Effect of Ionizing Radiation on Mechanical and Electric Properties of Polymer Composites Based on Polyvinyl ether of Ethyleneglycol

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Radiation technology is an effective way for regulating polymeric materials to physicochemical and mechanical properties. New polymeric hydrogels based on vinyl ethers have been synthesized by the γ-initiated polymerization method. In this paper, we have studied the effect of radiation on mechanical and electrochemical properties of new rubber-like polymeric composite materials based on polyvinylether of ethyleneglycol (PVEEG).

Keywords : Radiation, Polymeric materials, Physicochemical and mechanical properties, Hydrogel, Polyvinyl ether, Ethyleneglycol

1. INTRODUCTION

Radiation treatment of polymeric materials is one of the effective ways for regulation of their physico-chemical and mechanical properties. It was also found by our research team that the gamma-irradiation polymerization method is more effective to obtain both water-soluble and water-swelling co-polymers and the radical mechanism of reactions[1]. It is well known that the treatment of polymeric materials by high-energy radiation can induce two kinds of processes. The first one is a degradation, which is accompanied by decrease of polymeric molecular weight. The second process is a cross-linking, which leads to the formation of three-dimensional polymeric network. Usually both processes proceed simultaneously upon irradiation of polymers with domination of one of them. The nature of polymer affects significantly the processes, which occur in course of irradiation treatment[2]. At present the polymers of vinyl ethers attract considerable attention of researchers because of their unique physico-chemical and mechanical properties[3]. Recently it was shown that the polymeric films containing polyvinyl ether of ethyleneglycol (PVEEG) show the behavior typical for polymers in rubbery state at room temperature[4]. Very high elongations were observed at very low stress applied. The elongation at breakdown for these samples was about 400-500%. On removing the stress the films underwent a partial contraction, which is typical for rubbery state. In the present work we have studied the effect of radiation on mechanical and electrochemical properties of new rubber-like polymeric composite materials based on polyvinyl ether of ethyleneglycol.

2. EXPERIMENTAL

The hydrogel of polyvinyl ether of ethyleneglycol (PVEEG) was synthesized by gamma-irradiation polymerization of vinyl ether of ethyleneglycol with a help of ^{60}Co "MRX-γ-25M" at irradiation dose rate 1 Gy/s and absorbed dose 10 kGy as described in Refs[5]. To optimize the synthesis of polymeric gels based on vinyl ethers, the influence of cross-linking agent (CA) structure and nature as well as conditions of cross-linking process on the equilibrium swelling state, elasticity module and the basic parameters of hydrogels was studied[5]. The hydrogels based on vinyl ether of

ethyleneglycol (VEEG) and vinyl ether of diethyleneglycol (VEDEG) were synthesized in the presence of divinyl ether of diethyleneglycol (DVEDEG), N,N'-methylene-bis-acrylamide (BAA), N'N-bis(2-vinyloxyethyl)urea (BU), N'N-bis (2-vinyloxyethyl) ethylurethane (BEU) and allyl- oxyethylcellulose (AOEC), Mn120000 as cross-linking agents. BAA is bifunctional acrylic cross agent, which is widely used at the synthesis of hydrogels. BU and BEU are anologue to DVEDEG and they are vinyl ethers. AOEC is high molecular weight cross agent. At the using of the vinyl ethers with similar activities of double bonds as a cross-agent, practically same result takes place. In all cases, the increasing of the CA concentration and absorbed irradiation dose D leads to the increasing of gel fraction yield and cross-linking degree. Exception is only BAA, which has high reactivity of its double bounds[6]. Divinyl ether of diethyleneglycol (4 mol.%) was used as a cross-linking agent. After synthesis the hydrogel was washed by distilled water during 2 weeks to remove unreacted monomers. The equilibrium-swollen hydrogel was dispersed using the blender CONCEPT 7200 (Bosch, Germany) to obtain a microgel. Two kinds of samples were prepared. The first one was pure poly(vinyl ether of ethyleneglycol) microgel dried on air during several weeks. The second kind was prepared by mixing the microgel with aqueous solution of silver nitrate (20 mL of 0.005 M $AgNO_3$ was mixed with 250 mL of microgel) and subsequent drying. In course of drying the samples containing silver ions gained a dark color because of partial reduction of $AgNO_3$ into metallic Ag^0. The obtained dry samples were cut into pieces of 10 × 20 mm with a thickness 3-5 mm. Irradiation of compositions was conducted using the linear electron accelerator ELU-6 (Russia) with a medium energy of electrons 2 MeV. The absorbed dose was calculated methodology described in [2] according to the following empirical formula:

$$D = dE/dx \cdot 10^3 \cdot \tau \cdot j,$$

where dE/dx is a coefficient of energy absorption by the substance, τ - irradiation time (s), j – electric current density ($\mu A/cm^2$).

The dose rate was 1.56 kGy/s. The absorbed dose was varied within 10-100 kGy. Mechanical properties of the composites were studied using the facility 2167 P-50 (Russia) in a compression mode. Circular samples are cut and put in cylinder with diameter 10 mm and be pressed using cylindrical piston of different forces. After applying force the contraction of the sample sickness is microscopically measured with error factor 0.01 mm[8].

The rigidity index was calculated according to the following formula:

$$k = F/\Delta h \cdot S$$

where F is a force applied (N), Δh is a contraction of the sample thickness under stress (m) and S is a surface of the sample (mm^2). The dynamic compression was evaluated using the following formula[8]:

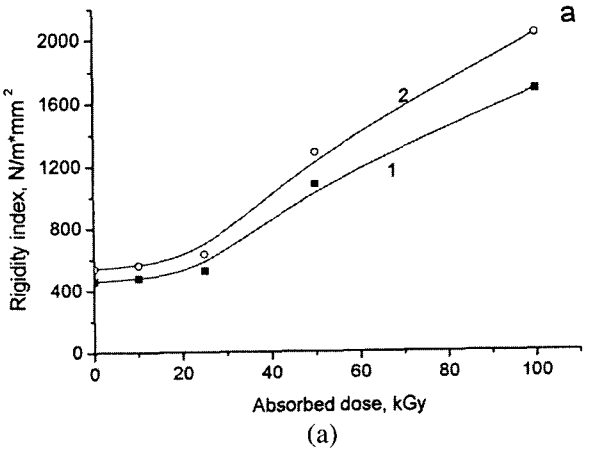
$$\varepsilon = (\Delta h/h_0 \cdot \Delta\tau) \cdot 100\ \%,$$

where h_0 is a starting thickness of the sample and $\Delta\tau$ is a time of compression.

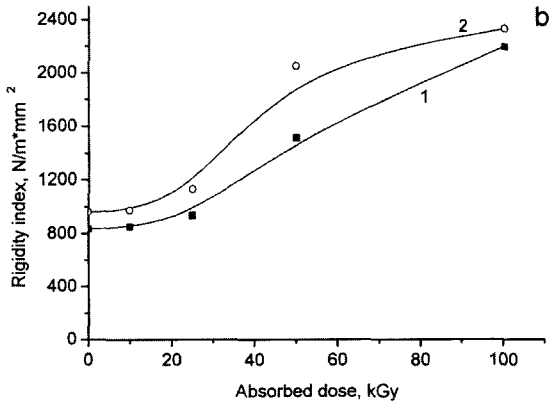
The electric resistance of the materials was measured with the universal voltmeter V-73-42 (Russia), where the samples were put between two similar Cu electrodes as described by K. P. Lee[9].

3. RESULTS AND DISCUSSION

The unique mechanical properties of polymers of vinyl ethers in dry state are due to very low glass transition point, which is below than -30°C[8,10]. Therefore at normal conditions the rubbery state is typical for these polymers with a possibility of very high elongations at very low stress applied. The main effect of radiation treatment of polymers of vinyl ethers is a cross-linking, which leads to the formation of polymeric networks [11-13]. The microgels obtained by pulverization of a macrogel of PVEEG using a blender after drying represent solid substances with rubber-like properties. We have studied the compressibility of the samples as a function of absorbed dose. The dependences of rigidity index of the pure polymer and the samples saturated by silver ions on absorbed dose is plotted in Fig. 1 (a, b, c).



(a)



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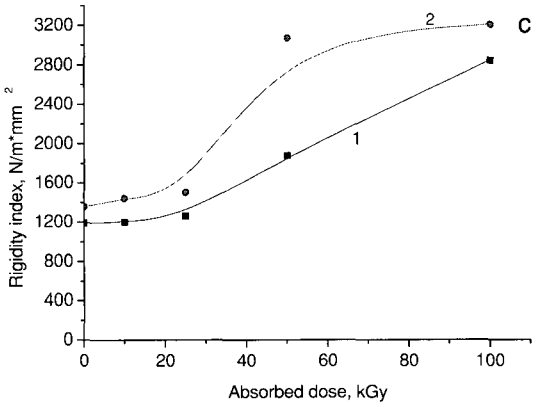
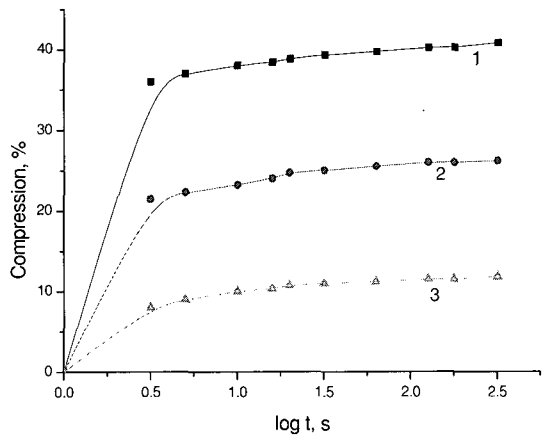


(c)

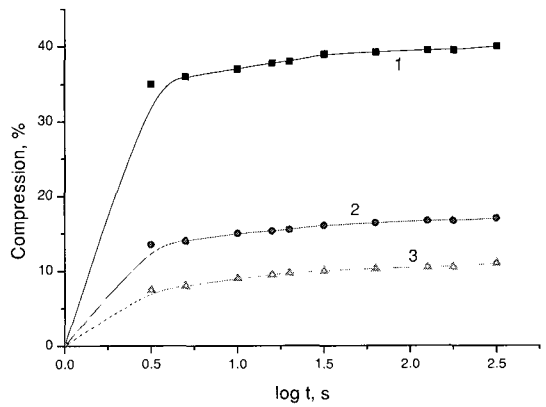
Fig. 1. Rigidity index of pure PVEEG (1) and PVEEG+$AgNO_3$ samples (2) with absorbed dose and 100 (a), 200 (b), 300 N (c) of applied force.

It is seen that an increase of absorbed dose leads to a decrease of the samples compressibility, which is caused by cross-linking of polymeric materials. The samples, which were preliminary saturated by $AgNO_3$ show higher rigidity than the samples based on pure PVEEG due to additional structure formation processes occurring in the materials. This additional structure may attribute to the increasing of cross-linking junctions amount in the structure of polymer network due to presence of $AgNO_3$.

The data on dynamics of compression are plotted in Fig. 2. It is seen that depending the absorbed dose the samples reduce their thickness considerably in the first few seconds of the stress and then their compression comes to a plateau. The maximal compression of the sample is about 35-37%, which is observed for unirradiated samples. It should be noted that the deformation of samples is reversible, which is typical for rubbery state.



(a)



(b)

Fig. 2. Compression of pure PVEEG (a) and PVEEG + $AgNO_3$ (b) samples with time variation and 0 (1), 50 (2), 100 kGy (3) of absorbed dose at 100 N of applied force.

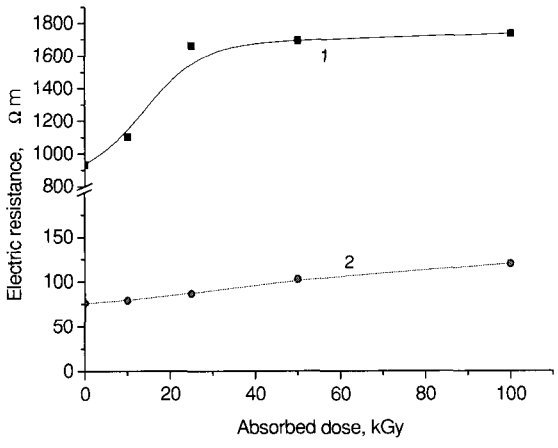


Fig. 3. Eelectric resistance of pure PVEEG (1) and PVEEG + $AgNO_3$ samples (2) with absorbed dose.

The samples saturated by $AgNO_3$ are characterized by lower compression values. The dependence of electric resistance of obtained polymeric materials on absorbed dose is shown in Fig.3. It is seen that the material saturated by $AgNO_3$ is characterized by lower electric resistance than the pure polymer, which is caused by appearance of ionic conductivity in the presence of Ag^+, NO_3^- and water traces. In both cases an increase of absorbed dose decreases the electric conductivity of the materials, which is probably connected with a cross-linking process and some loss of charge carriers mobility.

4. CONCLUSION

It has been shown that the γ-irradiation polymerization is one of the effective method for obtaining of various types of hydrogels on the basis of vinyl ethers of glycols. Physico-chemical and physico-mechanical properties of hydrogels can be regulated by variation of synthesis conditions. The polymeric materials prepared on the basis of poly (vinyl ether of ethyleneglycol) show the mechanical properties to be typical of rubbery-state. An irradiation treatment of the polymers results in additional cross-linking, which strengthens the mechanical properties. A saturation of obtained materials by $AgNO_3$ leads to a considerable decrease of electric resistance and increase in rigidity of polymers.

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