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The Effect of Ionizing Radiation and Magnetic Field on Deformation Properties of High Density Polyethylene/Acrylonitrile-Butadiene Composites

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Abstract: The effect of magnetic field and ionizing radiation on the mechanical properties of polymer blends consisting of high density polyethylene (HDPE) and acrylonitrile-butadiene rubber (NBR) has been investigated. The purpose of the work was to create HDPE/NBR blend composites of significantly different compositions (with an excess of HDPE, intermediate ones, and with an excess of NBR) and to investigate the role of composition on mechanical deformation properties under the influence of magnetic field. The investigation has importance from the engineering viewpoint, since thermoplastic composite materials have been used as structural elements in thermonuclear and engineering fields, like wires, insulation materials and others, which are frequently subjected to mechanical loadings under the effect of magnetic field greater than 1 T. One part of the blends has been irradiated with 5 MeV accelerated electrons up to absorbed dose D equal to 150 kGy. Unirradiated and the radiation modified blends have been exposed to a constant magnetic field with induction B equal to 1.0 T, 1.5 T and 1.7 T. It is found that the action of magnetic field decreases the elastic modulus of unirradiated materials. Decrement of elastic modulus is reduced with increase of the content of NBR in composites. It is also found that preliminary irradiation noticeably decreases the effect of magnetic field. Data of the influence of the magnetic field, radiation cross-linking, and the ratio of the components on the creep are also obtained.

Key words: Magnetic field, radiation modification, creep compliance, polyethylene, acrylonitrile-butadiene rubber.

1. Introduction

Acrylonitrile-butadiene rubber (NBR) consisting of acrylonitrile (ACN) and several butadiene isomers is known for about 50 years as a family member of unsaturated copolymers [1-2]. NBR has been used in industrial applications as manufactured products, insulation and packaging materials [1-4]. It has similar behaviour to ethylene-propylene-diene rubber (EPDM), except its polarity that increases with the content of ACN. The major parts of industrially applied NBR consist of 24 wt% to 30 wt% of ACN and have some advantages in comparison to other rubber like polymers. For example, NBR has a good processability, chemical resistance, especially resistance to hydrocarbons and oils, NBR has wide region of service temperature (from -35 ^{o}C up to 100 ^{o}C) [1-2].

There is a great difference of polarity between the base materials of NBR and HDPE due to the polar acrylonitrile groups in NBR affecting a large difference in surface energy [3-5]. The process of blending both the components may be attributed to some incompatibility, however, the morphology of composites depend on the ratio of both the components [3-5]. It was reported by Fu et al. [4] that small amount of NBR with the content of acrylonitrile 24 wt% improve the environmental stress crack resistance of HDPE, which may increase the wear resistance, that is

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important for coating and insulation materials. Vulcanization of NBR and HDPE/NBR polymer blends by chemical or ionizing irradiation (gamma rays, accelerated electrons) can significantly improve the durability of NBR and increase the compatibility of both the components [6-7]. Radiation modification especially the irradiation by electron beam (EB) has many advances (regulated cross-linking process, low costs, high purity of material, reduced oxidation during the irradiation process that precludes the process of chain breakage) [8].

In the recent years an increased interest has been attributed to the effects of constant and impulse magnetic fields on the physico-chemical and in particular the mechanical properties of polymer materials in the recent years attributed to the modern fields of engineering, mainly the construction and insulation materials (insulators of electrical wire cables, sealants, membranes, gaskets and other devices) of fusion reactors like the International Thermonuclear Experimental Reactor (ITER), the Demonstration Power Plant (DEMO) and the other future fusion reactors based on magnetic confinement of plasma in a high induction magnetic field over 1 Tesla [9-10]. There are a lot of design elements in reactor materials, including polymer materials based on cross-linked high density polyethylene and thermoplastic elastomers, epoxides, polyether and liquid crystal polymers that often have mechanical loadings [9, 11-12]. The main prerequisites for the use of these materials for nuclear applications are thermal stability (resistance to a temperature over 90 ^{o}C), excellent dielectrically properties, resistance to long-term radiation exposure and of course great mechanical properties.

The theoretical and experimental aspects of magnetic field effect on the deformation properties of polymers are discussed in Refs. [10, 13-18]. Some of the main aspects include magnetic field effect on elastic and viscoelastic properties mainly on crystalline and semi-crystalline polymers affecting increase of creep, decrease of mechanical properties like elastic modulus, the yield stress strain at the break and microhardness [10, 13-16]. Physical methods based on the studies of electron paramagnetic resonance have showed a high anisotropy of the diamagnetic susceptibility of the polymer chains and have revealed the presence of internal local magnetic field in a small region of ordered polymer (“physical units”) with non-chemical interaction between the adjacent molecular groups in macromolecules [10, 13-16]. The authors of Ref. [17-18] have found that the orientation action of magnetic field during the tension in respect to elastomer macromolecules can lead to appearance of so-called elastic forces during the strain contributed to micro Brownian motion that leads the ends of chains of elastomeric molecules moving closer each to other. That appears as increment of time of deformation, respectively increment of deformation in contrast with the material strained in the absence of magnetic field. The authors attribute it to elastomers that contain unsaturated bounds like double or triple bonds or polar functional groups like nitrile and halogen more sensitive to MF and that affect the magnetic susceptibility [17]. It is predictable that addition of NBR to HDPE can reduce the undesired effect of increased plasticity during the tension of HDPE under magnetic field.

2. Materials and Methods

2.1 Materials

High density polyethylene (HDPE) of trademark KS 10100 UE of density 0.955 g/cm^3, with a melt flow index 4.0 g/10 min and degree of crystallinity χ_c—62%, ρ—(DOW Chemical Co), and acrylonitrile-butadiene rubber of trademark CKH-26 (Russia) with a content of acrylonitrile 26 wt% have been used in composites.

HPE/NBR blend composites with a ratio of components 100/0; 90/10; 80/20; 50/50 and 20/80 wt% were obtained by thermoplastic mixing at 160 ^{o}C for a total duration of 6 min. Then, plates were obtained by pressure molding at 150 ^{o}C and a pressure of 5 MPa, which were further cut in dog-bone specimens with a length of the working zone 15 mm and a transverse cross section 0.4 × 5 mm.

2.2 Methods

Part of the blends were irradiated in a linear particle accelerator (LINAC) ELU-4 with accelerated electrons (the energy 5 MeV, and the dose rate 1.2 MGy/h) in air with irradiation dose D equal to 150 kGy.

Creep tests of samples were made in the creep measurement apparatus consisting of a stand made of non magnetic stainless steel of trademark 12X18H10T (Russia). The loading was located between the poles of an electromagnet obtained from nuclear magnetic apparatus of trademark TESLA BS 497 (Czechoslovakia) with an induction B in the range from 0.6 T to 2.5 T. The loading for a permanent mechanical stress was made of chemically pure cathode copper (grade MOOK, Russia), containing impurities, not more than 0.001%). Axis of the sample material was perpendicular to the vector of MF. Deformation was measured by a digital indicator of trademark MarCator 1086 Z supplied by Marh (Germany) with a resolution of 0.001 mm, equipped with the MarhCom-v2.1 program for the measurement of data process.

The short-term creep tests were carried out under the action of the constant loads for 10 minutes at 20 ^{o}C ± 0.5 ^{o}C temperatures. Mechanical loading of composite samples was carried out both in the absence of magnetic field and in a field with induction B equal to 1.0 T, 1.5 T and 1.7 T. These tests were performed to investigate the creep in the viscoelastic region of stress-strain relationship. With increased content of NBR, the created stress was gradually reduced from 5 MPa for the entire HDPE to 1 MPa for the composite with the content of NBR 80 wt%. The strain changes in time were calculated in the form of total creep compliance curves $D(t) = \varepsilon(t)/\sigma \times 10^3$ MPa^{-1} to compare the results of HDPE/CPE specimens with different component ratios.

The values of quasi-static elastic modulus E were determined from the results obtained in a fast stepwise loading of samples. Five parallel measurements for each specimen have been done.

3. Results and Discussion

3.1 Creep Tests in Magnetic Field

First, the changes of elastic modulus E and total strains after a 10-min creep which were averaged from five parallel measurements of unirradiated and radiation cross-linked entire high density polyethylene (the base material of the composites) loaded at stress equal to 5.0 MPa were investigated. Kinetics of strain with time under the influence of constant tension for HDPE is shown in Fig. 1.

As the curves of creep compliance $D(t) = \varepsilon(t)/\sigma \times 10^3$, where: $D(t)$ is the total creep compliance (the instantaneous plus the creep one), and t is the time. Results of elastic modulus and the total strain for unirradiated HDPE are shown in Fig. 2 (experimental curves in Fig. 3) and for radiation modified one in Fig. 4.

It is found that elastic modulus reduces notably with increase of induction B of magnetic field. For example, with increase the B from 0 T to 1.7 T the elastic modulus of unirradiated HDPE decreased 1.7 times (the value of E changed from 995 MPa for the entire HDPE at induction B = 0 T to 581 MPa at B = 1.7 T).

Achieved total strain ε of unirradiated polyethylene significantly increased after the time of loading under the influence of magnetic field in comparison to measured in the absence of it. For example, the values of total creep compliance measured at induction equal to 1.5 T and 1.7 T were 1.7 and 1.85 times greater than the values recorded in the absence of magnetic field (Fig. 1).

It should be noted that the results of HDPE almost coincide with the results obtained by Alexandrov et al. [10] and in our previous work [16] it was found that for composite blend of HDPE with chlorinated polyethylene (CPE) with the content of HDPE/CPE 80/20 with increase in induction of magnetic field from 0 T to 1.8 T the modulus of elasticity decreased almost

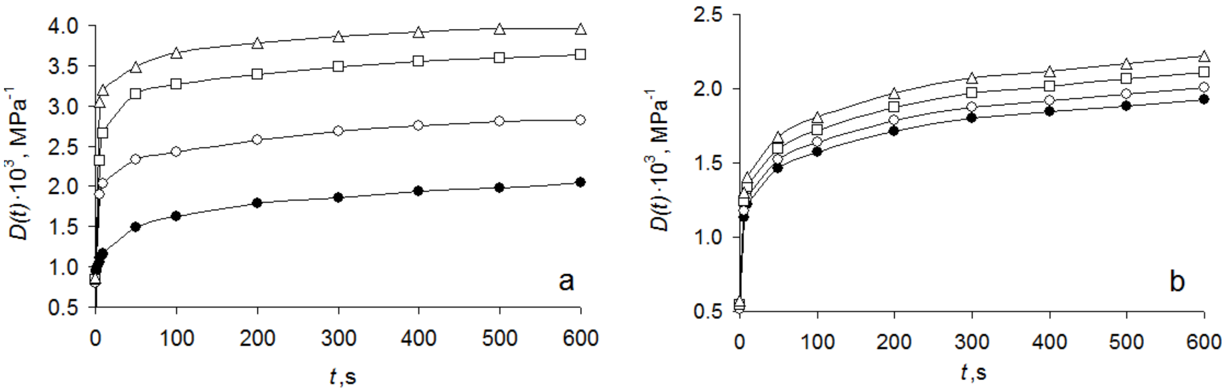

Fig. 1 Experimental curves of creep compliance D(*t*) of unirradiated HDPE (a) and HDPE irradiated up to the absorbed dose 150 kGy (b) in the absence of magnetic field (•) and in the case of induction equal to 1.0 T (○); 1.5 T (□) and 1.7 T (△).

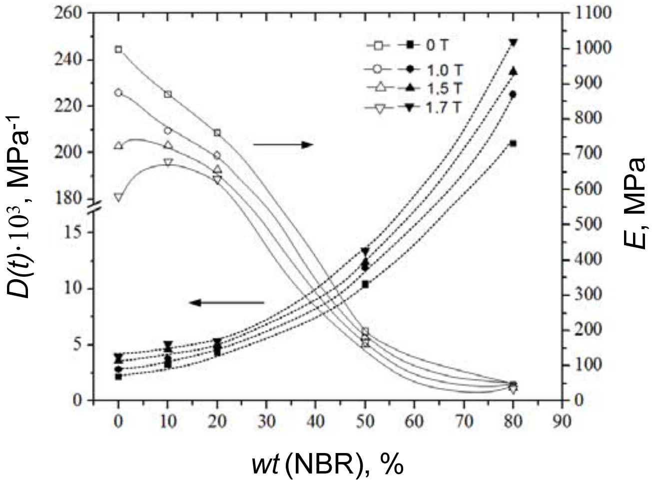

Fig. 2 Dependence of instantaneous total creep compliance *D(t)* and elastic modulus *E* of unirradiated HDPE/NBR composites with a different content of NBR.

1.25 times and the total strain decreased 1.53 times with increase B from 0 to 1.8 T.

It also follows from the data obtained that the preliminary irradiation of HDPE specimens considerably decreases the effect of magnetic field on high density polyethylene. With increase in the induction of magnetic field from 0 T to 1.7 T, the elastic modulus E contrary to that of the unirradiated specimens decreased only 1.22 times (the value of E changed from 1040 MPa at induction B = 0 T to 852 MPa at B = 1.7 T) and the creep strain grew only by 14%. It was also found that irradiated specimens have an increase in rigidity and elastic stifness in the absence of a magnetic field, i.e., at B = 0. At D = 150 kGy. The value of E increased by 4% but ε increased by 22% compared with those of unirradiated HDPE that may be attributed to radiation induced cross-linking of HDPE macromolecules. The effect is small for entire HDPE as the crystalline phase content in HDPE is rather high, that affects the morphology of cross-linked HDPE.

The further investigations are related to HDPE/NBR composite blends. The experimental curves of creep compliance $D(t)$ for HDPE/NBR compositions are seen in Fig. 3. Dependence of instantaneous total creep compliance $D(t)$ and elastic modulus E on induction of MF in the creep tests for 10 minutes for unirradiated specimens is compared in Fig. 2.

With increased content of NBR, the type of deformation behavior of HDPE/NBR compositions tends to the character of elastomer type. The values of

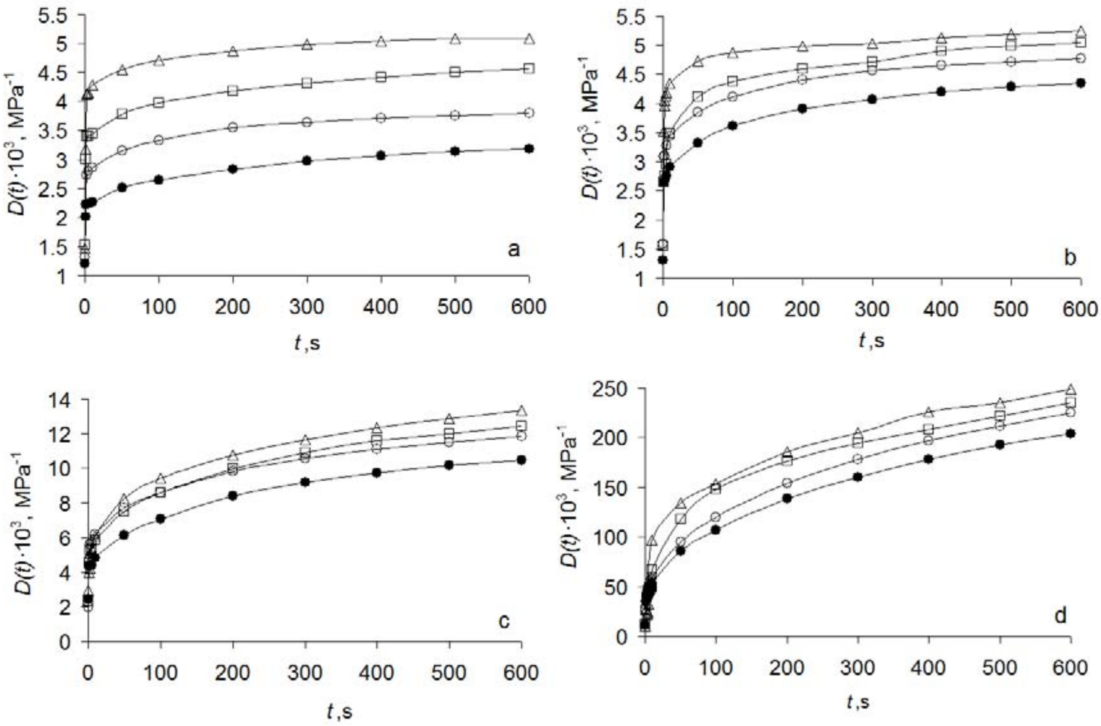

Fig. 3 Experimental curves of creep compliance for unirradiated HDPE/NBR composites with different ratio of the components: (a) 90/10; (b) 80/20; (c) 50/50; (d) 20/80 measured in the absence of magnetic field (•) and in a constant magnetic field with induction *B* equal to 1.0 T (□), 1.54 T (△) and 1.7 T (○).

elastic modulus slowly decrease for compositions with the content on NBR > 50 wt%—the values of E for compositions of HDPE/NBR decrease by 15% for composite 90/10 (average value of *E* is equal to 870 MPa) and by 31% for composite 80/20 (average value of *E* is equal to 760 MPa) in the absence of magnetic field, i.e., at *B* = 0. The value of *E* dramatically decreases for intermediate composition (the ratio of HDPE/NBR equal to 50/50, *E* equal to 200 MPa) and reaches the value 5 times lower than that of entire HDPE. It can be explained with the so-called synergism effect of individual components of the blend explained by morphological changes of a biphase material (Fig. 2). The values of total creep compliance gradually increase with increment in the content of NBR (Fig. 3). The composition of 20/80 has character of almost pure elastomer with the value of *E* 22 times lower than that of pure HDPE (*E* decreases to 45 MPa) and with the total creep compliance about 95 times greater than that of entire HDPE (Fig. 3).

The effect of magnetic field on the deformation properties partly reduces with increase of the content of NBR. For example, with increase in *B* from 0 T to 1.7 T the total creep compliance of unirradiated HDPE/NBR composite with the ratio equal to 90/10 decreased 1.5 times but with further increase of the content of NBR the values of E decrease only about 1.22 times that is almost by 50% in comparison to decrease of E for entire HDPE (Fig. 2) with increase *B* from 0 T to 1.7 T. The effect of magnetic field on decrease of elastic modulus with increase in *B* from 0 T to 1.7 T is reduced by 30-40 % with increase of the content of NBR.

Dependence of instantaneous total creep compliance *D(t)* and elastic modulus *E* on induction of MF in the creep tests of HDPE/NBR compositions irradiated with absorbed dose equal to 150 kGy is compared in Fig. 4. The experimental curves of the total creep compliance *D(t)* for these HDPE/NBR compositions are in Fig. 5.

Irradiated samples of HDPE/NBR compositions with the content of NBR > 80 wt% showed an increase

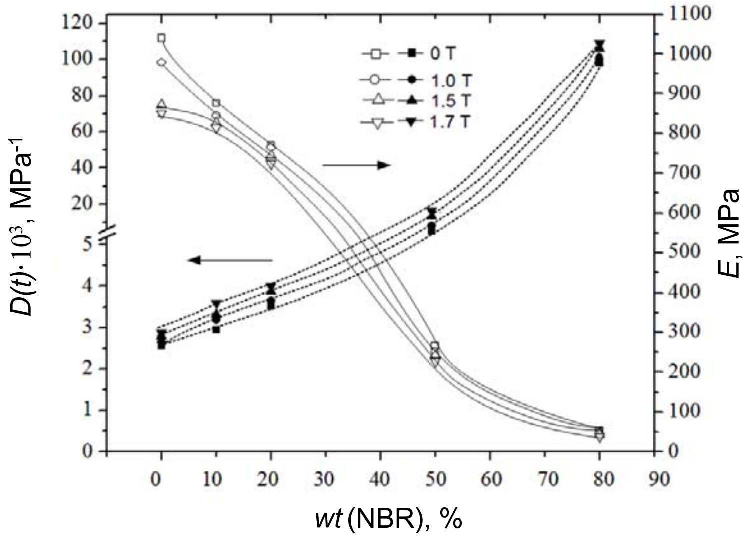

Fig. 4 Dependence of instantaneous total creep compliance *D*(*t*) and elastic modulus *E* of radiation modified (*D* = 150 kGy) HDPE/NBR composites with a different content of NBR.

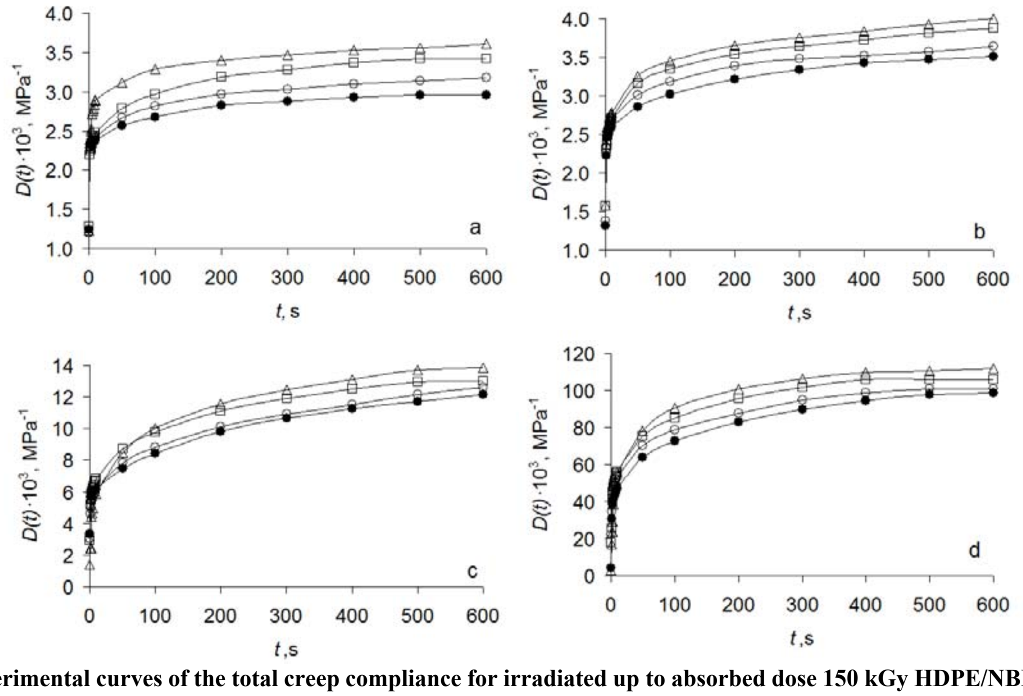

Fig. 5 Experimental curves of the total creep compliance for irradiated up to absorbed dose 150 kGy HDPE/NBR composites with different ratio of the components: (a) 90/10; (b) 80/20; (c) 50/50; (d) 20/80 measured in the absence of magnetic field (•) and in a constant magnetic field with induction *B* equal to 1.0 T (○); 1.5 T (□) and 1.7 T (△).

in stiffness in comparison to unirradiated samples. It is contributed to increase of the cross-linked macromolecule part with enrichment of amorphous phase of composite. As it is already known, the radiation induced cross-linking predominantly occurs in the amorphous region [7-8]. Elastic modulus did not change a lot for composites with HDPE as the dominant matrix, but increased by 35% in case of intermediate composition and by 16% in case of composite with the content of NBR 80 wt%. The values of total strain gradually decreased with increase of the content of NBR. For example, the total creep compliance decreased two times for composite with the ratio of HDPE/NBR equal to 20/80 in comparison to unirradiated sample.

It was found that the radiation modification of the samples led to a significant modification not only on reducing the deformability, but also effectively minimized the effect of MF on the creep. This is evident from approach of the curves each to other, as shown in Fig. 5. The values of elastic modulus for composites with the content of NBR 10% to 50% increased only by 7% to 10% with increase in the induction of magnetic field from 0 T to 1.7 T which are obviously less than that of unirradiated specimens. For composite with NBR as the dominant phase, the value of E increased by 17% which may be contributed to some increased plasticity of vulcanized part of composite as the morphology is more affected by the elastomer than by the part of polyethylene. It is confirmed by the discussed results [17]. The values of total creep compliance $D(t)$ at radiation dose equal to 150 kGy decreased with increase in the induction of magnetic field from 0 T to 1.7 T. For example, the value of total creep compliance decreased only by 14% for composites with the content of NBR 20-50 wt% and by 11% for composite with content of NBR 80 wt%.

Thus, the results of our tests point to a rather noticeable influence of magnetic field on the deformation properties of HDPE/NBR binary blends (decrease of elastic modulus, increase of creep strain). The effect of magnetic field on the creep process in the radiation-modified HDPE/NBR blend composites made it possible to draw the inference about a considerable decrease of magnetic field induced deformability as a result of introduction of the NBR into the composition, i.e., of an additional amorphous phase and continued with radiation cross-linking.

4. Conclusions

An experimental investigation into the effect of a constant magnetic field and ionizing radiation on the deformation properties (elasticity and the creep) of a blend composite consisting of a high-density polyethylene and nitrile-butadiene rubber binary composites at a wide ratio of components has been investigated.

It is established that exposure to magnetic fields causes a marked decrease in the modulus of elasticity of the unirradiated materials. A significant effect of the magnetic field was also identified on the creep of unirradiated polyethylene and its composites with acrylonitrile-butadiene rubber. It was concluded that the observed changes (increase of the total creep compliance and decrement of elastic modulus) induced by magnetic field with induction B equal up to 1.7 T reduced very remarkably with increase in the content of NBR content in HDPE/NBR blends and also with increase of the cross-links obtained by preirradiation modification by accelerated electrons of irradiation dose equal to 150 kGy. The results make it possible to adjust these polymer materials in areas under the tension in high magnetic fields that can be attributed to construction materials of thermo nuclear reactors and other engineering fields. Increase of the stiffness and rigidity of radiation cross-linked HDPE/NBR together with an excellent chemical properties show that it may be a promising composite for several properties, including the magnetic composite materials and other design elements.

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