УДК 621.1

М.І. Пилипець, В.Р. Паньків, М.Р. Паньків
Тернопільський національний технічний університет імені Івана Пулюя

ТЕРМОМЕХАНІЧНІ ВЛАСТИВОСТІ КОМПОЗИТНИХ МАТЕРІАЛІВ, ЯКІ БАЗУЮТЬСЯ НА ПОЛІМЕРАХ ТА ВУГЛЕЦЕВИХ НАНОТРУБКАХ

В створенні гвинтових робочих елементів виникає необхідність використання нових методів зміцнення поверхневих шарів матеріалу, як альтернатива відомим методам пропонується нанотехнологію. В статті розглянуто метод динамічного механічного аналізу наноматеріалів для вибору потрібного покриття поверхонь гвинтових робочих елементів.

Ключові слова: *динамічний механічний аналіз (ДМА), композитний матеріал, вуглецеві нанотрубки (УНТ), температура сканування, полімерний композит.*

Рис. 6. Літ. 5.

М.И. Пилипец, В.Р. Панькив, М.Р. Панькив

ТЕРМОМЕХАНИЧЕСКИЕ СВОЙСТВА КОМПОЗИТНЫХ МАТЕРИАЛОВ, ОСНОВАННЫХ НА ПОЛИМЕРАХ И УГЛЕРОДНЫХ НАНОТРУБКАХ

В создании винтовых рабочих элементов возникает необходимость использования новых методов упрочнения поверхностных слоев материала, как альтернатива известным методам предлагается нанотехнологию. В статье рассмотрен метод динамического механического анализа наноматериалов для выбора нужного покрытия поверхностей винтовых рабочих элементов

Ключевые слова: *динамический механический анализ (ДМА), композитный материал, углеродные нанотрубки (УНТ), температура сканирования, полимерный композит.*

M.Pylypets, V. Pankiv, M. Pankiv

THERMO-MECHANICAL PROPERTIES OF CONDUCTING POLYMERS AND CARBON NANOTUBES BASED COMPOSITE MATERIALS

In creation of screw working elements is necessary to use new methods to strengthen the material surface layers, as an alternative to known methods proposed nanotechnology. The article deals with method of dynamic mechanical analysis of nanomaterials to select the desired coating surfaces screw working elements.

Key words: *dynamic mechanical analysis (DMA), composite material, carbon nanotubes (CNTs), temperature scan, polymer composite.*

In modern conditions high competitiveness of screw working elements can be achieved primarily by improving quality, reducing of production costs and by the improvement of their production technologies. In particular, it is caused by a large number of manufacturing processes with low-quality materials, which results lead to reduction in service life. Known methods of surface hardening do not always provide this process for low-quality materials. So, promising is the use of nanotechnology for such strengthening.

Nanotechnology - an interdisciplinary area of fundamental, applied science and technology that deals with a set of theoretical study and practical methods of investigation, analysis and synthesis, manufacture methods and use of products with a given atomic structure by controlled manipulation of individual atoms and molecules. The starting point of the modern high technologies are new materials, mechanical, physical and chemical effects and processes. Production orientation on new technologies is characterized by different levels and trends in the use of specific functional properties of new materials, increment of processes productivity in the boundary areas of nanotechnology, technical intelligence equipment and ability of devices for conversion. With decreasing particle size in ultra-dispersed environments at favorable conditions significantly improve their mechanical properties such as hardness, strength, flexibility and yield strength increases, threshold of cold reduces.

If the size of nanoparticles is less than critical lengths, that characterize many physical phenomena, they may possess unique properties that are not peculiar to volumetric parts of the same substances. The development of nanotechnology promises massive expansion of new structural materials with unique properties and characteristics. It turned out that the control performance properties of structural materials can be performed not only by introducing dopant but also with the deformation of any nature. With such action, takes place fragmentation of non-metallic inclusions. Traditional annealing, tempering is nothing like nanotechnology in industry. As a result of these actions is possible to obtain steel where high strength

combined with ductility, i.e. precisely those features that are lacking in mechanical engineering and nanotechnology allow successfully receive such materials.

In perspective, already today created heavy-duty materials based on nanotechnology that are applied in engineering. Technological methods of strengthening the surface layers, using nanotechnology, providing change of their mechanical properties and play an important role in the creating of the transporting abrasive materials with high wear resistance and durability.

Introduction in manufacture of strengthening nanotechnology that ensure wear resistant structures, prior modeling work, installation of external factors on their performance, learning of processes that develop on the surfaces of friction, strengthened by the studied coatings.

Dynamic mechanical analysis (DMA), or dynamic mechanical thermal analysis (DMTA), is universal and sensitive testing technique that can provide us the data about thermo-mechanical properties of polymers depending on frequency, temperature or time. A big plus is that experiments required small amounts of the specimens [1].

The work principle of dynamic mechanical analysis (DMA). Machine apply sinusoidal stress or strain to a sample (of known geometry) and measure the resulting response of the material to stress, temperature, frequency and other values. Sinusoidal wave is generated with a force motor and that transmitted to the sample [2].

With this technique we can measure loss modulus (stiffness), tan delta (damping or dissipation of a material), storage modulus (elastic behavior). In this work, DMA was carried out using DMA8000 (Perking Elmer). The DMA8000 was attached to the computer in order to control the Pyris software for windows. Were conducted two types of experiments for all five samples and three tests for the control sample (pure polyurethane).

Temperature scan. With this type of test, we can observe strain response of the material while applying constant frequency and stress while sample temperature increasing. We used this test in order to characterizing thermally dependent behavior (loss modulus, storage modulus and Tg).

Temperature scan CNT 1%. For the first test, temperature range was from -104 ^{0}C to 100 ^{0}C, specimen size 10×9.5×1.8mm (length × width × thickness) the results we can observe on the Fig. 1.

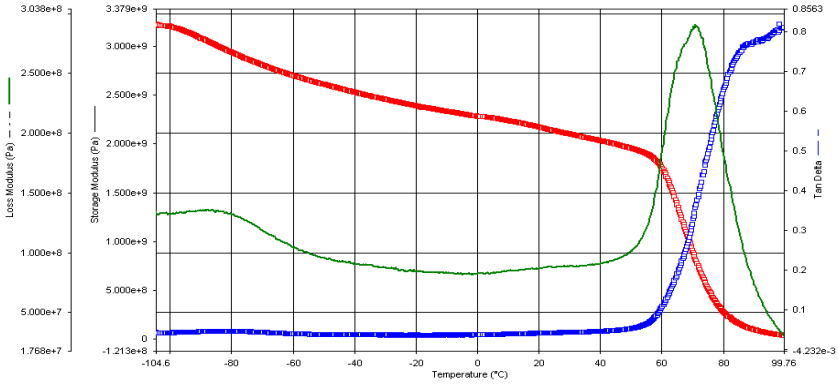

Fig. 1. **CNT 1%, temperature scan, first attempt**

On these graphs clearly pronounced only the peak of storage modulus also, we can see that loss modulus start to fall down at temperature 58^{0}C and tan delta starts to rise at the 55^{0}C. Therefore, a second experiment was conducted Fig. 2. Second attempt: temperature range from -50.00°C to 130.00°C, sample size 10×7×1.5. The second attempt showed us the full picture, storage modulus drop starts at the same temperature like in first test as well as peak of loss modulus and in addition, we can clearly see peak of tan delta 102.900C.

CNT 2. The results of testing specimens with 2.5% amount of CNT we can view of the Fig. 2. Samples dimensions and temperature range for first and second test respectively from 65.00°C to 100.00°C with 10×7.5×1.75 mm dimensions and from -20.00°C to 130.00°C, 10×9×1.93 mm. It must be said that second experiment was not necessary because all parameters we could took from the Fig. 3. Nevertheless, we sought that it is important to ensure that is singular peak of tan delta and with further heating in the material does not occur any anomalies. In bought experiments, we can see small differences in the indicators for example storage modulus at Fig. 3 start to fall sharply at temperature 40°C and on Fig. 4 the same indicator show 29°C. The same we can say about loss modulus in first case we can

observe peak at temperature 56°C in the second at 44°C but two tests indicate the same value of tg temperature 75.53°C.

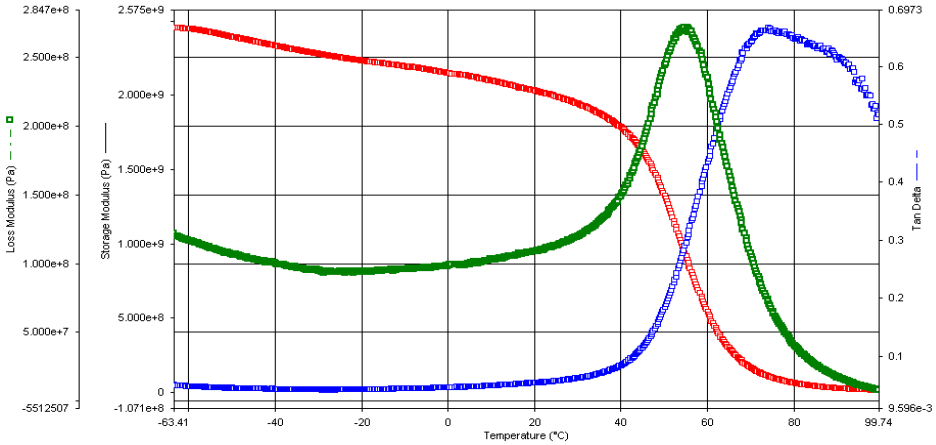

Fig. 2. **CNT 2.5% temperature scan, first attempt**

CNT 5. For this material was conducted only one test the results we can see on the Fig. 3. Sample dimensions 15×10.1×2mm and temperature rate from -100.00°C to 100.00°C. Speaking forward this showed the lowest temperature of tan delta peak. 26.28°C. Also we can see anomaly behavior of storage modulus curve it start to fall down, at temperature -50°C it start to rise up at 10°C was the peak and at 7°C is start to fall sharply again. Therefore, we can say that stiffness of particular material increase or stay at the same level in temperature range from -50°C to 10°C. Peak of the loss modulus is at 10°C.

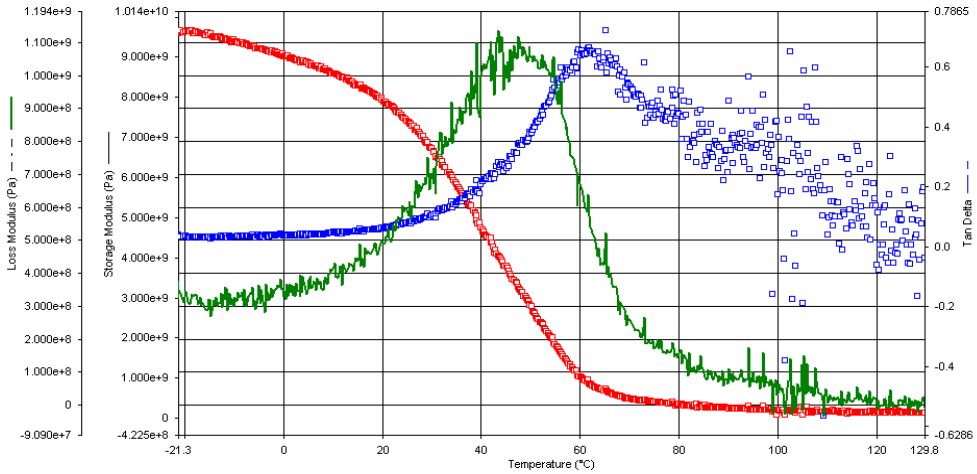

Fig. 31. **CNT 5% temperature scan**

CNT 7.5. For these samples were conducted two experiments, dimensions of specimens 15×5.5×1.1mm for the first and 15×5.8×1.2 for the second with temperature range from -100.00°C to 100.00°C and from -20.00°C to 130.00°C respectively. Two tests show virtually identical results for example rapid fall of storage modulus starts at the temperature 20°C for the first and 15°C for the second specimen, peak of loss modulus we can see at 43°C (Fig.4). Peak of tan delta we can observe at 61.65°C and 63°C respectively. However, on the Fig. 6 we can notice dispersion of tan delta curve that start right after the tg (peak tan delta) temperature.

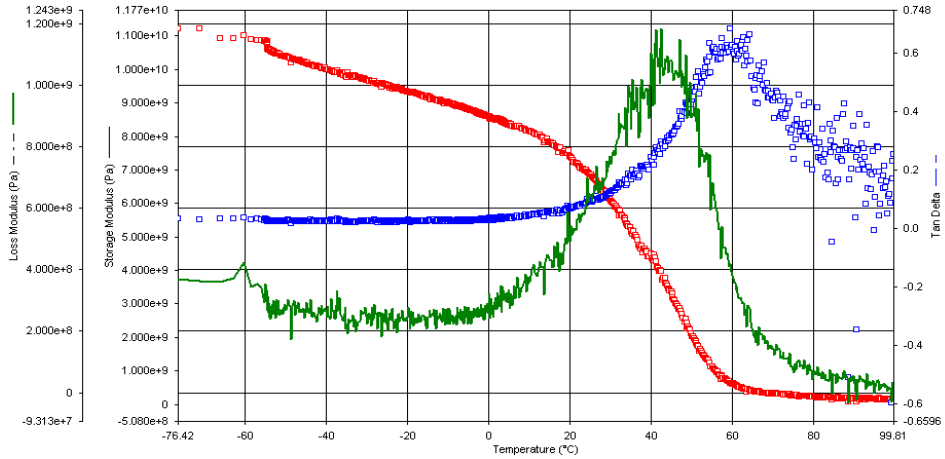

Fig. 4. **CNT 7.5% temperature scan, second attempt**

This may indicate that the material breaks down after the tg point of anomaly in the material. In second test temperature range was increased and as the result we can say that this material starts to break an the temperature approximately 64°.

CCNT 10%. Two experiments was conducted for these samples, dimensions of specimens 15×6.2×1.2 mm at temperature range -85.00°C to 60.00°C for the fist and 15×6.4×1.3 at -44.00°C to 70.00°C. Firs what we can say that this material is very unstable judging by the behavior of storage modulus amplitude and loss modulus dispersion. Firs reason for this can be a big percentage of carbon nanotubes in composite and second is the bad mixing and post curing of components. Nevertheless, both experiment shows almost the same results. Storage modulus star to drop at the -10°C in both tests. Peak of loss modulus in the first experiment is at the temperature 25°C in the second it hard to determinate exactly number but we can see that the value is in the same region. Based on the tan delta we can say that there is the same tendency but in case of this material is start break before the tg point, because peak of tan delta on Fig. 5 are in range
of temperatures from 40 to 45°C. Tan delta curve start to disband in bought experiments at -10°C.

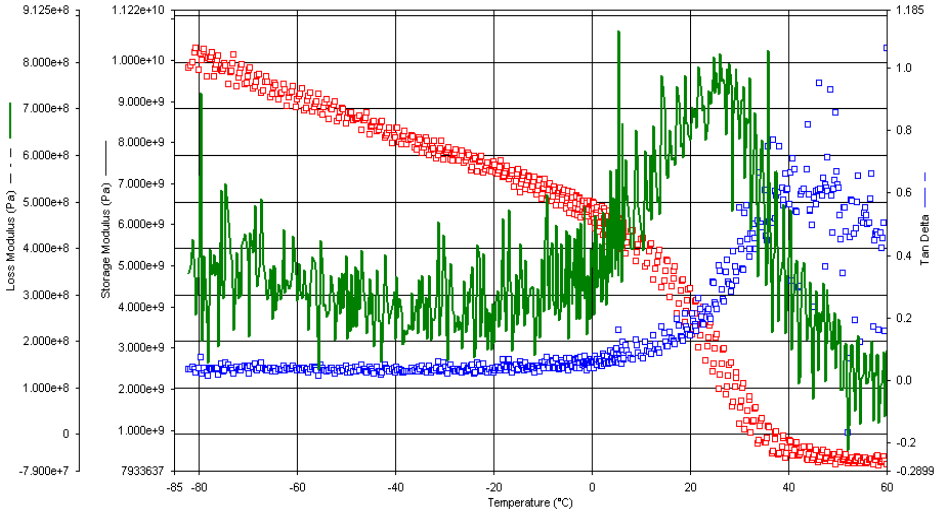

Fig. 5. **CNT 10% temperature scan, second attempt**

Control Pure PU sample pure polyurethane was also tested. Dimensions of specimen 15×7.3×2.3mm at temperature range from -70°C to 80°C. Results we can see on the Fig. 10. Sharply drop of storage modulus occur at -58°C, peak of loss modulus we can observe at -9.75°C and peak of tan delta at 6.35°C. As expected pure PU has the lowest glass transition temperature.

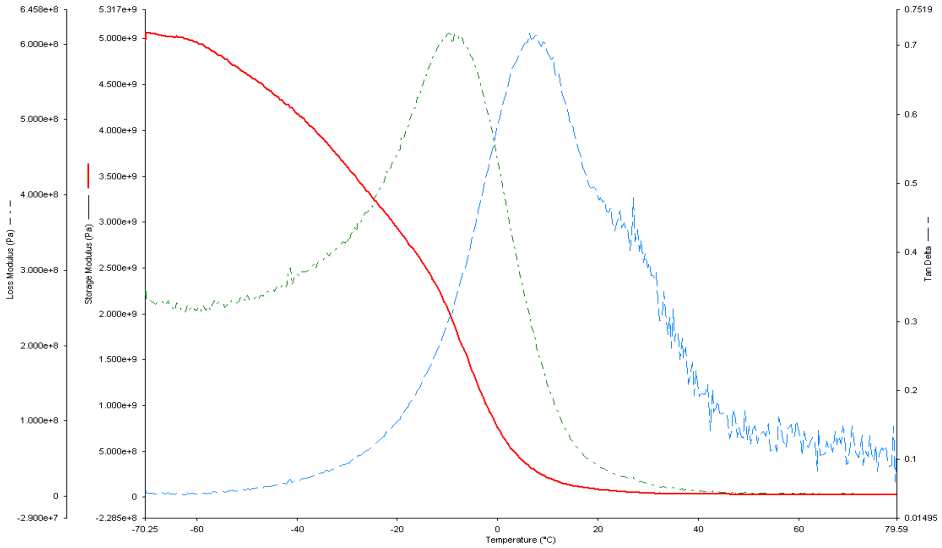

Fig. 6. **Pu temperature scan**

The results of temperature scan test showed that each composite has better performance than pure polyurethane. The highest value of glass transition temperature showed CNT 1% composite the lowest CNT 5% composite. By knowing this information, we can choose the optimal working temperatures for our materials. In total ten tests was conducted. Using this method it is possible with a small number of tests pick up coating material with the required parameters.

1. 1.Shiqiang Denga, Meng Houb, Lin Yea. Temperature-dependent elastic moduli of epoxies measured by DMA and their correlations to mechanical testing data. Polymer Testing. 2007, Vol. Volume 26, Issue 6.
2. Introduction to Dynamic Mechanical Analysis (DMA). Waltham, MA 02451 USA : PerkinElmer, Inc., 2008.
3. 3.Byrne, M.T., Guin'Ko, Y.K. Recent advances in research on carbon nanotube - polymer composites. 2010, Vol. Volume 22, Issue 15, pp. 1672-1688.
4. Hua Deng, , Lin Lin, Mizhi Ji, Shuangmei Zhang, Mingbo Yang, Qiang Fu. Progress on the morphological control of conductive network in conductive polymer composites and the use as electroactive multifunctional materials. Progress in Polymer Science. April 2014, Vol. Volume 39, Issue 4.
5. Costa, L.C.a , Valente, M.a, Sá, M.A.b, Henry, F. Electrical and magnetic properties of Polystyrene doped with Iron nanoparticles. 2006, Vol. Volume 57, Issue 6, pp. 881-887.

Стаття прийнята до друку 25.03.2015.