Andrej Demšar,
Vili Bukošek,
Alenka Kljun

University of Ljubljana,
Faculty of Natural Sciences and Engineering,
Department of Textiles,
Snezniska 5, 1000 Ljubljana, Slovenia
E-mail: andrej.demsar@ntf.uni-lj.si

Dynamic Mechanical Analysis of Nylon 66 Cord Yarns

Abstract
The viscoelastic properties of three different nylon cord yarns were analysed, and the dependence on the temperature of the annealing process was examined with the use of dynamic mechanical analysis (DMA). The research showed that the initial moduli of temperature-treated nylon cord yarns in a clamped state decrease after temperature treatment. The results also demonstrated that it is recommended to perform the vulcanisation of rubber composites at temperatures between 160 ℃ and 180 ℃, where segmental motion is at minima. Likewise, it is not recommended to mechanically load cord yarns between 90 ℃ to 130 ℃. This study demonstrated that DMA can be used to analyse the viscoelastic properties of cord yarns, which enables us to detect subtle differences between different materials and to interpret changes in the material at a supermolecular level. DMA can aid in determining optimal process conditions and materials.

Key words: *nylon, cord yarns, dynamic mechanical analysis, viscoelastic properties.*

■ Introduction

Synthetic yarns made from semi crystalline polymers, such as nylon, are used in a variety of applications ranging from textiles to the reinforcement of composites. Today, the consumption of composite materials, including rubber composites, is constantly increasing. Rubber composites [1] are composed of a load-bearing core (which is usually made of yarn) surrounded by a rubber matrix. The physical, mechanical and dynamic properties of rubber composites typically vary based on the intended application. Different rubber composite products require different load bearing cores with various physical and mechanical properties. Cord yarns [1] can be used as load-bearing cores in rubber composites, as well as in applications such as transmission belts, conveyer belts, and tires. Cord yarns are produced using a combination of spinning synthetic polymer filaments, stretching, plying, twisting, after-stretching, fixation and treatment with special agents to achieve better adhesion between rubber and fabric. Furthermore, a specific procedure can be tailored to achieve the properties of the end material required. The conditions under which rubber composites are produced and used (e.g. temperature, pressure, time) can affect the physical and mechanical properties (e.g. modulus, elongation, tensile strength, elastic recovery) of the textile portion of the composite. In many applications heat exposure occurs in at least one stage of the manufacturing process. It is desirable to minimise these changes so that an optimum performance can be realised from the textile reinforcements. For successful use as a reinforcement material, a well-oriented fibre structure is necessary to realise sufficient tensile properties and to remove large irreversible deformations inherent in un-oriented flexible polymers. The typical production process for nylon yarns is complex and time dependent due to the crystallisation, orientation and stress relaxation phenomena taking part in it. To achieve a well-oriented structure, additional hot drawing of the spun fibre is necessary to achieve the fibre properties desired (e.g. modulus, tenacity, elongation). During drawing, an increase in amorphous and crystalline orientation is observed. The consequence of a lack of the complete reorientation of macromolecules during the production process of yarns is the forced energetic state of the macromolecules, giving rise to internal stresses and, thus, thermodynamic instability. The macromolecules tend to reach a more thermodynamically stable state, which is achieved when the yarns are treated at elevated temperatures under tension (heat setting). By appropriately selecting the heat setting conditions, the general physical properties of the resulting cord can be adjusted to the level required. During the heat setting process, the super-molecular structure of cord yarn is stabilised, reducing the potential for subsequent property changes upon additional heat exposure. The thermal stability of yarns is important because they are subjected to a variety of thermal conditions during their manufacture and application. The annealing process (time, temperature and the stress-controlled yarn production stage) can provide enough energy and time for the system to move towards a state of equilibrium (lowest free energy) under a given set of conditions.

The super-molecular structure of nylon yarns and its influence on their behaviour has been extensively studied by various authors [2 - 18] who have all contributed to a better understanding of the production, structure, properties and application of nylon yarns.

The deformation and recovery characteristics of textile products upon the application or removal of forces are of great importance. To analyse these characteristics, dynamic mechanical analysis (DMA) can be used. Although DMA has been extensively used on a variety of different materials, little work has been done on cord yarns. The purpose of the following work is to determine the dynamic viscoelastic properties of commercially available nylon 66 cord yarns and their dependence on the manufacturing process and application conditions, specifically regarding the temperature applied and the state. Dynamic mechanical analysis (DMA) was used to analyse dynamic viscoelastic properties, such as the storage modulus - E', the loss modulus - E", tan δ and the glass transition temperature - Tg. This research was meant to answer the question: what changes take place in nylon 66 cord yarns at a super-molecular level after temperature treatment, and additionally what is the extent of these changes.

■ Experimental

Materials

The three different nylon cord yarns (PA66) analysed in this study come from a rubber composites producer who did not give any additional information about the technology of cord yarn production or properties. Raw cord yarn samples

Demšar A., Bukošek V., Kljun A.; Dynamic Mechanical Analysis of Nylon 66 Cord Yarns.
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29

Table 1. *Cord yarn properties: number of filaments in cord yarn – $n_{filaments}$, linear density – Tt, yarn twist, breaking stress - σ_{br}, breaking strain - ε_{br}, Young modulus – E, stress at yield point - σ_y, strain at yield point - ε_y, and modulus at yield point - E_y.*

Sample	$n_{filaments}$, /	Tt, tex	Twist, t.p.m	σ_{br}, N/tex	ε_{br}, %	E, N/tex	σ_y, N/tex	ε_y, %	E_y, N/tex
A	216 x 2	319,9	400	0.49	20.0	2.00	0.046	2.80	1.34
B	204 x 2	319,7	308	0.69	24.8	2.54	0.042	1.98	1.80
C	204 x 2	327,0	308	0.65	23.6	2.34	0.037	1.80	2.04

were designated as A, B and C. Some raw cord yarn properties are presented in **Table 1**. Additionally, the samples were temperature treated, and annealing conditions (temperature, time and state) were selected to simulate those of rubber composite production and applications. The yarns were temperature treated in an electric oven at three different temperatures: 150 °C, 170 °C and 190 °C, in a clamped state for 15 minutes. The yarns were stored in room conditions prior to and after temperature treatment.

Methods

Dynamic mechanical analysis (DMA) is an analytical technique used to study the dynamic viscoelastic nature of polymers, composites and other materials [19]. The method is very sensitive to segmental mobility and energetic transitions in materials that are usually temperature and time dependent. In DMA, dynamic mechanical properties, such as the modulus, glass transition temperature (Tg), sub- Tg transitions (e.g. beta, gamma, and delta transitions) in polymers, stiffness, damping, etc., are measured as a function of the temperature and frequency. DMA can be used to predict material behaviour over a wide frequency and time interval and allows for the possibility of analysing the influence of filling materials, additives and technological processes on the dynamic viscoelastic properties of the material. Using DMA, dimension stability, creep, relaxation of stresses, thermo mechanical properties, and other properties can be measured.

With this technique the sample undergoes repeated small-amplitude deformations caused by sinusoidal, cyclic oscillation. By measuring the time lag in the displacement compared to the force applied, it is possible to determine the dynamic viscoelastic properties of the material. The time lag is reported as a phase lag, which is an angle - tan delta (the tangent of the phase lag). For viscoelastic materials the angle is between $0° < \delta < 90°$. The ratio of the sinusoidal stress change and deformation is referred to as com-

plex modulus E* (E* = E′ + iE″), which contains the elastic modulus E' (storage modulus - measure of the energy stored elastically, component in phase) and the loss modulus E'' (loss modulus - measure of the energy lost as heat, a component that is 90° out of phase). Modulus E' represents the real elastic component of a material with stored energy. Modulus E'' represents the imaginary component of a material and describes the dissipated thermal energy and viscous behaviour of the material. The loss factor is defined as tan δ = E″/E′, where δ is the angle between the in-phase and out-of-phase components of the module in a cyclic motion. Tan δ is a measure of dissipated deformation energy in the form of heat.

DMA tests were carried out on TA equipment - DMA Q800 (USA) [20], with a controlled gas cooling accessory (GCA). The samples were heated from −10 °C to 260 °C at a constant rate of 3 °C/min. During heating, the test specimen was deformed (oscillated) at a constant amplitude of 10 μm at a single frequency of 1 Hz. The mechanical properties were then measured. The strain deformation values were sufficiently small (< 0.10%) to ensure that the mechanical response of the specimens was within the linear viscoelastic range.

■ **Results and discussion**

Comparison of different cord yarns

In *Figures 1 – 3*, the temperature dependence of the storage modulus (E'), the loss modulus (E'') and tan δ of the cord yarns are presented in the region of linear viscoelasticity and deformation change.

In *Figure 1* the dynamic mechanical properties of sample A are presented as a function of the temperature. A well-defined drop in the storage modulus can be seen between 21 °C - 60 °C, accompanied by increased segmental mobility, which is suggested by the shoulder on the tan δ curve at 62 °C and the increase in loss modulus E'', with a maximum at 47 °C. This behaviour shows that the

transition is accompanied by the emission of heat and loss of elastic properties.

A second decrease in the storage modulus of cord A, accompanied by an increase in softness, can be observed between 97 °C and 130 °C. Due to this drop in the storage modulus, a shoulder can be observed on the loss modulus curve (at 105 °C) as well as a maximum on the tan δ curve at 115 °C, corresponding to increased segmental mobility and Tg transition. A small increase in the storage modulus can be seen from 200 °C to 238 °C. An increase in segmental mobility can clearly be seen as maxima on the tan δ curve (at 218 °C) and loss modulus curve (at 223 °C), which can be attributed to the impregnation system on cord yarn.

Heating sample A to 260 °C caused a 24.77% contraction, from 60 °C to 185 °C - a 9.47% contraction, and from 185 °C to 260 °C it contracted by 15.31%.

In *Figure 2* the dynamic mechanical properties of sample B are presented as a function of the temperature. The glass transition temperature can be seen at 98 °C, and a rapid decrease in the storage modulus is observed between 68 °C and 119 °C. The glass transition temperature on the storage modulus curve is accompanied by maxima on the loss modulus curve (at 84 °C) and on the tan δ curve (at 105.6 °C).

Above the glass transition temperature and below the melting temperature at 256 °C, the two moduli decrease, and the softness of the cord increases. The tan δ curve shows the increased mobility of molecular segments above 180 °C and below the melting temperature, with a poorly defined maximum at 239 °C which is accompanied by small maxima on curve E''. Near the melting point, the tan δ curve increases very rapidly, which is again a consequence of the marked increase in molecular segment mobility (viscous component).

Heating cord sample B to 260 °C caused a 24.84% contraction. A more pronounced contraction was observed at 80 °C, and by 190 °C the sample had contracted by 6.73%. From 190 °C to 256 °C the sample contracted by an additional 18.11%.

Figure 3 shows the dynamic mechanical properties of sample C as a function of the temperature. A decrease in modulus E' is accompanied by an increase in seg-
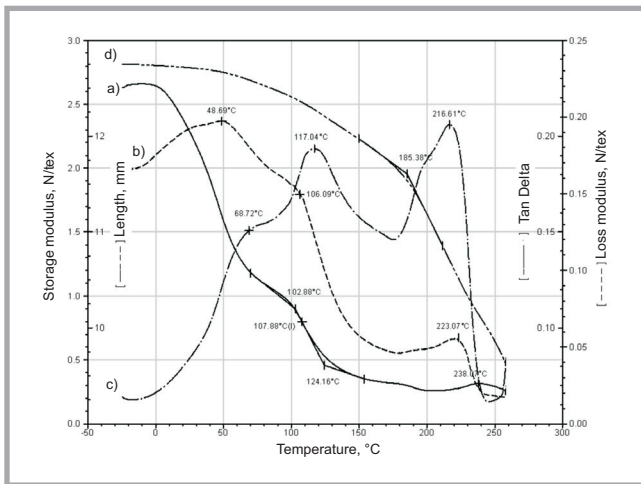
Figure 1. *Dynamic mechanical analysis of nylon 6.6 cord – sample A; a) storage modulus [——], b) loss modulus [– – –], c) length [—— – –], d) tan delta [—— ·].*
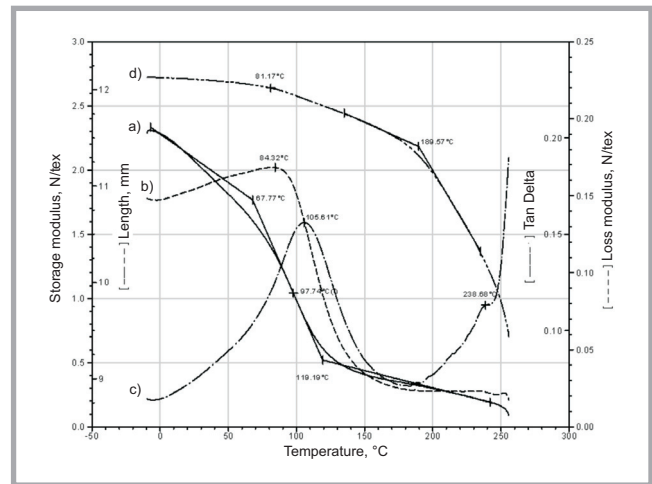

Figure 2. *Dynamic mechanical analysis of nylon 6.6 cord – sample B; a) storage modulus [——], b) loss modulus [– – –], c) length [—— – –], d) tan delta [—— ·].*
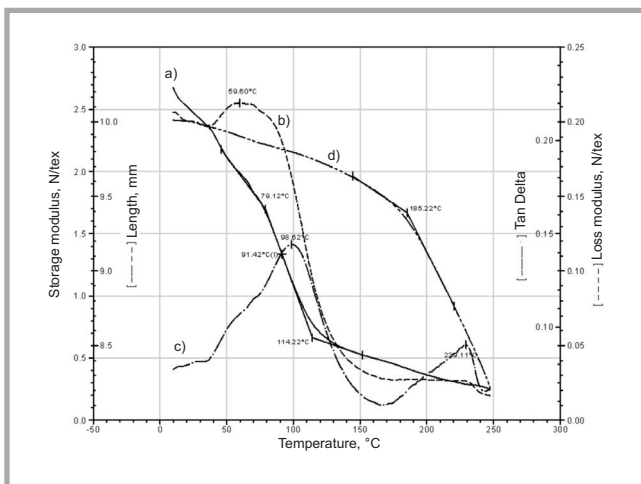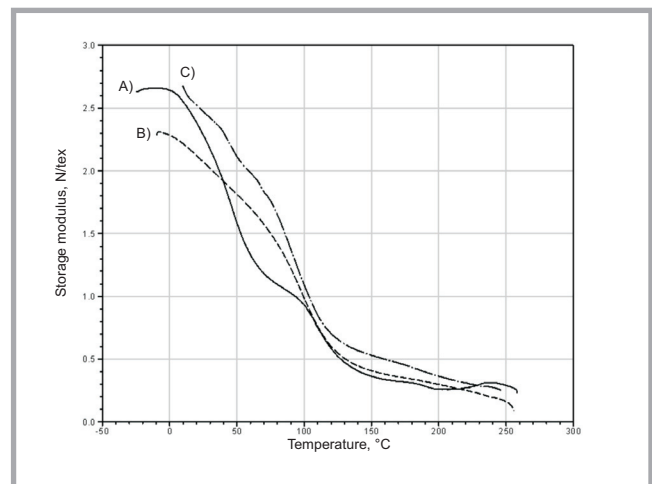

Figure 3. *Dynamic mechanical analysis of nylon 6.6 cord – sample C; a) storage modulus [——], b) loss modulus [– – –], c) length [—— – –], d) tan delta [—— ·].*

Figure 4. *Storage modulus E' of samples A, B and C.*

mental mobility, which can be seen as a shoulder on the tan δ curve at 70 °C. Loss modulus E'' concurrently increases, with the maxima at 60 °C, which can be explained as an accompaniment to transition by heat emission and loss of elastic properties.

A second marked decrease in the storage modulus and a concomitant increase in the softness of the material can be seen between 79 °C and 114 °C. This is accompanied by a marked maximum on the tan δ curve at 99 °C, which corresponds to increased molecular segment mobility and Tg transition. After glass transition, the storage modulus and loss modulus decrease. Increased molecular mobility can be observed on the tan δ curve between 165 °C and the maximum at 229 °C (on the E'' curve at 228 °C), which may be a

consequence of the impregnation system applied to the cord yarn.

The heating of sample C caused a contraction of 23.45%. The contraction monotonically increased until 178 °C, where the contraction was 5.91%. Above 178 °C and below the melting temperature, the contraction was 17.54%.

Comparison of the dynamic mechanical properties of the three different nylon 66 cord yarns shows that the cord yarns have, as expected, relatively similar properties, but different behaviour in different temperature regions. In **Figure 4** a comparison is presented of the storage moduli of all three cord yarns with respect to the temperature. It can be seen that sample C achieved the highest value of storage modulus E'. At room temperature the differences in moduli were between

2,3 N/tex and 2,7 N/tex in the decreasing order C, A, B. In the temperature interval from 50 °C to 100 °C, differences between samples can still be seen because of the quick decrease in the storage modulus of sample A, in the sequence C, B, A.

Above 100 °C the sequence of the decreasing storage moduli of the samples remains the same; however, the differences between storage moduli are less significant, especially between samples A and B. The storage moduli of samples B and C decrease relatively evenly, with the fastest decreases occurring between 68 °C and 119 °C (sample B) and between 79 °C and 114 °C (sample C). For sample A, two regions of a decrease in the storage modulus can be observed. The first decrease in the storage modulus is below 60 °C, and in the second region it is between 100 °C to 130 °C. The first
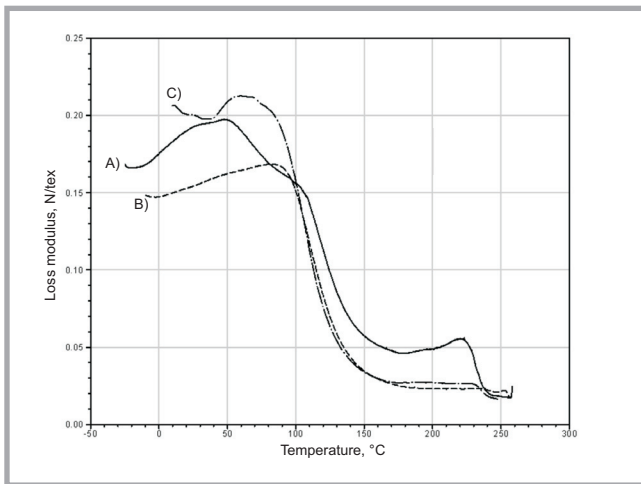
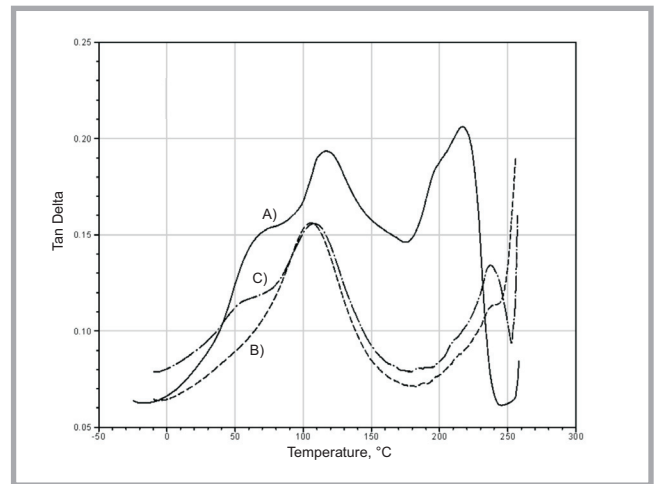*Figure 5. Loss modulus E" of samples A, B and C.*

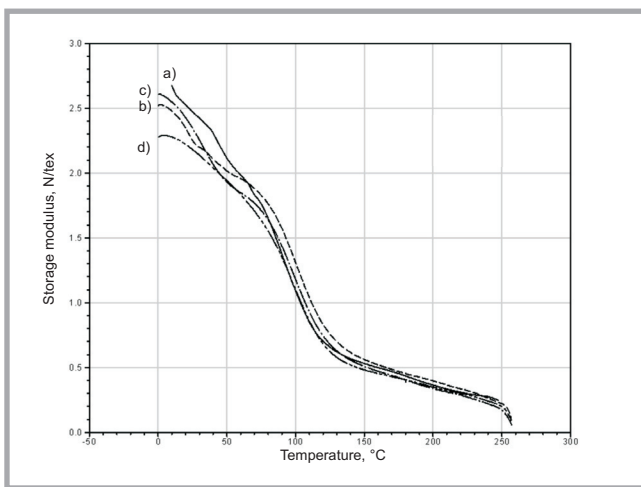*Figure 6. Tan δ curves of samples A, B and C.*

Figure 7. *Storage moduli of untreated and temperature-treated cord yarn C in a clamped state (a) at three different temperatures: 150 °C (b), 170 °C (c) and 190 °C (d).*
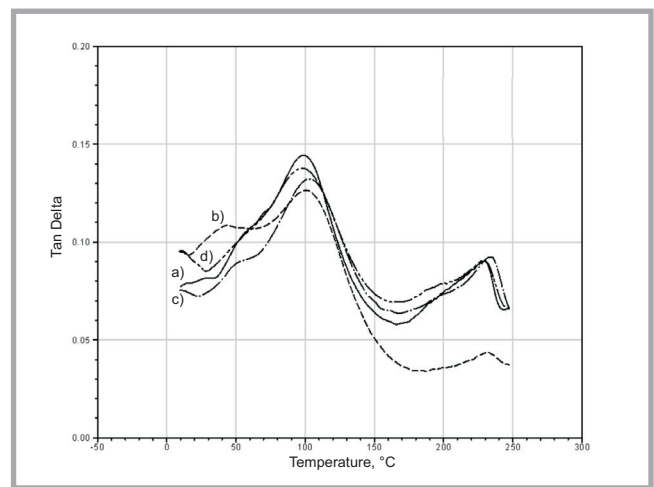

Figure 8. *Tan δ curves for untreated and temperature-treated cord yarn C in a clamped state (a) at three different temperatures: 150 °C (b), 170 °C (c) and 190 °C (d).*

region of a decrease in the storage modulus of the samples is connected with a sub-Tg transition at 69 °C (on E" curve at 49 °C), which is not observed on the tan δ curve at this temperature; however, it is more pronounced as a Tg transition at 117 °C.

In ***Figure 5***, the loss modulus E" of samples A, B and C are presented as a function of the temperature. The evolution of the loss modulus curves with respect to the temperature can be divided into two parts: above and below 100 °C. The loss moduli of the samples are in accord with the storage moduli shown in Figure 4 since the complex storage modulus is composed of both the storage modulus and loss modulus: E* = E' + iE", where a higher E' means a lower E" and vice versa.

In the region below 100 °C, the storage moduli (***Figure 4***) and loss moduli (***Fig-***

ure 5) vary between samples. Sample A shows the highest loss modulus E" above 100 °C (the lowest storage modulus E'), which means that the non-elastic component of sample A in the temperature region above 100 °C is much higher compared to samples B and C. Sample A has the worst elastic properties.

In ***Figure 6*** the tan δ curves of samples A, B and C are presented as a function of the temperature. The segment mobility of molecules in the amorphous regions can be explained by these tan δ curves. Material with lower storage moduli, and consequently lower elasticity, have higher loss moduli as a consequence of the increased segment mobility of molecules. This can be seen in ***Figure 6,*** where tan δ curves follow this relationship. Over the entire temperature interval, the segmental mobility of molecules of sample A is the highest (lowest E'), followed by sam-

ple B and then by sample C (the highest E'). The tan δ curves of samples A and C show small shoulders at 69 °C and 70 °C, which may be attributed to sub-Tg transitions, which continue into the two well-defined maxima at 117 °C (sample A) and 99 °C (sample C), indicating the glass transition of both samples. Only sample B has one well-defined maximum (Tg) on the tan δ curve, at 106 °C.

Sample A has another pronounced maximum at 218 °C, and samples B and C have less-defined maxima at 230 °C and 239 °C, respectively, which is a likely consequence of the adhesive system applied to cord yarn A. Molecular segmental motion minima on the tan δ curves can be seen for sample A at 179 °C, for sample B at 180 °C and for sample C at 167 °C. It is recommended that the vulcanisation of rubber composites be performed at temperatures between 160 °C

and 180 °C, where segmental motion is at a minimum. Furthermore, temperatures between 90 °C and 130 °C are not recommended for the mechanical loading of cord yarns A, B and C.

Influence of the temperature treatment of the samples in a clamped state

Rubber composites are exposed to elevated temperatures in their manufacture and in applications. During the cord production process, the cord yarns are temperature stabilised, and, as a consequence, only minor changes in viscoelastic properties are expected. Additionally, rubber composite cord yarns are surrounded by a rubber matrix, and it is not expected that the cord yarns will contract when subjected to elevated temperatures; consequently, the dynamic mechanical properties should not change much either. To establish possible changes in the dynamic mechanical behaviour of cord yarns, a 15-minute temperature treatment of cord yarn C was performed at three different temperatures: 150 °C, 170 °C and 190 °C in a clamped state. Annealing conditions (temperature, time and state) were selected to simulate the production (vulcanisation) temperatures of rubber composites.

Figure 7 shows the storage modulus E' of non-treated cord yarn C and temperature-treated cord yarn C in a clamped state at three different temperatures: 150 °C, 170 °C and 190 °C. As can be seen, the storage modulus of the cord yarn changed after the temperature treatment. The influence is more evident at lower temperatures (below 50 °C). At higher temperatures changes are less evident, and above 50 °C the moduli are comparable. The highest initial modulus (below 50 °C) was observed for the cord yarn that was not temperature treated (2,7 N/tex), whereas the lowest was observed for the temperature-treated cord yarn at 190 °C (2,3 N/tex). From these results it can be stated that exposure to high temperatures causes a decrease in the storage modulus. Since a decrease in the modulus marks the beginning of the breakdown of the entanglement network and breakage of inter-molecular bonds in the amorphous region, it can be assumed that temperature treatment decreases the number of entanglements among molecules in the amorphous region (Gupta [21]), and hence the amorphous orientation. Secondary crystallisation during

temperature treatment occurs at the expense of the oriented amorphous fraction.

Figure 8 shows the tan δ curves of untreated and temperature-treated cord yarn C. As can be seen, only minor changes occur in the tan δ curves; thus, the effect of the temperature treatment seems to decrease the intensity of maxima on the tan δ curve, which may be explained by the onset of additional crystallisation during temperature treatment, thereby increasing the order of the amorphous portion and decreasing segmental mobility. These changes are only minor, which is supported by the observation that the glass transition temperatures are all between 98 °C and 103 °C.

The structure of drawn fibres does not typically correspond to a thermodynamic equilibrium state, and cord yarns tend to shift to more stable formations after exposure to an elevated temperature. The heat of the temperature treatment breaks inter-molecular bonds, and the energy of molecular segments that are not firmly tightened decreases according to the law that the free energy of crystallisation is a function of the degree of molecular coiling β, G = f(β) (Elyashevich [22]). The oriented segments become loose and can shift to a more stable equilibrium state, which is accomplished by structural changes in the super-molecular structure of the fibres, such as the reorientation and re-crystallisation of macromolecular segments, changes in inter-crystalline and intra-crystalline structures (folded chains, additional crystallisation), crystallisation of the amorphous phase, the perfection of crystals through the migration of defects (e.g. the chain ends in the amorphous regions), and the thickening of crystals. Temperature treatment decreases the number of entanglements among molecules in the amorphous regions, and hence the amorphous orientation. Secondary crystallisation occurs during temperature treatment at the expense of the oriented amorphous fraction, which is then exhibited as a decrease in the modulus. On the other hand, additional crystallisation occurs during temperature treatment in amorphous parts of cord yarns, thereby increasing the order of the amorphous regions and decreasing segmental mobility (the decreasing intensity of maxima on the tan δ curve).

The clamped state mainly influences inter-fibrillar and intra-fibrillar tie molecules and the relaxation of inner stresses.

Thus, the higher the accumulated stress (higher load) in the yarns during the temperature-treatment process, the lower the relaxation of internal forces and shrinkage in the cord yarns.

■ Conclusions

The results of this study demonstrated that DMA can be used to analyse the viscoelastic properties of cord yarns and to interpret changes in the material at a supermolecular level caused by the temperature treatment. The research showed that the initial moduli of temperature-treated nylon cord yarns in a clamped state decrease after temperature treatment. Temperature treatment decreases the number of entanglements among molecules in the amorphous region, thus decreasing the amorphous orientation. On the other hand, additional crystallisation occurs in the amorphous regions of cord yarn during temperature treatment, which increases the order of the amorphous regions, thereby decreasing the segmental mobility of molecules. The decrease in the initial modulus during temperature treatment (vulcanisation of the rubber composite) is relatively low and should not affect the final properties of the rubber composite.

On the basis of the dynamic mechanical analysis and comparison of E', E'' and tan δ of samples A, B and C, it can be concluded that despite only minor differences between the different cord yarns, slight differences can be detected using this methodology. Of the three different nylon cord yarns, sample C exhibited superior elastic and dynamic mechanical properties.

The results of this study also demonstrated that it is recommended to perform the vulcanisation of rubber composites at temperatures between 160 °C and 180 °C, where segmental motion is at the minima. Likewise, it is not recommended to mechanically load cord yarns A, B and C between 90 °C and 130 °C.

Thus, it can be concluded that dynamic mechanical analysis enables the detection of subtle differences in materials (at a molecular level) and aids in determining optimal process conditions for given materials and, similarly, optimal materials for given applications.

Refrences

1. Wootton D. B.; The application of textiles in rubber. Shawbury, Shrewsbury, Shropshire [Great Britain]: Rapra Technology, 2001.
2. Prevoršek D. C.; Visokozmogljiva vlakna iz gibkih polimerov :teorija in tehnologija. Naravoslovnotehniška fakulteta, Oddelek za tekstilstvo, Ljubljana, 1998 (in Slovenian).
3. Lewin M., Pearce E. M.; Handbook of Fiber Science and Technology; Volume IV.: Fiber Chemistry, Marcel Dekker, Inc., New York and Basel, 1985.
4. Starkweather H. W., Jones G. A. J.; Polym. Sci. Polym. Phis. Ed., 19, 1981, pp. 467-477.
5. Prevoršek D. C., Oswald H. J.; Melt Spinning of PET and Nylon Fibers. In the book Solid State Behaviour of linear Polyesters and Polyamides, Prentice Hall, New Jersey (1990), pp. 131-208.
6. Dreyfuss P., Keller A. J.; Macromol. Sci.-Phys.: B4, 4, 1970, 811-836.
7. Dreyfuss P., Keller A., Willmouth F. M.; J. Polym. Sci.: A2, 10, 1972, pp. 857-861.
8. Atkins E. D. T., Keller A., Sadler D. M.; J. Polym. Sci.: A2, 10, 1972, pp. 863-875.
9. Dreyfuss P., Keller A. J.; Polym. Sci. Polym. Phis. Ed., 11, 1973, pp. 193-200.
10. Dreyfuss P.; J. Polym. Sci. Polym. Phis. Ed., 11, 1973, pp. 201-216.
11. Colclough M. L., Baker R. J.; Materials Sci., 13, 1978, pp. 2351-2540.
12. Magill J. H., Girolamao M., Keller A.; Polymer, 22, 1981, pp. 43-55.
13. Bukošek, V. Ph.D. thesis; Ljubljana, 1997 (in Slovenian).
14. Bukošek V., Prevoršek D. C.; Int J Polym Mater, 47 (4), 2000, pp. 569-592.
15. Murthy N. S.; et al. Polymer, 36 (20), 1995, pp. 3863-3873.
16. Peterlin A.; Textile Research Journal, 42 (1), 1972, pp. 20-30.
17. Peterlin A. J.; Journal of Applied Physics, 48 (10), 1977, pp. 4099-4107.
18. Prevoršek D. C., et al.; Ruber Chem Tech, 60, 1987, p. 59.
19. Kevin P. Menard; Dynamic Mechanical Analysis: A Practical Introduction, Second Edition; CRC Press: Boca Raton, 2008.
20. http://www.tainstruments.com/product.aspx?id=12&n=1&siteid=11.
21. Gupta V. B., In Textile Fibers: developments and innovations, Volume 2, Kothari, V.K., Ed.; IAFL Publications: New Delhi, 2000, pp. 11-118.
22. Elyashevich G. K., Baranov V. G., Frenkel S. Y.; J Macromol Sci – Physics, B13 (2), 1977, pp. 255-289.