

## Effect of Gamma-Irradiation on the Electret Properties of Poly(L-lactide)

Temenuzhka Yovcheva, Mariya Marudova, Asya Viraneva, Elena Gencheva, Nikola Balabanov, Georgi Mekishev

Department of Experimental Physics, University of Plovdiv, 24 Tzar Assen Str., 4000 Plovdiv, Bulgaria

Correspondence to: T. Yovcheva (E-mail: temiov@uni-plovdiv.bg)

**ABSTRACT:** Electret stability of poly(L-lactide) (PLA) films, gamma-irradiated up to 100 kGy has been investigated by measuring the surface potential during the storage period. PLA samples—40- $\mu\text{m}$  thick films—were prepared by the casting method and then irradiated in a  $^{60}\text{Co}$  radiation facility at a dose rate of 0.25 kGy/h. The structural changes during the irradiation were estimated by viscometric, differential scanning calorimetry and scanning electron microscope measurements. Random chain scission and appearance of end radicals are the most probable results of the irradiation process. After irradiation, the samples were charged in a corona discharge system and surface potential was measured by the method of the vibrating electrode with compensation. The values of the surface potential of the irradiated samples were higher in comparison with the non-irradiated samples. This effect could be related to the degradation of the macromolecules and changes in the crystal state of PLA during the irradiation. Both of the mentioned factors lead to structural defects that increase the number of discrete trapping levels. The effect of low pressure on the surface potential drop was also investigated. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** gamma-irradiation; poly(L-lactide); corona; films; differential scanning calorimetry

Received 20 April 2011; accepted 31 May 2012; published online

DOI: 10.1002/app.38140

### INTRODUCTION

Poly(L-lactide) (PLA) is well-known biodegradable, biocompatible, and nontoxic polyester, which can be produced from renewable resources. PLA offers the potential for an attractive combination of mechanical properties, biocompatibility, and cost and finds a wide variety of applications.<sup>1–3</sup> PLA possesses polar uniaxial orientation of molecular dipoles and shows electro-active properties such as shear piezoelectricity.<sup>4</sup> Corona-charged polylactic acid films with different degree of crystalline were investigated in respect to their electret properties.<sup>5</sup> The results obtained show that films with preliminary determined surface potential values could be formed through changing of the degree of crystallization, corona charging conditions, and lower pressure values. PLA electrets charged in corona discharge are used as polymeric implants in medicine,<sup>6</sup> drug release matrices<sup>2,3</sup> and as biodegradable electric filter media.<sup>7</sup>

The effect of gamma-irradiation on structure, crystallization behavior and thermal properties of PLA are investigated in Refs. 8 and 9. Poly(L-lactic acid) (PLA), was irradiated with gamma-rays in air and in vacuum at 25°C. Melting point  $T_m$ , glass transition temperature  $T_g$ , and number-average molecular weight  $M_n$  decreased with increasing the irradiation dose. At low doses,  $T_m$ ,  $T_g$ , and  $M_n$  decreased sharply and then the rate

became slower. Up to 200 kGy, PLA was predominantly degraded by random chain-scission. Extensive chain scission, as a dominant effect of gamma-irradiation has as a consequence a growth of new thin crystal lamellae and occurrence of the second low-temperature melting peak. Above 200 kGy, recombination reactions or partial crosslinking may occur in addition to chain-scission. The decrease in  $M_n$ ,  $T_m$ , and  $T_g$  of the sample in air was faster than in vacuum because of oxidative chain-scission. Biodegradation of PLA was retarded with increasing dose due to the introduction of crosslinking during irradiation.

Unfortunately, we could not find any information about the influence of gamma-irradiation on the charge decay of PLA electret films in the published papers.

The present article reports the effect of gamma irradiation (up to 100 kGy) on the structural modifications and the electrets' charge decay of PLA films.

### EXPERIMENTAL

#### Preparation of PLA Films

PLA ( $M_w = 85,000$ – $160,000$  g/mol) was purchased from Sigma and used without further purification or characterization. A polylactide film was prepared by casting of 1 g/dL PLA solution

in chloroform. The solution was poured into glass dishes and then dried at room temperature for 48 h in vacuum drying chamber Bioblock Scientific 45003. All the dishes are placed onto a horizontal leveled surface. The film's thickness was about  $40 \pm 1 \mu\text{m}$  measured by electronic micrometer Micromaster IP54, TESA SA, Switzerland. The samples with 30-mm diameter were cut from this film.

### Gamma Irradiation

Right after the samples were prepared they were irradiated at different gamma irradiation doses. The samples were placed in special holders inside a metal tube under the  $^{60}\text{Co}$  gamma source. The irradiations were performed in air at room temperature by a  $^{60}\text{Co}$  source with total doses of 5, 25, 50, and 100 kGy at dose rates of 0.25 kGy/h. It was checked by thermometric control that the sample temperatures during the irradiation did not appreciably increase above room temperature. This was expected because of the low dose rate of the irradiation (0.25 kGy/h).

### Charging the Samples

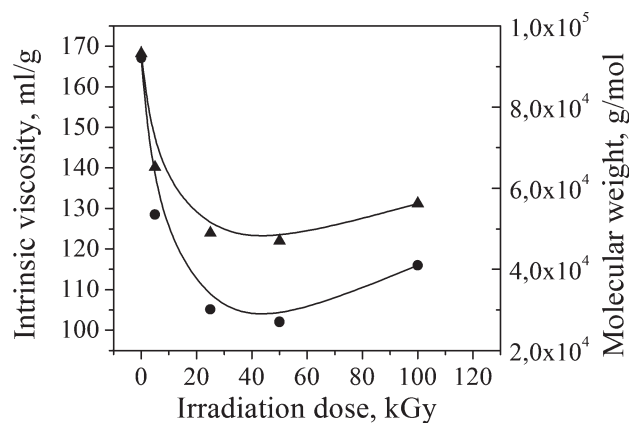
The corona charging of the samples was carried out by a three-electrode system consisting of a corona electrode (needle), a grounded plate electrode and a grid placed between them. The experimental set up is described in Ref. 10. The samples of the non-irradiated (0 kGy) and gamma-irradiated PLA films were charged at a room temperature for 3 min. Positive or negative 5 kV voltage was applied to the corona electrode. Voltage of 1 kV of the same polarity as that of the corona electrode was applied to the grid. The electret surface potential of the charged samples was measured by the vibrating electrode method with compensation<sup>11</sup> by which the estimated error was less than 5%. By this method, the electrode vibrations induce variations in the electret-electrode gap which causes periodic changes of the induce charge on the electrode, and we have alternating current in the outer circuit. If we supply appropriate outer voltage to the vibrating electrode its potential becomes equal to the electret surface potential and the value of the electric field in the gap gets zero, that is, the electrode vibrates in a zero electric field and there is no current running in the outer circuit. That outer voltage determines the electret surface potential.

### Characterization of Structural Changes of Films

**Viscometry.** Measurements of the specific viscosity as a function of the concentration of poly(lactic acid) (0.01–0.1%, w/w) in chloroform were carried out using an Ubbelohde viscometer with 0.40 mm internal capillary diameter at 25°C. The details of viscometer measurements are given in Ref. 12. The efflux time for chloroform was 76 s and no shear rate corrections were made. The intrinsic viscosity [mL/g] was calculated by the extrapolation of reduced viscosity to zero concentration.

**Differential Scanning Calorimetry.** Some thermal characteristics of the PLA films—glass transition temperature, temperatures and enthalpies of cold crystallization, and melting, as well as degree of crystallization were examined by a differential scanning calorimetry (DSC) method. The samples were heated from 25 to 250°C at a constant rate of 10 K/min.

**Scanning electron microscopy.** Morphological investigation of the surface was carried out using a scanning electron micro-



**Figure 1.** Intrinsic viscosity (circle) and molecular weight (triangle) of irradiated PLA samples.

scope (SEM-515, Philips, Belgium). The samples were sputter-coated by a very thin gold layer at a thickness of 14 nm prior to examination to allow conductivity.

## RESULTS AND DISCUSSION

The structural changes during the irradiation were estimated by viscometric determination of the molecular weight and some thermal characteristics determined by means of the DSC method.

### Molecular Weight Analysis

Molecular weight of PLA films was determined by a viscometric measurement, using the Mark–Houwink equation:

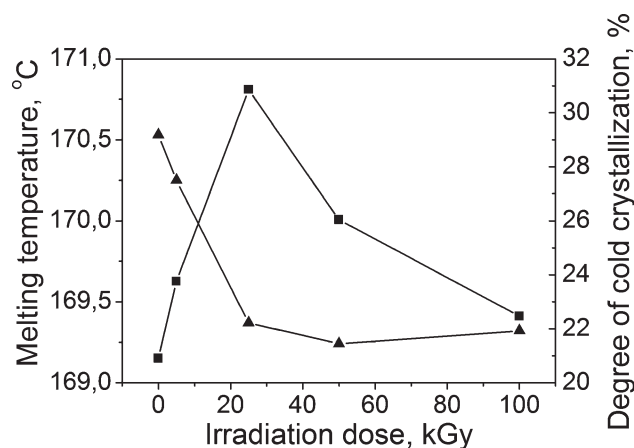
$$[\eta] = K \times M_w^\alpha,$$

where  $[\eta]$  is the intrinsic viscosity,  $K$  and  $\alpha$  are specific for the material positive constant. For PLA  $K = 4.41 \times 10^{-4}$  dL/g and  $\alpha = 0.72$  were chosen.<sup>13</sup>

The dependences of irradiation dose on the intrinsic viscosity and molecular weight are presented in Figure 1. The increase of the irradiation dose up to 50 kGy leads to decrease of the PLA intrinsic viscosity (molecular weight respectively) and degradation of the PLA. A common phenomenon in radiation-induced processing of polymers is the scission of weaker bonds in macromolecules.<sup>14</sup> The exposed material absorbs the energy supplied by irradiation and excited macromolecules are produced. Degradation of PLA was predominantly chain-scission. Further increase of the irradiation dose above 50 kGy leads to increase of the intrinsic viscosity (Figure 1) that is experimental evidence for increasing of the molecular weight of the sample. We assume that irradiation dose above 50 kGy initiates a cross-linking process expressed in a slight growth of the molecular weight. The results obtained are in good agreement with previously published references.<sup>15,16</sup>

### Thermal Analysis

Further information about the degradation and cross-linking processes and also for changes of degree of crystallization during the irradiation was obtained by evaluating the thermal characteristics of irradiated and non-irradiated PLA samples.

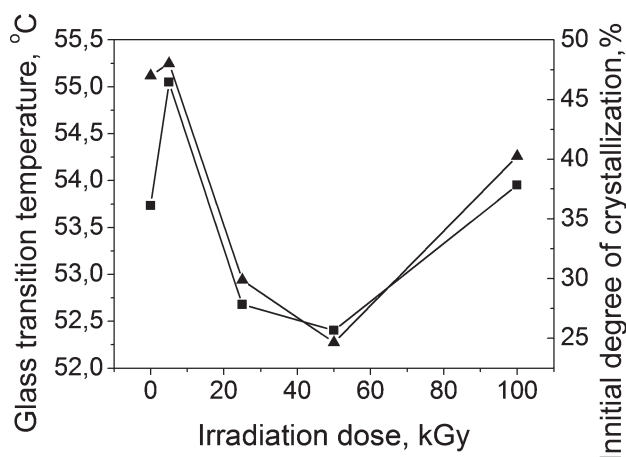


**Figure 2.** Melting temperature (▲) and degree of cold crystallization (■) of PLA films.

The melting temperatures of the gamma-irradiated PLA samples followed the same tendency as the intrinsic viscosity-irradiation dose dependence (Figure 2). The melting peaks shifted to a lower temperature and became broader as the irradiation dose increased, which implied that further degradation or introduction of irregularities proceeded from the crystalline surfaces to the inside. Increasing of the irradiated dose above 50 kGy led to a slight increase of the melting temperature, hence, less degraded crystal components with smaller irregularities had been grown due to the cross-linking process.<sup>16</sup>

The highest degree of cold crystallization was observed at the irradiation dose of 25 kGy (Figure 2). It corresponded to the relative high degree of polymer degradation and low molecular weight. The lower molecular weight was a precondition for the increase of the mobility of macromolecules and reinforced their potential for reorganization and crystallization.

The initial degree of crystallization is lowest at the irradiation dose of 50 kGy, where the polymer degradation is highly marked and the crystal structure is partially destroyed (Figure 3). The initial degree of crystallization is highest at the irradiation dose of 5 kkGy. The presence of higher amount of amorphous phase and the lower degree of polymerization at irradiation dose of 50 kGy leads to increase of the free volume in the PLA samples. The increase of the free volume is related to



**Figure 3.** Glass transition temperature (▲) and initial degree of crystallization (■) of PLA films.

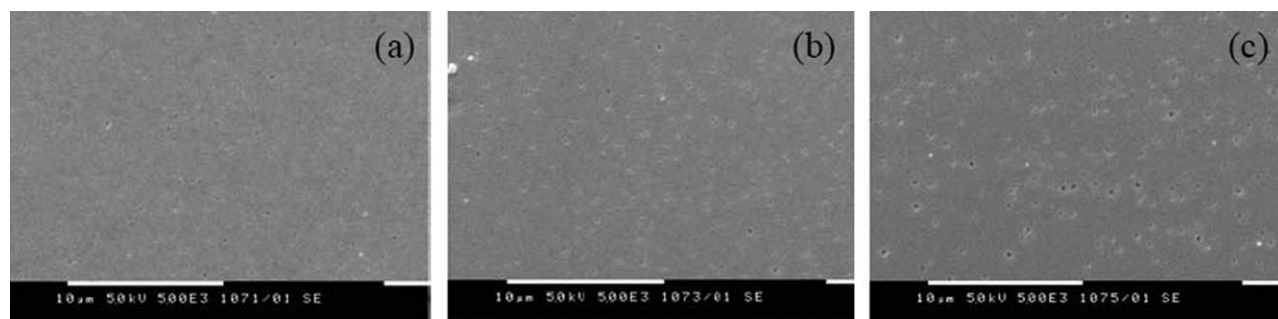
decrease of the glass transition temperature. Therefore, the glass transition temperature—irradiation dose dependence follows the same tendency as the initial crystallization degree.

#### SEM Measurements

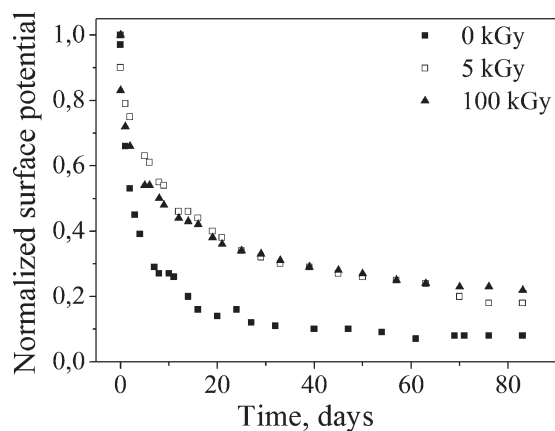
To examine the influence of irradiation on the microstructure, the surface morphology of PLA samples was analyzed by a SEM. Microstructures of non-irradiated and irradiated samples are shown in Figure 4(a–c). The SEM analysis clearly shows that gamma irradiation influences the changes in PLA surface morphology—appearance of a defect/damage, which is almost uniformly distributed on the samples' surfaces. These objects are quite clear for higher doses—100 kGy. The radiation-induced increase in defects at lower doses can be attributed to degradation; in particular, the scission of strained tie molecules is the most probable process. At higher doses, the introduction of crystal defects is additionally expected. The results obtained are in good agreement with the previously published references.<sup>17</sup>

#### Effect of Irradiation on Electrets' Properties

The time dependences of the sample surface potential under room conditions had been studied for 85 days. After this period, steady state values of the surface potential were established for all of the samples. The surface potential has been measured once a week except for the first 10 days when it was measured more often because the charge rapidly decayed. The samples



**Figure 4.** Scanning electron microscopy pictures of PLA samples at high magnification,  $\times 5000$ : (a) non-irradiated; (b) 5 kGy gamma irradiated; (c) 100 kGy gamma irradiated.

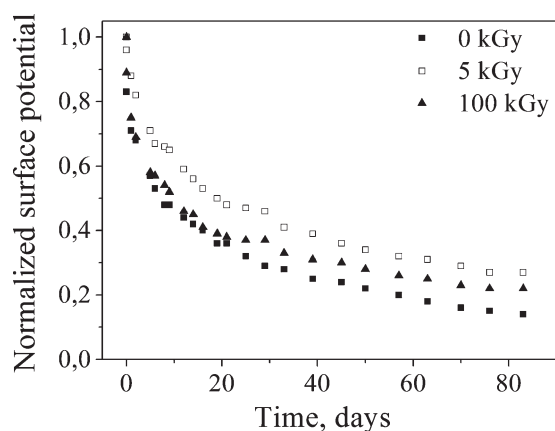


**Figure 5.** Time dependences of surface potential of negatively charged PLA electrets.

were kept in a desiccator at controlled circumstances –  $T = 25^{\circ}\text{C}$  and relative humidity (RH) = 54%, between measurements.

Figures 5 and 6 present a classical result concerning potential decay on non-irradiated and gamma-irradiated corona charged PLA films. For the negatively charged samples, the curves of surface potential decay are nearly the same for irradiation dose from 5 to 100 kGy. For the positively charged samples, the potential decay curve at 5 kGy dose of irradiation is located a higher than the one for 100 kGy.

The surface potential values of the irradiated samples, independently of the corona polarity and irradiation dose, were higher in comparison with the non-irradiated samples. The atoms and atom groups that build the polymer chains are bound together by weak covalent bonds that are disrupted easily by gamma ray irradiation. As the polymer absorbs the energy of irradiation, the bonds are broken and polymer radicals are formed.<sup>18</sup> In practice, degradation and cross-linking often occur simultaneously, and the dominant one determines the reaction results.<sup>19</sup> Our experimental results (Molecular weight analysis, SEM, and DSC measurements) show that for PLA the degrada-

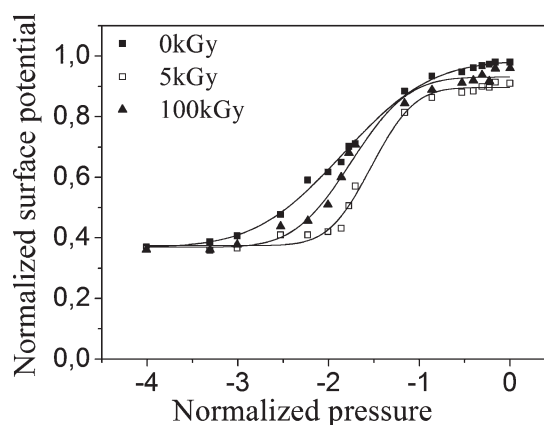


**Figure 6.** Time dependences of surface potential of positively charged PLA electrets.

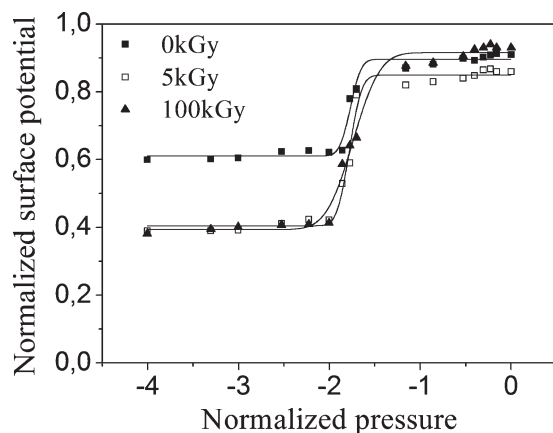
tion reaction exceeds the cross-linking reaction up to 100 kGy dose of irradiation, in contrast to gamma irradiated polybutylene naphthalate where the cross-linking reaction is dominant.<sup>20</sup> Consequently, the potential decay of PLA films mainly relies on the process of degradation. It is known<sup>21</sup> that the density of surface states can be increased by degradation. These surface states become traps of the charges, and hence, the charge density can be increased. Based on this, it is likely to understand why the normalized surface potential increased by the gamma-irradiation.

PLA is a highly crystalline material and this structural characteristic also affects the changes introduced to the surface potential stability of the samples after their treatment. DSC-thermograms of the samples indicated the highest glass transition temperature and crystallinity for the samples, irradiated by 5 kGy. The crystal structure was related to unhomogeneities in the PLA structure, which could behave like charged traps and lead to stability of the surface potential. Because of the change and complexity of crystalline structure induced by crystallinity, the kinds of structural defects enlarge, resulting in the increase of the number of discrete trapping levels. Similarly, results were found for the electret state of other polyesters with similar to the PLA structure, like PET.<sup>22</sup>

It should be physical processes which are responsible for the potential decay of the electrets: surface processes—surface conduction and atmospheric neutralization; volume processes—sample polarization and injection of the deposited charge.<sup>23</sup> To clarify what kind of discharge processes (surface or volume) is predominant the effect of low pressure on the surface potential drop was also investigated. Low pressure is one of the conditions that propose the presence of surface discharge processes. Initially the PLA samples were charged in a corona discharge. After that the electrets were placed in a vacuum chamber at various low pressures (from 0.1 to 1013 mbar). The dependences of the normalized surface potential on normalized pressure for the non-irradiated and gamma irradiated PLA electrets charged in a negative or in a positive corona, respectively, are presented in Figures 7 and 8. The “normalized surface potential” is the ratio  $V/V_0$  where  $V_0$  indicates the initial value of the surface



**Figure 7.** Dependence of the normalized surface potential of negatively charged PLA samples on the normalized pressure.



**Figure 8.** Dependence of the normalized surface potential of positively charged PLA samples on the normalized pressure.

potential, measured just after the sample had been charged,  $V$  indicates the surface potential, measured after removing the electrets from the vacuum chamber. The “normalized pressure” is the ratio  $p/p_0$  where  $p_0$  is the atmospheric pressure,  $p$  is the low pressure under which the electrets were stored in the vacuum chamber. Each point in the figure is a mean experimental value from six samples. The maximum standard deviation from the average value at 95% confidence level was 5%.

The results obtained show that three parts exist in each curve. Similar behavior has been observed by Mekishev et al.<sup>24,25</sup> The values of surface potential at a pressure of 0.1 mbar [ $\log(\text{Normalized pressure}) = -4$ ] for the non-irradiated samples charged in a positive corona are higher than those for the non-irradiated samples charged in a negative corona. The values of surface potential at a pressure of 0.1 mbar for the non-irradiated and the gamma-irradiated PLA samples charged in a negative corona are the same. The surface potential values at a pressure of 0.1 mbar are higher for the non-irradiated PLA samples charged in a positive corona than those for PLA gamma-irradiated samples, independently of the irradiation dose (5 or 100 kGy). The experimental results are well described by the equation, analyzed in Ref. 26. This equation is analogous to the equation that described linear desorption accompanied by surface diffusion. The solid line in Figures 7 and 8 is the theoretical curve, fitted by this equation. The really good agreement between the theoretical curves and the experimental data (Figures 7 and 8) shows that the surface potential decays due to the desorption of ions from the electret surface accompanied by surface diffusion. These results can be explained if we suppose the presence of a different type of surface traps formed during the positive and negative corona charging processes. The energy distribution for the traps of negatively and positively charged samples is different. The pressure range where the surface potential of positively charged samples decays sharply is relatively narrow,  $P = (40 - 10)$  mbar, while the corresponding one for the negatively charged samples is quite wider,  $P = (70 - 1)$  mbar. Hence, the surface processes rather than charge injection, may explain the observed potential decay.

However, the results obtained do not show clearly the effect of charge trapping, which can be induced by gamma-irradiation in

air. Consequently, further investigations are required to clarify the influence of gamma-irradiation on the PLA electret behavior.

## CONCLUSION

The gamma irradiation effects on the electret behavior of corona charged biobased polymer films of PLA were investigated at energies of up to 100 kGy. It was shown by viscometric, DSC, and SEM studies (examination) that the degradation process is predominant. It was observed that the values of the surface potential of the irradiated samples, independently of the corona polarity and irradiation dose, were higher in comparison with the non-irradiated samples. We suppose that gamma-induced degradation and enlarged crystallinity form new surface states that become traps for the charges and those new surface states explain why the normalized surface potential increases by gamma irradiation. It was established by low pressure measurements that the surface processes rather than charge injection, may explain the observed potential decay.

## REFERENCES

- Liu, L. S.; Finkenstadt, V. L.; Liu, C. K.; Jin, T.; Fishman, M. L.; Hicks, K. B. *J. Appl. Polym. Sci.* **2007**, *106*, 801.
- Thomas, K. A.; Toth, J. M.; Crawford, N. R.; Seim, H. B. *Spine* **2008**, *33*, 734.
- Grayson, A.; Voskerician, G.; Lynn, A.; Anderson, J.; Cima, M.; Langer, R. *J. Biomater. Sci.* **2004**, *15*, 1281.
- Fukada, E. *IEEE Trans. Ultrason. Ferroelectr.* **2000**, *47*, 1277.
- Gencheva, E. A.; Yovcheva, T. A.; Marudova, M. G.; Viraneva, A. P.; Bodurov, I. P.; Mekishev, G. A.; Sainov, S. H. *AIP Conf. Proc.* **2009**, *1203*, 495.
- Valentini, R. US Patent, **1998**, No 5,759,205.
- Tokuda, S. Jpn Patent, **2004**, No. JP 2004-57976 A.
- Nugroho, P.; Mitomo, H.; Yoshii, F.; Kume, T. *Polym. Degrad. Stab.* **2001**, *72*, 337.
- Milicevic, D.; Trifunovic, S.; Galovic, S.; Suljovrujic, E. *Radiat. Phys. Chem.* **2007**, *76*, 1376.
- Yovcheva, T. A. *Corona Charging of Synthetic Polymer Films*, Nova Science Publishers, Inc: New York **2010**, 7.
- Reedyk, C. W.; Perlman, M. M. *J. Electrochem. Soc.* **1968**, *115*, 49.
- Kulicke, W.; Clasen, C. *Viscosimetry of polymers and polyelectrolytes*, Springer-Verlag, Berlin-Heidelberg: Germany, **2004**.
- Doi, Y.; Fukuda, K. In *Biodegradable Plastics and Polymers*, Elsevier Science: New York, **1994**.
- Gupta, M. C.; Deshmukh, V. G. *Polymer* **1983**, *24*, 827.
- Kodama, Y.; Lima, N. B.; Luci D. B. Machado, L. D. B.; Nakayama, K. International Nuclear Atlantic Conference – INAC 2007, Brazil, **2007**.
- Nugroho, P.; Mitomo, H.; Yoshii, F.; Kume, T. *Polym. Degrad. Stab.* **2002**, *72*, 337.

17. Milicevic, D.; Trifunovic, S.; Galovic, S.; Suljovrujic, E. *Therm. Rad. Phys. Chem.* **2007**, *76*, 1376.
18. Banford, H. M.; Fouracre, R. A. *IEEE Electr. Insul Mag.* **1999**, *15*, 19.
19. Du, B. X.; Suzuki, A.; Kobayashi, S. *Trans. IEE Jpn.* **1996**, *116*, 461.
20. Du, B.; Gao, Y.; Huo, Z. J. *Electrostat.* **2009**, *67*, 22.
21. Prutton, M. *Introduction to Surface Physics*, Oxford University Press: USA, **1994**.
22. Xingyuan, Z.; Yiqin, Z. *Chin. J. Mater. Res.* **1992**, *6*.
23. Moulinie, P. J. *Electrostat.* **1999**, *45*, 265.
24. Mekishev, G. A.; Yovcheva, T. A.; Viraneva, A. P. *J. Non-Cryst. Solids* **2007**, *353*, 4453.
25. Viraneva, A. P.; Yovcheva, T. A.; Gencheva, E. A.; Mekishev, G. A. *J. Non-Cryst. Solids* **2010**, *356*, 560.
26. Viraneva, A. P.; Yovcheva, T. A.; Pisanova, E. S.; Gencheva, E. A.; Mekishev G. A. *AIP Conf. Proc.* **2010**, *1203*, 382.