საქართველოს მეცნიერებათა ეროვნული აკადემიის მოამბე, ტ. 12, №4, 2018
BULLETIN OF THE GEORGIAN NATIONAL ACADEMY OF SCIENCES, vol. 12, no.4, 2018

Organic Chemistry

Investigation of Free Volume of Oriented Electrical Conducting Polymer Composites by Spin Probe Method

Jimsher Aneli[*] and Levan Nadareishvili [**]

[*]*Department of problems of machine building, R.Dvali Institute of Machine Mechanics, Tbilisi, Georgia*
[**]*Laboratory of optical-chemical investigations, V.Chavchanidze Institute of Cybernetics, Georgian Technical University, Tbilisi, Georgia*

(Presented by Academy Member Giorgi Tavadze)

ABSTRACT. The spine probe method based on electron spin resonance (ESR) is used for investigation of free volume of the oriented polyvinyl alcohol films filled with high dispersive carbon black. After introduction of nitroxide stable radicals by diffusion to oriented with different degree polymer films the samples were tested by noted method via definition of the measuring of correlation times of rotation of stable radicals around their axes. It is established that the lower is free radicals concentration and their correlation time in local regions of the films, the higher is the orientation (stretching) degree of the films, which is directly connected with the volume of micro-empties in the polymer matrix. These phenomena correlate with the analogical ones in the same polymer containing high dispersive electrical conducting filler (carbon black). In this case the diffusion of free radicals to the polymer matrix is more difficult than in pure polymer. The values of correlation time and diffusion coefficients of the stable radicals decrease because of additive interactions of these radicals with the filler particles. *© 2018 Bull. Georg. Natl. Acad. Sci.*

Key words: spin probe method, stretched polymer composite, diffusion of stable radicals, correlation time, electric conductivity

ESR is a spectroscopic method able to detect paramagnetic centers, unpaired electrons, stable radicals, etc. in different low and high molecular substances of inorganic or organic media (particularly in polymers, biological bodies, etc.) [1,2]. Important application of this method is the investigation of different structural-morphological changes in the polymer materials by ESR spectra of stable radicals introduced to the polymer matrix via diffusion (so called method of spin probes). Most commonly free radicals of the nitroxides types are used in this method. Thanks to its structure the nitroxide radicals are rather stable in organic substances. Nitroxide radical possesses a free (unpaired) electron that belongs to the nitroxide group and occupies the pz orbital of the nitrogen atom. The nitrogen group is often surrounded by four methyl groups, substituted

in α position, which sterically protect the paramagnetic center from a possible attacking reagent and hence contribute to the stability of a free nitroxide radical. The choice of an adequate nitroxide for investigation of a given polymer system is particularly important. Therefore, it is necessary to take into account care not only miscibility of the nitroxide radicals in polymer matrix, but also the nitroxide size, shape, polarity and flexibility of the nitroxide radicals [3,4]. The chosen nitroxide radical must be compatible with polymer chain segment in order to be able to follow its motional behavior.

There are many investigations, where the ESR method is successfully used for studying of the problems of influence of the polymer materials microstructure on their physical and chemical properties [5, 6].

In the presented work we investigated effect of micro-empties (free volume), in which the stable radicals are localized, on the character of electrical conductivity of polymer composites based on polyvinyl alcohol with the use of the above considered spin probe method.

Experimental. The films – the composites based on polyvynylalcohol (PVA) and high dispersive carbon black were obtained via introduction of filler powder (40 wt%) to the water solution of PVA with the following evaporation of the solution at room temperature. The orientation of the films (width 20 mm, thickness 0.3 mm) was conducted in an oven under conditions of temperature 90oC at the rate 0.1 cm/min with the following slow cooling. The films stretched on 50, 100 and 150% were obtained. The specimen is stretched as one whole along the entire length. In the film the distribution of deformation in stretching direction is heterogeneous - the relative deformation increases and thickness decreases from clamps up to central region. After this we apply the rectangle greed (5x5mm) to the stretched film. Then we cut the strip from the film in stretching direction with sizes 5 x 45 mm. Three types of samples are obtained with 5 mm width corresponding to stretching degree 50, 100 and 150% and different length. Analogical manipulations were provided on obtaining of stretched films without filler (carbon black).

There were measured two parameters: electrical resistance and the stable radical concentrations in each elemental square of the central strip (Fig.1).

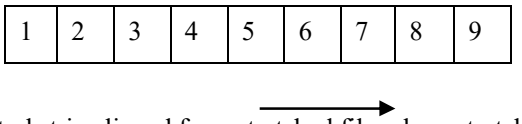

Fig.1. Central strip clipped from stretched film along stretching direction.

The electric conductivity of each elemental square of this strip was measured with the use of impedance spectroscopy. The value of electrical resistance R was determined for each local square from one side up to other side in terms of unit volume of the squares with the use of two contact method.

At the next stage the doping of the same strip of the film was conducted with stable nitroxide radical (2,2, 6, 6-tetramethyl -4-carboximethylpiperidin-1-oxide) in the vacuum (10^4Pa) stove at 60°C during 30 min. The radical concentration varied in the range of 10^{-3} -10^{-4} mol/l. After doping the electric resistance of each square of the film was repeatedly measured.

On the next stage the measuring of ESR spectra of the stable radicals localized in each elemental square of the strip was provided. With this aim the probes from each squares of the strip were cut and then the ESR spectra of stable nitroxide radicals were recorded by standard method on the spectrometer of the type the Varian at room temperature. Values of rotational diffusion coefficient of the radicals in the polymer matrix were determined using formula $D_r = 1/6\tau$, where τ is a correlation time of radical rotation. With the use of the spatial atlas of ESR spectra obtained via theoretical calculation of all experimentally permissible

ESR spectra of the nitroxide radicals it is possible to obtain numerical estimation of the corresponding correlation time and diffusion coefficient of the stable radicals in the polymer medium [7].

Results and Discussion

The measuring of the specific volumetric electrical resistance value of the separate regions of the film shows that this parameter depends on the coordinates of the elemental squares in all horizontal strip from one side of the film up to another side (Fig. 1). The average resistance of squares increases exponentially in stretching direction with the maximum at central square (N5). On the basis of character of the curves in the Fig. 2 it can be concluded: 1) exponential increasing of electrical resistance value is in accordance with well known law for the resistance of linearly elongated electric conducting polymer composites (exponential dependence of the resistance on the distance between conducting particles) [8]; 2) The higher the degree of elongation the higher is the maximum of the electric resistance; 3) The resistances of the squares containing stable radicals are higher than that at the equivalent squares in the films without stable radicals. This result is explained by phenomenon of capture of the charge particles by stable radicals, which leads to the decrease of the amount of charge carriers in the polymer matrix and, consequently, to the decrease of the electric current to some extent [9].

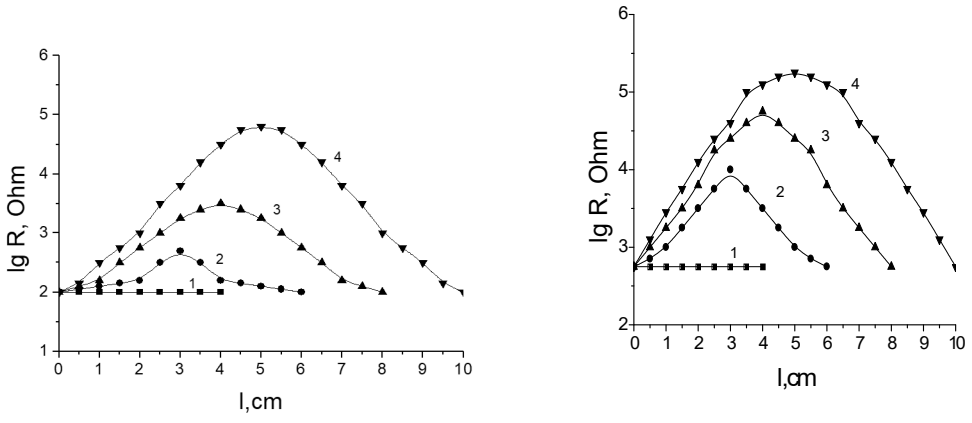

Fig. 2. Dependence of the electrical resistance R of the PVA filled with CB without (a) and with nitroxide radicals (b) for unstretched (1) and stretched on 50 (2), 100 (3) and 150 % (4) films.

It is known that the spectrum of nitroxide radicals containing fragment > C-(N - O·)-C < with four methyl groups and unpaired electron in the liquid medium present a symmetric triplet. However, this symmetry damages at increasing of viscosity of the medium - the more it is the less is the free volume around of the stable radical.

By view of the shape of spectrum it is possible to estimate the viscosity or the density of the radical surrounding medium. Besides, it is known that the rate of rotation of radicals depends on segmental mobility of macromolecules [5]. The obtained ESR spectra and calculated diffusion coefficients of rotating nitroxide radicals show that the values of these parameters decrease and reach to the minimum near the middle of the stretched on 50, 100 and 150 % film for both pure and filled with carbon black (Table 1). With the aim of comparison of the correlation times significances it was conducted the measuring of this parameter for radicals localized in each square from the central strip. It is clear that because of the density of filled polymer

films is higher than for pure analogues this gradation of spectra ESR shape for composites is stronger than in pure ones.

Table. Values of the correlation times of nitroxide radicals localized in unstretched and stretched on 150% polymer film strips of four regions with equal sizes from left to right up to middle region of the strips*

N of square from strip (see Fig.1)	PVA		PVA +CB	
	t,s	Dr, s^{-1}	t,s	Dr, s^{-1}
Unstretch.	$1x10^{-10}$	$1x10^{10}$	$3x10^{-10}$	$3x10^{9}$
1	$2x10^{-10}$	$5x10^{9}$	$6x10^{-10}$	$1x10^{9}$
2	$5x10^{-10}$	$2x10^{9}$	$2x10^{-9}$	$5x10^{8}$
3	$1x10^{-9}$	$1x10^{9}$	$1x10^{-8}$	$1x10^{8}$
5	$8x10^{-9}$	$1x10^{8}$	$9x10^{-8}$	$2x10^{7}$

*The data for right part of the stretched films are not given, because they reflect left part.

The Table shows that the diffusion process of free stable radicals are fastest in polymers without fillers, which indicates relatively weak interaction of these radicals with macromolecules. Other reason of this result may be the presence of structural defects (empties) in the polymer microstructure, in which the radical movement proceeds with least difficulties. The decrease of both parameters enhances in the composites with carbon black because of increase of the separate regions density and, respectively, decrease of the free volume, as well as increasing of interaction of radicals with active groups on the surface of carbon black particles.

Conclusions

With the use of ESR spectra of stable radicals it is shown that as a result of the increase of orientation degree the correlation time of radical rotation of the local squares in the stretching direction from one side till middle square of the film correspondingly increases, which is due to decreasing of the free volume in the composite material.

By study of electrical conductivity it was established that in result of the increasing of orientation degree of the polymer composite a specific electrical resistance of the materials increases, which is due to increase of the average distance between conducting particles in stretching direction.

ორგანული ქიმია

ორიენტირებული ელექტროგამტარი პოლიმერული კომპოზიტების თავისუფალი მოცულობის კვლევა სპინური ზონდის მეთოდით

ჯ. ანელი* და ლ. ნადარეიშვილი**

**რ.დვალის სახ. მანქანათა მექანიკის ინსტიტუტი, მანქანათმშენებლობის პრობლემათა განყოფილება, თბილისი, საქართველო*
*** საქართველოს ტექნიკური უნივერსიტეტი, ვ.ჭავჭანიძის სახ. კიბერნეტიკის ინსტიტუტი, ოპტიკურ ქიმიურ კვლევათა ლაბორატორია, თბილისი, საქართველო*

(წარმოდგენილია აკადემიის წევრის გ. თავაძის მიერ)

მაღალდისპერსიული ტექნიკური ნახშირბადით შევსებული ორიენტირებული პოლივინილის სპირტის თავისუფალი მოცულობა შესწავლილია ელექტრონული სპინური რეზონანსის სპინური სინჯის მეთოდით. ორიენტირებულ პოლიმერულ ფირებში აზოტჟანგა სტაბილური რადიკალების პოლიმერულ მატრიცაში დიფუზიით შეყვანის შემდეგ აღნიშნული მეთოდის გამოყენებით გაანგარიშებულია ამ რადიკალების საკუთარი ღერძის გარშემო ბრუნვის კორელაციის დროები და, შესაბამისად, მათი დიფუზიის კოეფიციენტები, რაც უშუალო კავშირშია პოლიმერულ მატრიცაში არსებული მიკროსიცარიელეების მოცულობასთან. დადგენილია, რომ თავისუფალი რადიკალების კონცენტრაცია და მათი კორელაციის დროები ფირის ლოკალურ უბნებში დაბალია იმდენად, რამდენადაც მაღალია ფირის ორიენტირების (გაჭიმვის) ხარისხი. ეს პროცესები კარგად კორელირებენ ანალოგიურ მოვლენებთან დენგამტარი შემვსების (ტექნიკური ნახშირბადი) შემცველი იმავე ტიპის კომპოზიტებში. ამ შემთხვევაში სტაბილური რადიკალების დიფუზია პოლიმერულ მატრიცაში უფრო შეფერხებულია, ვიდრე სუფთა პოლიმერში - სტაბილური რადიკალების კორელაციის დროები და, შესაბამისად, დიფუზიის კოეფიციენტები მცირდება რადიკალებსა და შემვსების ნაწილაკთა შორის დამატებით ურთიერთქმედებათა გამო.

REFERENCES

1. Kovarski A.L., Sorokina O.N. (2013) Update on paramagnetic sensors for polymers and composites research. Rapra, UK.
2. Dragutan I., Dragutan V., Caragheorgheopo A. (2001) Nitroxide spin probes for magnetic resonance characterization of ordered systems. *Science Direct.***183:** 767.
3. Warwar N., Mor A., Fluhr R., Pandian R. (2011) Detection and imaging of superoxide in roots by an electron spin resonance and spin-probe method. *Biophysical Journal*, **101:** 1529.
4. Valic S. (2010) Rubber nanocomposites. Chapter 15: 391.Academic Press, New-York.
5. Veksil Z., Andries H., Rakvin B. (2000) ESR spectroscopy of the study of polymer heterogeneity [Review]. *Progress in Polymer Science,* **25**, 3: 949.
6. Jeschke G. (2002) Determination of the nanostructure of polymer materials by ESR spectroscopy. *Macromolecular Rapid Communications,* **23**: 227.
7. Editor A.L.Buchachenko (1977) Atlas spektrov EPR spinovikh metok i zondov, M. (in Russian.).
8. Aneli J.N., Khananashvili L.M., Zaikov G.E. (1998) Structuring and conductivity of polymer composites. New-York.
9. Masuda Kohzoh, Susumu Namba (1974) Contribution of free radicals to electrical conductivity. In book: energy and charge transfer in organic semiconductors.

Received June, 2018