stress, $\sigma/\dot{\varepsilon}$. In the case of LVE, the dependence $\sigma/\dot{\varepsilon} - \ln t$ is common for every $\dot{\varepsilon}$. Besides, if one presents the data in double logarithmic axes, $\ln \sigma/\dot{\varepsilon} - \ln t$, then this dependence is close to linear in a common region of strain rates. This allows one to determine the stress values uniquely with a fair degree of accuracy [16].

It has to be pointed out, that stress and strain are interrelated time-dependent functions and their limit values are strongly influenced by a test rate and action of temperature (moisture, etc). In order to combine the effects of both stress and strain into one physical function initiating nonlinear behaviour and in such a way to exclude the time effect, it is advisable to use a concept of an energy threshold as a criterion of LVE limit [9, 16, 17]. Analogously to the energy based failure criteria [18, 19], the energy limit of LVE is assumed to be a material characteristic independent of time and action of external factors.

According to the energy approach firstly developed in [17], it is stated that transition from linear to nonlinear viscoelastic behaviour appears when stored deviatoric energy of the material reaches a certain value which is a material property. However, taking into account some simplifications for isotropic materials in simple loading cases (high contribution of the deviatoric energy component compared to the isotropic one and smallness of dissipative energy compared to the stored one) it is suggested to consider the total energy of deformation for the energy threshold of LVE [18]. Then, the general energy relation for the case of quasi-elastic linear approximation is written as following

$$W_{LVE} = C \frac{\sigma_{LVE} \varepsilon_{LVE}}{2} \qquad (1)$$

where σ_{LVE} and ε_{LVE} are limit stress and strain of linear viscoelasticity, respectively. Parameter C characterizes a contribution of time-dependent components to the total energy or, in other words, an amount of deviation from the elastic behavior. A procedure for determining W_{LVE} from the data of tension tests consisted of two steps. First, σ_{LVE} was determined from

the rate independent stress curves at points where deviation from the linear trend, which corresponds to the case of linear viscoelastic behaviour, was about 1% for $\ln \sigma/\dot{\varepsilon}$ value. Then, original σ-ε curves were integrated up to $\sigma = \sigma_{LVE}$ and corresponding values of W_{LVE} were determined. The procedure for evaluating the effects of temperature and moisture was the same.

Before proceeding, it is worth noting that in the present study the nonlinear viscoelastic response does not assume in itself a presence of irreversible deformations, i.e. physical nonlinearity is only considered.

4. RESULTS AND DISCUSSION

Typical stress-strain diagrams of neat PA and PA/TiO$_2$ nanocomposite obtained at different strain rates are shown in Fig. 1. Character of tension diagrams is similar for both materials, while a slight difference in the ultimate and elastic characteristics is observed. The elastic modulus, stress and strain at yield for all test conditions are summarized in Table 1. Incorporation of the nanoparticles leaded to a noticeable increase of the elastic modulus and stress at break, and decrease of the yield strain and strain at break. The effect of strain rate is quite pronounced and similar for both materials: the higher the strain rate, the higher the elastic modulus and stress at yield and the lower the strain at yield.
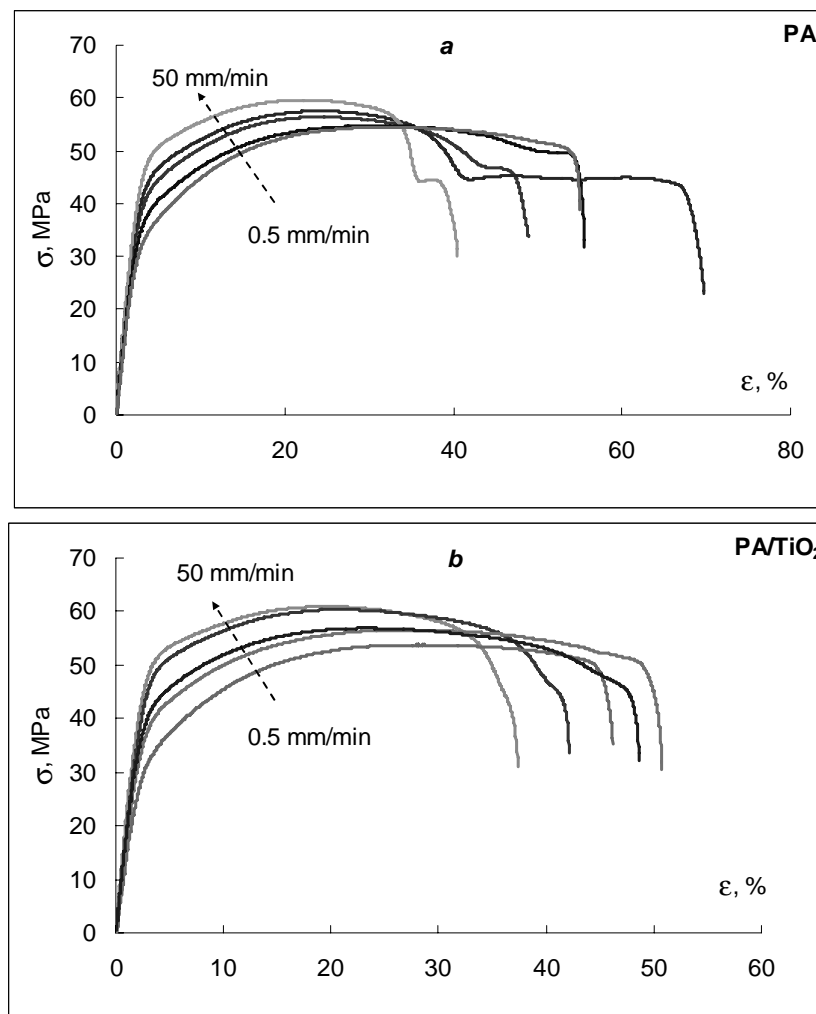

Fig. 1. Stress-strain diagrams of neat PA (*a*) and PA/TiO$_2$ (*b*) at different strain rates.

The diagrams of the rate independent stress are shown in Fig. 2 for neat PA as an example. It is seen, that the individual curves for different strain rates fit on a common curve covering a wide time interval of 3 decades. Deviation of an individual curve from the common curve indicates to a significant contribution of nonlinear effects, i.e. to a transition from linear to nonlinear viscoelastic behavior. The stress limits of LVE, σ_{LVE}, determined at these points are as higher as higher the strain rate is. Difference in σ_{LVE} values for the slowest and fastest test conditions amounts up to 15% for both materials. Presumably, nanoparticles restrict segmental motion of macromolecule chains and hamper development of nonlinear mechanisms of viscoelastic deformation. This appears in increase of σ_{LVE} for about 20% with respect to the neat polymer. The limit stress and strain values, up to which values the deformation behavior generally remains linear viscoelastic are listed in Table 1. It is determined that the corresponding energy values, W_{LVE}, for all strain rates are 0.08 and 0.10 ($\pm$ 0.002) N·mm/mm^3 for neat PA and PA/TiO$_2$, respectively. Thus, the effect of strain rate is slightly pronounced for the limit stresses and strains of LVE, but is not observed for the energy threshold. Besides, W_{LVE} for the nanoreinforced polymer is for 20% higher than that for the neat polymer.
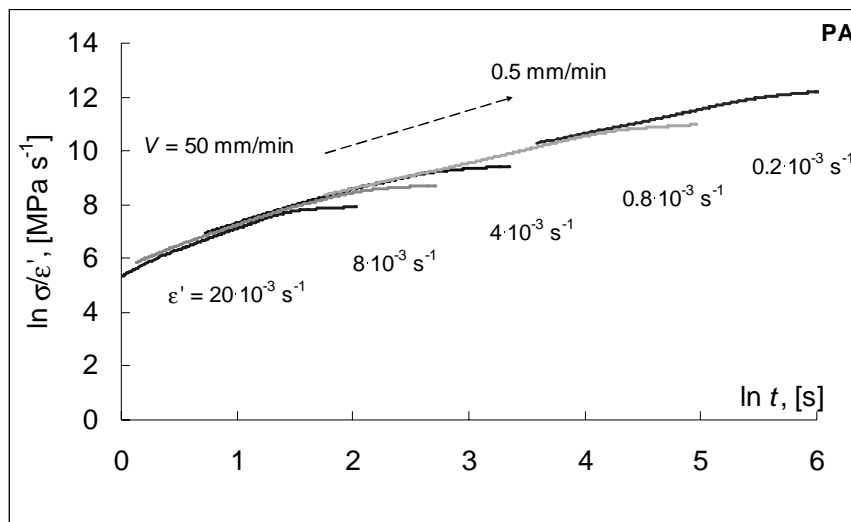

Fig. 2. Diagrams of the rate independent stress of neat PA for different strain rates.

Temperature effect on deformability of the neat and filled polymers was generally similar. Typical tension diagrams of PA/TiO$_2$ at different temperatures are shown in Fig. 3. Character of the tension diagrams significantly changes with an increase of temperature. At low temperatures, the behavior is typical for glassy polymers: high elastic modulus and the ultimate stress, small deformations, and brittle fracture. Obviously, that with a temperature growth the glass transition region is nearly approached. This appears in a drop of the elastic modulus and yield stress, noticeable necking, and large deformations. Temperature increase for 23 °C (from room temperature up to 45 °C) leads to a decrease of the elastic modulus for 50%, decrease of yield stress for 40%, and increase of yield strain for 40%. Temperature decrease for 42 °C (from room temperature down to -20 °C), in turn, leads to an increase of the elastic modulus and yield stress for about 40%, and twofold drop of the yield strain. Values of the corresponding elastic and yield characteristics at different temperatures are shown in Table 1.

Table 1. Elastic, yield and LVE limit characteristics of the materials at different test conditions.

ε', 10^{-3} s^{-1}	T, °C	w, %		E, GPa		σ_y, MPa		ε_y, %		σ_{LVE}, MPa		ε_{LVE}, %		W, N·mm/mm^3	
		PA	PA/TiO$_2$	PA	PA/TiO$_2$	PA	PA/TiO$_2$	PA	PA/TiO$_2$	PA	PA/TiO$_2$	PA	PA/TiO$_2$	PA	PA/TiO$_2$
0.2	22	1.6	1.45	1.38	1.47	54	54	35	28	14.7	16.9	1.02	1.17	0.08	0.1
0.8				1.67	1.76	55	55	30	26	15.9	19.2	0.96	0.99		
4				1.89	2.06	57	57	23	23	16.2	18.8	0.94	1.01		
8				1.82	2.14	58	59	24	21	16.5	19.2	0.92	1.01		
20				1.92	2.11	59	60	22	20	16.7	21.0	0.89	0.91		
4	-20	1.6	1.45	3.42	3.44	95	92	12	10	22.8	26.2	0.65	0.73	0.08	0.1
	0			3.05	3.17	77	81	17	15.5	21.6	25.3	0.68	0.77		
	22			1.89	2.06	57	57	23	23	16.2	18.8	0.94	1.01		
	35			1.44	1.60	47	50	27	27	13.5	17.0	1.04	1.08		
	45			0.98	1.10	34	36	42	42	11.8	13.2	1.25	1.39		
4	22	0	0	2.73	3.21	74	74	12	5	21.8	25.0	0.7	0.77	0.08	0.1
			0.78		2.30		70		16		22.2		0.85		
		1.6	1.45	1.89	2.06	57	57	23	23	16.2	18.8	0.94	1.01		
		8.4	7.6	0.52	0.65	30	32	44	40	8.9	10.1	1.74	1.81		
relative error, %*				7		3		5		1		1		2	

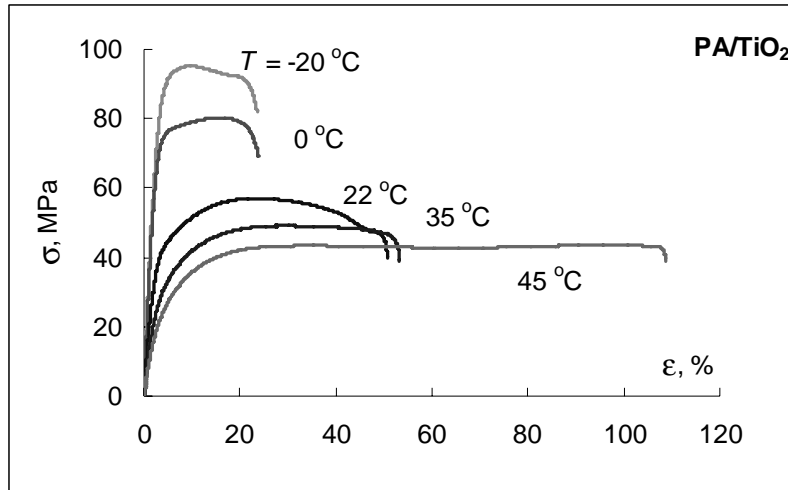* Relative error in different tests did not exceed this value.

Fig. 3. Stress-strain diagrams of PA/TiO$_2$ for different temperatures.

The diagrams of the rate independent stress are shown in Fig. 4 for PA/TiO$_2$. It is seen, that action of temperature does not change character of the curves significantly, but leads only to their shift relative to each other. The limit stresses decrease, but the limit strains increase with a temperature growth for both materials as it is seen from the data of Table 1. The limit stresses of the filled polymer are higher than those of the neat polymer, although magnitude of the temperature effect is the same as demonstrated in Fig. 5. Besides, similarly to the data for different strain rates, it is verified that W_{LVE} values determined at points, where the deviation from the linear curve appears, do not change with a temperature growth and keep within an error interval too.
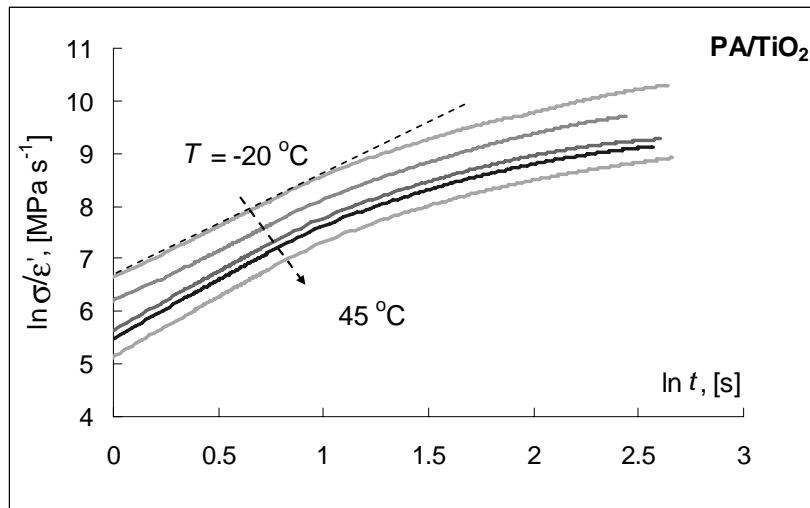

Fig. 4. Diagrams of rate independent stress for different temperatures.

Typical stress-strain diagrams of PA/TiO$_2$ samples with different moisture contents are shown in Fig. 6. The effect of moisture on deformation behavior of the materials is very high. Sorbed moisture leads to a plastification and "softening" of the materials that appears in dramatic changes of the elastic and yield characteristics (see Table 1). Presence of appr. 8% of moisture in materials leads to a reduce of the elastic modulus and yield stress for 80 and 60%, respectively. An extremely high increase of the yield strain is also observed. Sorbed moisture leads to an essential decrease of the limit stress too: σ_{LVE} of maximally moistened and dry samples differ for more than 50%. At the same time, W_{LVE} values are not influenced by sorbed moisture.
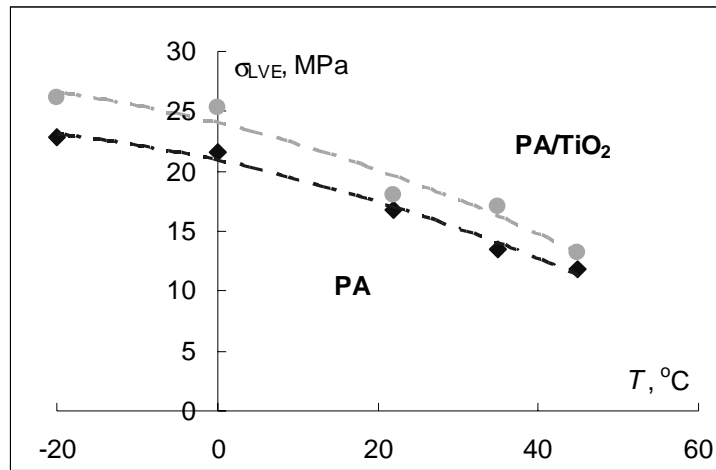
Fig. 5. Temperature dependence of the limit stress of LVE.

Let us present the limits of LVE behavior in stress-strain axes. The results are shown in Fig. 7 for the neat and filled polymers. It is seen that the data obtained at different tension rates, temperatures, and moisture contents of samples finely fit to a common curve for each material. This curve represents a quasi-linear energy approximation Eq.(1) with parameter C = 1.07 (note, that C is the same and close to a unit for both materials, since tension curves in the region of LVE are practically linear for all test conditions).
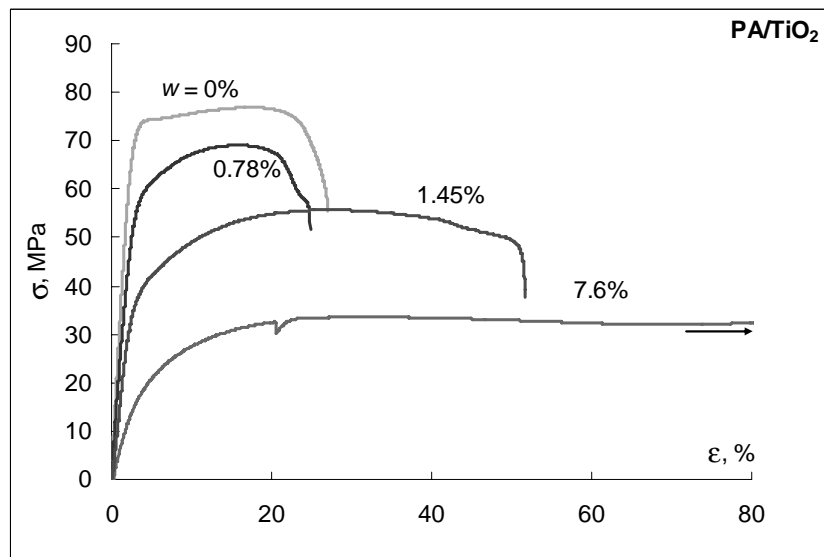

Fig. 6. Stress-strain diagrams of PA/TiO$_2$ samples with different moisture contents.

Decrease of the test rate or growth of temperature or moisture content of samples leads only to a shift along the energy curve to lower stress limits and higher strain limits. Transition from linear to nonlinear viscoelasticity takes place when this curve will be crossed at given loading conditions. Obviously, the higher the energy value, the wider the region of applicability of LVE theory. Thus, it is quantitatively shown that incorporation of TiO$_2$ nanoparticles into the neat polyamide leads to an extension of the limits of applicability of LVE theory and W_{LVE} of the filled polymer is for 20% higher than that of the neat one. In other words, viscoelastic behaviour of the nanoreinforced polymer remains linear at higher stresses and strains that is in agreement with the creep data [5, 6]. Moreover, it is shown that W_{LVE} values are not influenced by the effect of strain rate, temperature and moisture. Thus, the energy limit can be considered as the material characteristic at least in the region of test conditions considered within the study.

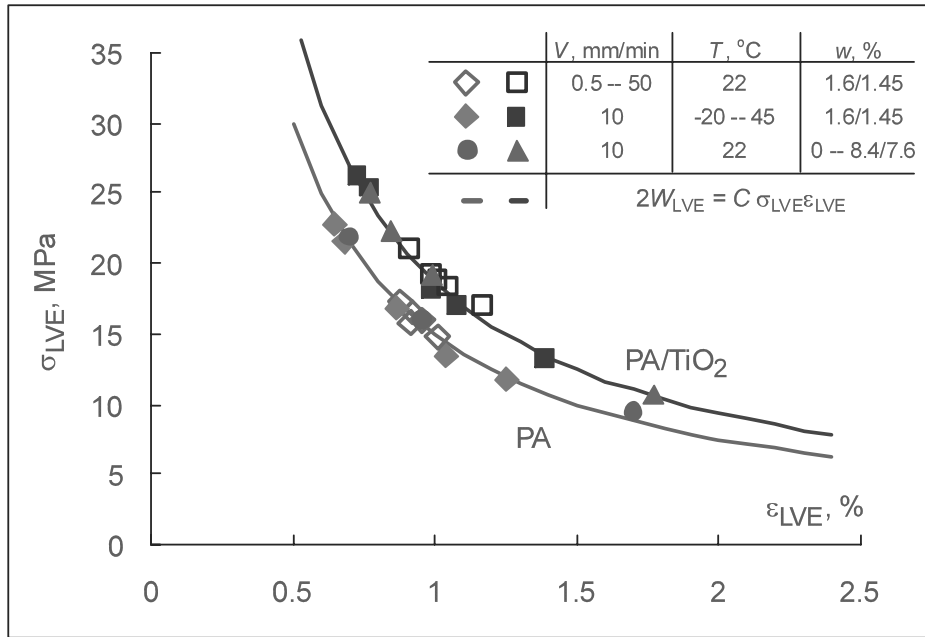|		V, mm/min	T, °C	w, %
◇	□	0.5 -- 50	22	1.6/1.45
◆	■	10	-20 -- 45	1.6/1.45
●	▲	10	22	0 -- 8.4/7.6
–	–	$2W_{LVE} = C\,\sigma_{LVE}\varepsilon_{LVE}$		

Fig. 7. Limits of LVE determined in tests at different strain rates, temperatures and moisture conditions. Symbols are experimental data, solid lines are calculations.

Use of the energy approach gives one a possibility of comparing the regions of linear viscoelastic behaviour of polymers under different test conditions. This will allow one to choose appropriate test conditions for reliable modeling of deformation behavior for a certain material; to simplify the prediction procedure and raise its accuracy; to reduce a number of the required tests for general characterization of long-term behavior covering a wide interval of test time, temperatures, moisture contents etc.

6. CONCLUSIONS

Deformational behaviour of neat polyamide 66 and filled with TiO_2 nanoparticles was investigated in uniaxial tension tests under different test conditions. The elastic and yield characteristics are noticeably higher for the filled polymer, while character of the effects of strain rate, temperature and moisture is similar for both materials. Quantitative estimation of the limits of linear viscoelastic behaviour is performed. The stress limits were determined by constructing the rate-independent stress diagrams. Their values are as lower as higher temperature and moisture content of samples are, and as lower as lower the strain rate is. The stress limit of the filled polymer is higher than that of the neat one. A concept of the energy threshold of linear viscoelastic behaviour is used for comprehensive characterisation of the limits in a wide range of test conditions. It is determined that the energy limit is not influenced by the effect of strain rate, temperature and moisture and its value for the filled polymer is higher than that for the neat one. When plotted in the stress-strain axes, the data obtained for each material at different tension rates, temperatures and moisture contents fall on the common curve described by quasi-linear energy approximation. Decrease of the test rate or growth of temperature or moisture content of samples leads only to a shift along the energy curve to lower stress limits and higher strain limits. The higher the energy value, the wider the region of linear viscoelastic behaviour. It is quantitatively shown that the limits of applicability of the theory of linear viscoelasticity are noticeably extended by incorporation of the nanoparticles into the neat polymer.

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