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Electret materials based on an epoxy oligomer and multi-walled carbon nanotubes (MWNT-1020)

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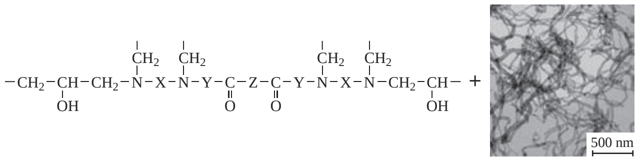
The characteristics of thermal electrets based on epoxy resins were adjusted by varying curing agent and filler contents. The addition of carbon nanotubes (MWNT-1020) reduced the electret characteristics of the epoxy composites due to a higher electrical conductivity and improved the mechanical properties of the epoxy composites.

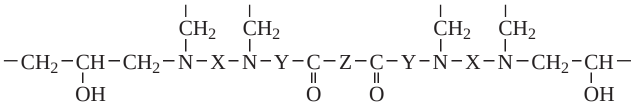


A wide range of electret applications in different industries[1,2] stimulates academic and applied research on new electret materials. Epoxy resins and their composites are frequently used for this purpose.[3–8] To produce materials with high and stable electret characteristics, different polymer modifications are employed: chemical grafting, elastication, filling, simultaneous synthesis (curing) and polarization, *etc*.[3–10] Moreover, both the electret and performance (strength, deformation and rheological) characteristics of materials depend on their structure, composition and production method. Thus, studying the effect of an epoxy composition on the electret properties is of great interest.

Here, we describe the possibility to adjust the characteristics of thermal electrets based on epoxy resins by varying curing agent and filler contents. The test materials were a DER-331 epoxy oligomer, an L-20 polyaminoamide as a curing agent and multi-walled carbon nanotubes (MWNT-1020) as a filler. Thermoelectrets were manufactured by the simultaneous curing of DER-331 with L-20 (in a stoichiometric ratio)[6] with the addition of MWNT-1020 and polarization at a constant electric field strength (between two flat electrodes) of 5 kV for 2 h followed by cooling in the field for 30 min. The temperature of simultaneous polarization and curing (thermoelectret treatment) was changed from 100 to 125 °C. Electrostatic field parameters of the polymer (the surface potential V_s, the electric field strength E and the effective surface charge density σ_eff) were measured by an IPEP-1 electrostatic field meter with the periodic shielding of the receiving electrode.

Previously,[9] we studied the electret properties of composites based on DER-331 oligomer with different curing agent (diethylenetriamine) contents and found that, under the same curing and polarization conditions, the highest values of V_s, σ_eff and E correspond to the maximum effective cross-link density of the three-dimensional network.

When L-20 (oligoamide) was used as a curing agent, additional amino groups appeared in the structure of a node of the three-dimensional network with hydrogen atoms in these groups being positive charge carriers. The most probable negative charge carriers are oxygen atoms in C=O groups (Figure 1). Under the given conditions, the introduction of additional functional groups into the structure of the three-dimensional network node (L-20 curing agent) is the dominant factor compared to the effective cross-link density of the polymer matrix.



$$-\mathrm{CH_2}-\underset{\underset{\mathrm{OH}}{|}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\overset{|}{\mathrm{CH_2}}}{\overset{|}{\mathrm{N}}}-\mathrm{X}-\overset{\overset{|}{\mathrm{CH_2}}}{\overset{|}{\mathrm{N}}}-\mathrm{Y}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{Z}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{Y}-\overset{\overset{|}{\mathrm{CH_2}}}{\overset{|}{\mathrm{N}}}-\mathrm{X}-\overset{\overset{|}{\mathrm{CH_2}}}{\overset{|}{\mathrm{N}}}-\mathrm{CH_2}-\underset{\underset{\mathrm{OH}}{|}}{\mathrm{CH}}-$$

Figure 1 Polymer matrix node of the composite based on DER-331 oligomer cured by L-20.

The study of the epoxy thermal electrets obtained at a thermoelectret treatment temperature of 120 °C revealed that the maximum values of electret characteristics on the 60th day of storage conform to a stoichiometric ratio of the curing agent L-20 (V_s = 0.847 kV, σ_eff = 0.803 μC m^{-2} and E = 62.3 kV m^{-1}).[9] It is clear that an increase in the curing agent content of the epoxy composite results in more functional groups that can participate in polarization involving dipole-segmental fragments under a polarizing field. However, an increase in the curing agent content above a stoichiometric ratio does not lead to the growth of a proportion of functional groups able to participate in polarization processes involving dipole-segmental fragments under a polarizing field since these groups are not fixed by a three-dimensional network, and they can cause additional steric hindrances in the formation of the network node.

Thus, a lack or excess of the curing agent reduces the surface potential and other electret properties of the epoxy polymer; for this reason, a further study was conducted at a stoichiometric ratio between the epoxy oligomer and curing agent.

The effect of thermoelectret treatment conditions on electret characteristics was examined for composites based on the DER-331 oligomer cured by a stoichiometric ratio of L-20 without a filler. Figure 2(*a*) shows that an increase of the treatment temperature from 100 to 120 °C accounted for the growth of electret surface potential. Maximum values on both the 40th (V_s = 0.901 kV, σ_eff = 0.819 μC m^{-2} and E = 66.87 kV m^{-1}) and 60th days of

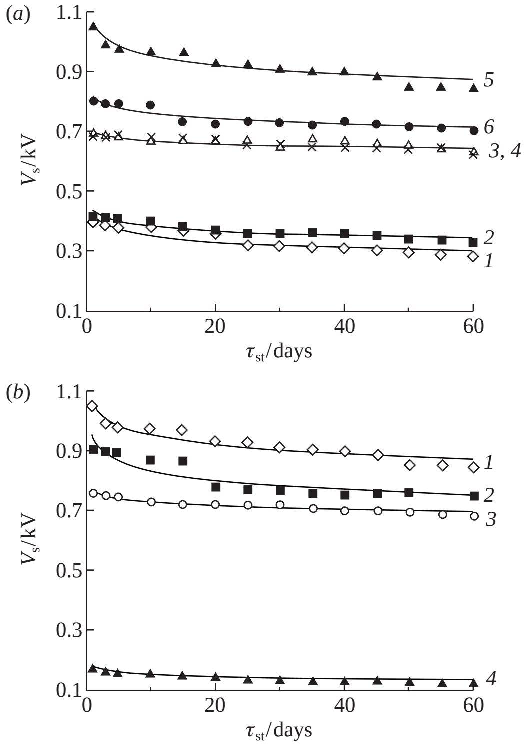


Figure 2 Surface potential of the composites based on DER-331 oligomer cured by a stoichiometric ratio of L-20 during thermoelectret treatment at a polarization voltage of 5 kV for 2 h (*a*) at (*1*) 100, (*2*) 105, (*3*) 110, (*4*) 115, (*5*) 120 and (*6*) 125 °C and (*b*) at 120 °C and MWNT-1200 concentration of (*1*) 0, (*2*) 0.06, (*3*) 0.1 and (*4*) 1 wt%.

storage (V_s = 0.847 kV, σ_{eff} = 0.803 μC m^{-2} and E = 62.3 kV m^{-1}) correspond to a temperature of 120 °C. A slight decrease of the electret properties of the composites obtained at 125 °C can be explained by the appearance of two competitive factors: the three-dimensional network density of the composite[11] and the mobility of the functional groups that are able to participate in polarization involving dipole-segmental fragments. The increase of thermoelectret treatment temperature results in the growth of both the density of the three-dimensional network that creates additional steric hindrances in polar group orientation and the mobility of functional groups capable of participating in polarization processes.

In the meantime, to create high-quality composite materials and devices, multi-walled carbon nanotubes are used.[12] The carbon nanotubes were considered as long ones: the length-to-diameter ratio was about 1000–5000, the diameter ranged from 60 to 80 nm, and the bulk density was about 0.165 g cm^{-3}.

Figure 3 shows the micrographs of MWNT-1020 obtained by transmission electron microscopy (TEM) using JEM-2010 (JEOL).

The Raman spectra (Figure 4), measured using a T64000 Horiba Jobin Yvon instrument (wavelength of 514 nm), revealed two main peaks D (1345 cm^{-1}) and G (1573 cm^{-1}) attributed to the disorder and graphitic structures of multi-walled carbon nanotubes, respectively. The intensity ratio I(D)/I(G) shows the disorder degree of carbon nanotubes.[13] The disorder degree of the material was 1.0, which is high for carbon nanotubes and connected with the high amount of defects sites. These defect sites can improve the filler-matrix interaction and mechanical properties. In addition, the defectiveness of MWCNTs promotes a better distribution of the filler in composites than that of well-ordered nanotubes.

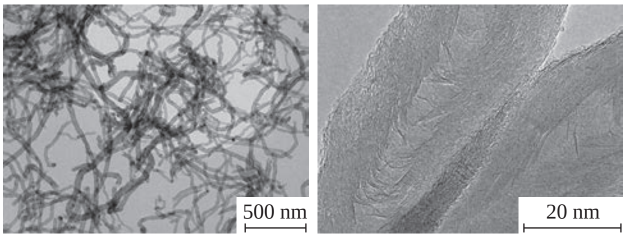


Figure 3 TEM micrographs of MWNT-1020.

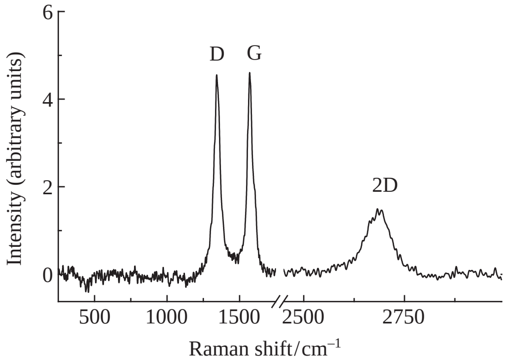


Figure 4 Raman spectrum of MWNT-1020.

Recently, it was reported that the electrical properties of epoxy/carbon nanofiber composites depend on preparation technique.[14] The defectiveness, aspect ratio and conductivity of carbon nanofibers can be changed during the composite preparation. Moreover, the composite preparation technique affects a filler distribution in the epoxy matrix. In this work, the mechanical mixing of MWNT-1020 in epoxy resin was used for composite preparation.

Figure 2(*b*) demonstrates the time dependence of the surface potential of the composites based on DER-331 oligomer with different MWNT-1020 contents cured and charged at 120 °C. It is clear that the behavior of V_s is similar to that shown in Figure 2(*a*) for the polymer without the filler. Table 1 summarizes the electret properties (V_s, σ_{eff} and E) of the test samples on the 60th day of storage at room temperature.

The addition of carbon nanotubes reduces the electret performances of epoxy composites (Table 1). The higher the NWMT-1020 content, the lower the values of V_s, σ_{eff} and E. This decrease is not monotonic and not proportional to electret characteristics, *i.e.*, various composites differ in thickness and electrical conductivity. Changes in the electret properties of polymers due to filler addition are well known.[15–17] At a nanotube content of 1.0 wt%, a drop of the thermo-electret characteristics occurs owing to an increased electrical conductivity of the composition. High carbon nanotube loadings (above 0.5–1.0%) of the polymer lead to the formation of percolation clusters in composites, which negatively affect the electret properties. Percolation clusters increase the composite conductivity.

However, the mechanical properties of the epoxy composites with carbon nanotubes were improved.

Therefore, the prescription and technological conditions for the production of epoxy composites with good electret properties (surface potential, effective surface charge density and electric

Table 1 Electret characteristics of the polymer composites based on a DER-331 oligomer cured by a stoichiometric ratio of L-20 at different MWNT-1020 contents after 60 days.

Nanotube content (wt%)	V_s/kV	σ_{eff}/μC m^{-2}	E/kV m^{-1}
0	0.847	0.803	62.3
0.02	0.470	0.275	29.3
0.06	0.750	0.238	27.5
0.10	0.681	0.319	38.5
1.00	0.130	0.132	8.3

field strength) were optimized. The addition of carbon nanotubes reduces the electret characteristics of epoxy composites due to a higher electrical conductivity of the compositions. The experimental data make it possible to manufacture materials with predefined mechanical strength, electrical and electret properties for traditional and new fields of polymer electret applications.

References

1 *Electrets*, ed. G. M. Sessler, Springer, Berlin, 1987.

2 V. Kestelman, L. Pinchuk and V. Goldade, *Electrets in Engineering: Fundamentals and Applications*, Kluwer, London, 2000.

3 K. Ren, Y. Liu, X. Geng, H. F. Hofmann and Q. M. Zhang, *IEEE Trans. Ultrason. Ferroelectr. Freq. Control*, 2006, **53**, 631.

4 T. A. Vakhonina, S. M. Sharipova, N. V. Ivanova, O. D. Fominykh, N. N. Smirnov, A. V. Yakimansky, M. Yu. Balakina and O. G. Sinyashin, *Mendeleev Commun*., 2011, **21**, 75.

5 V. N. Studentsov, E. A. Skudaev and R. V. Levin, *Int. Polym. Sci. Technol*., 2014, **41** (11), T/11.

6 E. N. Mochalova, N. A. Limarenko, M. F. Galikhanov and R. Ya. Deberdeev, *Dizain Materialy Tekhnologiya*, 2014, **4** (34), 60 (in Russian).

7 G. N. Nazmieva, T. A. Vakhonina, N. V. Ivanova, A. Sh. Mukhtarov, N. N. Smirnov, A. V. Yakimansky, M. Yu. Balakina and O. G. Sinyashin, *Eur. Polym. J*., 2015, **63**, 207.

8 G. N. Nazmieva, T. A. Vakhonina, S. M. Sharipova, N. V. Ivanova, A. Sh. Mukhtarov, M. A. Smirnov, M. Yu. Balakina and O. G. Sinyashin, *Mendeleev Commun*., 2015, **25**, 101.

9 E. N. Mochalova, N. A. Limarenko and R.Ya. Deberdeev, *Vestn. Kazan. Tekhnol. Univ*., 2013, **16** (21), 178 (in Russian).

10 E. N. Mochalova, N. A. Limarenko, M. F. Galikhanov and R. Ya. Deberdeev, *Polym. Sci., Ser. D*, 2016, **9**, 396.

11 E. N. Mochalova and R. M. Garipov, *Vestn. Kazan. Tekhnol. Univ.*, 2012, **15** (8), 82 (in Russian).

12 M. M. Tomishko, O. V. Demicheva, A. M. Alekseev, A. G. Tomishko, L. L. Klinova and O. E. Fetisova, *Ross. Khim. Zh. (Zh. Ross. Khim. Ob-va im. D. I. Mendeleeva)*, 2008, **LII** (5), 39 (in Russian).

13 K. Varshney, *Int. J. Eng. Res. Gen. Sci*., 2014, **2**, 660.

14 A. G. Bannov, N. F. Uvarov, S. M. Shilovskaya and G. G. Kuvshinov, *Nanotechnologies in Russia*, 2012, **7** (3–4), 169 [*Ross. Nanotekhnologii*, 2012, **7** (3–4), 91].

15 B. Yu, J. Han, X. B. He, G. P. Xu and X. B. Ding, *J. Macromol. Sci., Part B: Phys*., 2012, **51**, 619.

16 I. Bodurov, T. Yovcheva and S. Sainov, *Colloid Polym. Sci.*, 2014, **292**, 3045.

17 A. A. Guzhova, M. F. Galikhanov, Yu. A. Gorokhovatsky, D. E. Temnov, E. E. Fomicheva, E. A. Karulina and T. A. Yovcheva, *J. Electrostat.*, 2016, **79**, 1.

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