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## تأثير التعرض لأشعة جاما على الخصائص الذاتية لبوليمر خلات السليولوز

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### الملخص:

الإشعاع المؤين للبوليمرات هي تقنية واحدة وقد وجدت لها تطبيقات في مختلف المجالات مثل حفظ الأغذية، وإنتاج الأدوية والصناعات وغيرها. تمتلك تكنولوجيا التشعيع العديد من المزايا مثل التحكم في درجة التحلل، تكوين توزيع بوزن جزيئي متجانس، توفير المواد الكيميائية وأنها عمليات صديقة للبيئة. وقد أجريت هذه الدراسة لتقييم تأثير تشعيع جاما على الخصائص الفيزيائية والتركيبية لبوليمر خلات السليولوز. تم تكوين أقراص صلبة من خلات السليولوز وتعرضها إلى مصدر الكوبالت 60 لفترات زمنية مختلفة. كما تم تحضير محاليل مخففة من البوليمر ودراسة معاملات الإنكسار واللزوجة لكل منها. أظهرت النتائج بأن تعرض خلات السليولوز لأشعة جاما يؤدي إلى انخفاض في قيم كل من الكتلة المولية، الحجم الهيدروديناميكي، الأبعاد الحقيقية والمثالية والنسبة المميزة لخلات السليولوز. وعلى عكس ذلك فإن تشعيع جاما يزيد من قيم ثابت شولتز بلاشكة، التركيز الحرج والتفاعل بين كل من المذاب والمذيب. ومع ذلك، فلقد أدى تعرض بوليمرات خلات السليولوز لأشعة جاما في المحاليل المخففة إلى انخفاض قيم معامل الانكسار، ثابت العزل الكهربائي، متغيرات الذوبانية وكثافة طاقة التماسك.



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ORIGINAL ARTICLE

# The influence of gamma irradiation on the intrinsic properties of cellulose acetate polymers

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**Abstract** Ionizing radiation of polymers is a promising technique that has found applications in various fields such as food preservation, pharmaceutical production and natural bioactive agent industries. Irradiation technology has several advantages like controlling the degree of degradation, producing uniform molecular weight distribution, saving chemicals and environmentally friendly process. This study was carried out to evaluate the effect of  $\gamma$ -irradiation on the physical and structural properties of cellulose acetate (CA) polymer. Solid disks of CA were exposed to a cobalt-60 source (50 kGy) for different periods of time. Dilute solutions of irradiated and non-irradiated CA were prepared and studied viscometrically and refractometrically.  $\gamma$ -irradiation of CA causes a decrease in the values of relative, specific, reduced and intrinsic viscosities. In addition, there is a reduction in the values of molar mass, hydrodynamic volume, real and ideal chain dimensions and the characteristic ratio of CA. On the contrary,  $\gamma$ -irradiation increased the values of Schulz–Blaschke constant, critical concentration and solute–solvent interaction. However, the values of refractive index, dielectric constant, solubility parameters and cohesive energy density of the polymer in dilute solutions are decreased due to the effect of  $\gamma$ -irradiation.

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## 1. Introduction

Polymers have replaced conventional materials in packaging applications due to their functionality, lightweight, ease of processing, and low cost (Risch, 2009). Thus, research in polymer science is developing to producing a plethora of new elastomers, plastics, adhesives, coatings, and fibers. It has been reported that

(Byun et al., 2008) polymers can be degraded by acidic hydrolysis or enzymatic treatment. Although these methods are effective in decreasing the molecular weight, they do have certain disadvantages such as high cost, low yield, long processing time, and acidic wastes from the chemical or enzymatic treatment. Another method used for polymer degradation is irradiation using negative or neutral rays. Irradiation in polymers destroys the initial structure by way of cross linking, free radical formation, irreversible bond cleavages, etc., resulting in the fragmentation of molecules and formation of saturated and unsaturated groups. All these processes introduce defects inside the material that are responsible for change in the physical and chemical properties of the material (Sharma et al., 2007; Alwan, 2012).  $\gamma$ -irradiation is used for the final biological sterilization (Hugo, 1995) of materials that can be subsequently used for

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manufacturing biomedical products. In addition, ionizing radiation leads to the degradation of polysaccharides such as starch, cellulose, and pectin by the cleavage of the glycosidic bonds. The basic advantages of degradation of polymers by radiation include the ability to promote changes reproducibly and quantitatively, without the introduction of chemical reagents and without the need for special devices to control temperature, environment, and additives (Charlesby, 1981). Thus, this technology is simpler and more environmentally friendly than conventional methods. Over the past decades, interest in controlling of degradation effects in radiation processing of polymers has increased continuously (Hon and Chan, 1982; Ershov, 1998; Gladus, 2001; Mowery et al., 2005; Alwan, 2012).

Cellulose acetate (*CA*) is a polymer derived from cellulose, which is one of the most abundant polysaccharides on earth (Rimdsut et al., 2008). *CA* is one of the most commercially important cellulose derivatives. It has been used in several applications such as textiles, cigarette industries, and in separation processes such as dialysis, reverse osmosis, gas separation, and hemodialysis (Cao et al. 2007; Cerqueira et al. 2007). Moreover, *CA* is used in medical applications, such as membrane material for desalination, while other cellulose derivatives such as cellulose acetatebutyrate are being used in capsule form as drug-releasing (Hoenich, 2006). Bio-tech industry of these polymers is closely connected with their solubility, processability, bioactivity and applicability. Therefore, it is based on their intrinsic properties. One can hypothesize that the conformational-intrinsic property relationships of each specific polysaccharide can be manipulated by irradiation in order to adjust their applications.

Although several methods such as sulfation, phosphorylation, and carboxymethylation, acid and alkaline hydrolyses, enzymatic digestion, and ultrasound irradiation have been applied for the depolymerization of polymers and polysaccharides (Leung et al., 2006; Moradali et al., 2007; Sandula et al., 1999; Shin and Lee, 2003),  $\gamma$ -irradiation with high energy has not been used broadly in the research of *CA*. Hence, the aim of the present study is to apply radiation technology to *CA*, so that its intrinsic properties have been studied.

## 2. Experimental

### 2.1. *CA* discolor preparation

The powder material of cellulose acetate (*CA*) has been supplied by a local Libyan company (JOWF) and used without further purification; The samples were ground with a mortar and pestle, the powder samples were spread onto one face of a home-made stainless steel die, in which the die is a Perkin–Elmer product, the powder was placed between two mica sheets to avoid samples sticking to the die, and pressed by a manually operated Perkin–Elmer hydraulic press. After placing the second mica sheet on the top of the powder, the plunger was carefully inserted, and the die cylinder was rotated to remove the air present. The sample was then pressed under a pressure in the range of 3–5 ton/in<sup>2</sup> for 5 min to produce *CA* solid disks (0.5 cm thickness and 2.5 cm diameter).

### 2.2. Solutions preparation

Acetone was used as a solvent for the native and irradiated *CA*-disks. The solvent was then, also, used to make different concentrations by diluting the native and  $\gamma$ -irradiation mother

solutions. The native and  $\gamma$ -irradiation solutions were labeled  $M_0$  and  $M_1$ ,  $M_2$  and  $M_3$ , respectively.

### 2.3. $\gamma$ -Irradiation

Irradiated in air at room temperature by a Canadian <sup>60</sup>Co  $\gamma$ -source (Theratron 780; Theratronics Ltd.) located in the Radiodiagnosis and Radiotherapy Center at Benghazi city. Each *CA* discolor was exposed to the radiation at a constant dose rate of 50 rad/min for different periods of time. Monitoring the change in each sample was made immediately after irradiation, and at intervals afterward for each sample, by using the solution viscometric technique.

### 2.4. Measurements

#### 2.4.1. Viscosity measurements

In determining the efflux time of the solutions, methodology stated by ASTM (1989) was used. The efflux time for solvent ( $t_{acetone}$ ) and cellulose acetate solution ( $t_{CA}$ ) were measured by glass capillary viscometer made by Brand at W-Germany (Kulicke, 2004). The accuracy of the viscosity measurements was  $\pm 0.015$ .

The measured values have been expressed in terms of relative,  $\eta_r$ , specific,  $\eta_{sp}$ , and reduced,  $\eta_{red}$ , viscosities of dilute cellulose acetate in acetone as follows:

$$t_{CA}/t_{acetone} = \eta_r \quad (1)$$

$$\eta_{sp} = \eta_r - 1 \quad (2)$$

$$\eta_{red} = \frac{\eta_{sp}}{C} \quad (3)$$

where  $C$  is the mass concentration of *CA* in acetone.

#### 2.4.2. Refractive index measurement

Refractive indexes of solutions have been measured by refractometer (Bausch and Lomb, New York) with a precision of 0.01%. The technique is described in detail elsewhere (Kratovichil, 1987). The Measurements have been thermostated to  $\pm 0.1$  °C; at 25 °C.

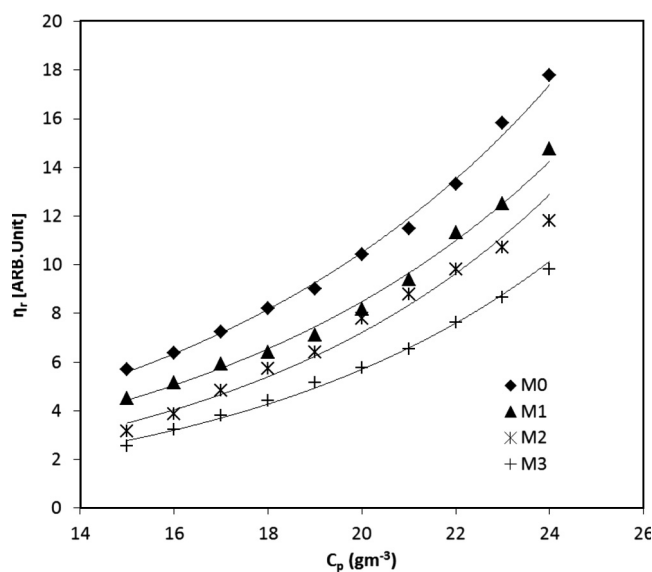
## 3. Results and discussion

### 3.1. Weight parameters and their kinetic behavior

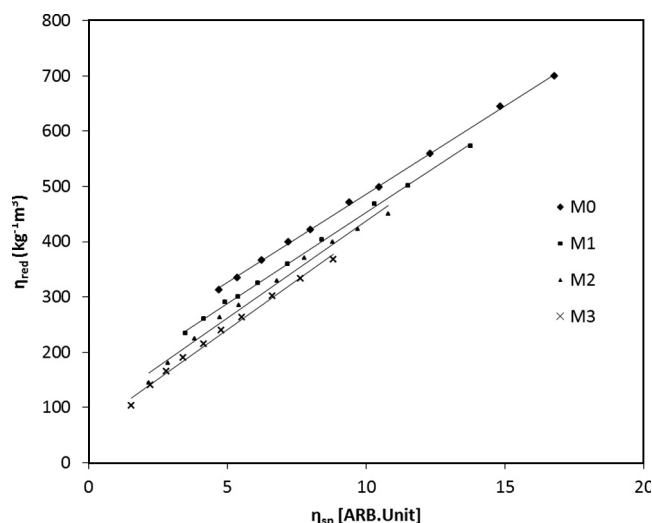
Fig. 1 shows plot of native ( $M_0$ ) and irradiative ( $M_1$ – $M_3$ ) relative viscosity values against mass concentration ( $C_p$ ). This figure demonstrates that viscosity increases monotonically with the increase of concentration of the *CA* solution. Furthermore, consideration of the plots indicates that the rate of increment in the viscosity values after  $\gamma$ -irradiation is less than those before irradiation. This could be attributed to the reduction in the polymer chains (O'Donnell, 1991).

Thus it is clear that  $\gamma$ -irradiation produces significant changes in the viscosity of the *CA* solution and as the absorbed dose increases, the *CA* solution shows a significant decrease of viscosity. The decrease in the viscosity occurs by the radiolysis of *CA*. This result is consistent with other studies on starch, agar, alginate, and carrageenan (Aliste et al., 2000; Graham et al., 2002).

The linear plots of Fig. 2 show agree with Schulz–Blaschke equation for native ( $M_0$ ) and  $\gamma$ -irradiated ( $M_1$ – $M_3$ ) samples (Schoff, 1999).



**Figure 1** Relative viscosity vs. concentration for native and different degradable *CA* in acetone solution at 25 °C.



**Figure 2** Reduced viscosity vs. specific viscosity for native and different degradable *CA* in acetone at 25 °C.

$$\eta_{red} = [\eta] + k_{sb}[\eta]\eta_{sp} \quad (4)$$

where  $\eta_{red}$  is reduced viscosity,  $[\eta]$  intrinsic viscosity,  $k_{sb}$ , Schulz–Blaschke constant and  $\eta_{sp}$ , specific viscosity.

However,  $[\eta]$  and  $k_{sb}$  before and after  $\gamma$ -degradable *CA* were estimated from the typical linear plot of Schulz–Blaschke.

The values of relative average viscosity molar mass  $\langle M_v \rangle_r$ , in Tables 1–3 were calculated according to the following form of Mark–Houwink equation (Johnston and Sourirajan, 1973).

$$[\eta] = 4.46 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1} \langle M_v \rangle_r^{0.731} \quad (5)$$

Reduction in the values of intrinsic viscosity and average relative molar mass could be attributed to the marked scission effect on the polymer chain (Reichmanis et al., 1993).

Thus for the *CA* in acetone solution, the solute–solute contact is greater than that for degradable one and consequently,

**Table 1** Mark–Houwink parameters.

Sample	$t_{\text{exposure}}/\text{min}$	$[\eta]/\text{cm}^3 \text{ g}^{-1}$	$\langle M_v \rangle_r$
M <sub>0</sub>	0.00	1656.6	1784583.73
M <sub>1</sub>	30.00	1232.2	1190420.7
M <sub>2</sub>	60.00	857.2	724613.973
M <sub>3</sub>	90.00	622.3	467566.682

**Table 2** The average number of bonds for *CA* in acetone at 25 °C.

Sample	$N$
M <sub>0</sub>	6890.30
M <sub>1</sub>	4596.22
M <sub>2</sub>	2797.74
M <sub>3</sub>	1805.30

**Table 3** The characteristic ratio for *CA* in acetone at 25 °C.

Sample	$C_\infty$
M <sub>0</sub>	195.57
M <sub>1</sub>	160.96
M <sub>2</sub>	157.74
M <sub>3</sub>	152.37

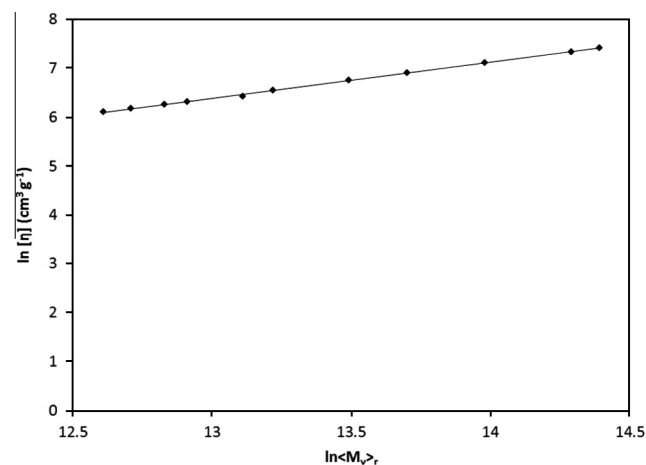
for irradiated *CA*, the solute–solvent interaction is greater than that of the non-irradiated one (Kurata and Tsunashima, 1999; Fujita, 1997).

The linearity increases in the Logarithm of relative average viscosity molar mass vs. Logarithm of intrinsic viscosity of *CA* in acetone solution in the plot of Fig. 3 verifying Mark–Houwink equation.

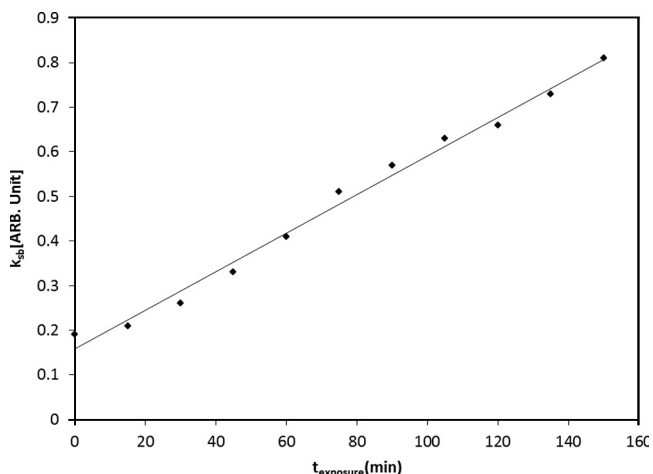
Fig. 4 shows plot of Schulz–Blaschke constant  $k_{sb}$  values against exposure time, it reflects how far the values of Schulz–Blaschke constant of the polymer increase with increasing the exposure time. This could be attributed to scission on the polymer chains.

### 3.2. Size parameters and their kinetic behavior

The values of hydrodynamic volume ( $V_h$ ), average number of bonds ( $n$ ), root-mean-square end-to-end distance  $\langle r^2 \rangle^{1/2}$ , and



**Figure 3** Mark–Houwink plot for *CA* in acetone at 25 °C.



**Figure 4** Schulz–Blaschke constant vs.  $\gamma$ -exposure time for CA in acetone at 25 °C.

root-mean-square radius of gyration  $\langle S^2 \rangle^{1/2}$  of CA in acetone were calculated according to the following mathematical expression, respectively (Debye, 1946; Flory, 1949):

$$V_h = (2/5)[\eta] \langle M_v \rangle / N_A \quad (6)$$

$$n = 2 \langle M_v \rangle_r / M_u \quad (7)$$

$$[\eta] = \phi \langle r^2 \rangle^{3/2} / \langle M_v \rangle_r \quad (8)$$

$$\langle S^2 \rangle^{1/2} = \langle r^2 \rangle^{1/2} / (6)^{1/2} \quad (9)$$

where  $M_u$  is the molar mass of CA repeating unit, and Flory viscosity constant,  $\Phi$ , is defined as (Kurata and Tsunashima, 1999):

$$\Phi = 2.1 \times 10^{23} \text{ mol}^{-1} \text{ before irradiation and } \Phi = 2.7 \times 10^{23} \text{ mol}^{-1} \text{ after irradiation.}$$

Indeed, the study of the relation of real root-mean-square radius of gyration vs.  $\gamma$ -exposure time for CA, in acetone at 25 °C, demonstrates the reduction in root-mean-square radius of gyration with increasing  $\gamma$ -time. This is in accordance with the previously discussed results on this work.

Fig. 5 represents the linear plot of Stockmayer–Fixman equation (Van Krevelen, 1997):

$$[\eta] / \langle M_v \rangle_r^{1/2} = K_o + B \langle M_v \rangle_r^{1/2} \quad (10)$$

in which the intercept ( $K_o = 0.5433 \text{ cm}^3 \text{ g}^{-1}$ ) is the ideal Mark-Houwink constant and the slope ( $B = 0.5A_2 = 5 \text{ cm}^3 \text{ kg}^{-1}$ ) is the interaction parameter, while  $A_2$  is the second virial coefficient.

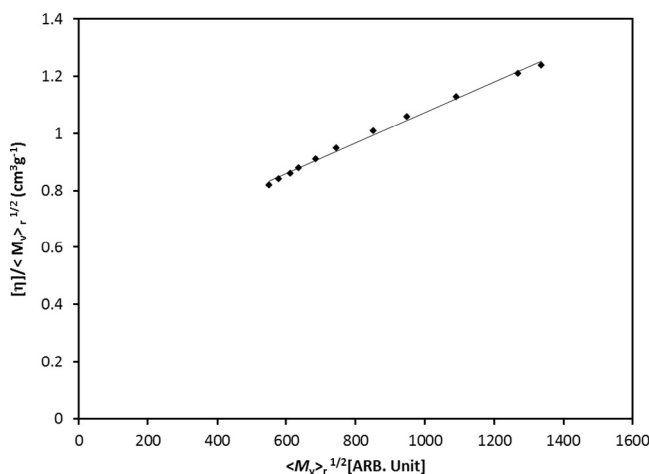
Therefore, the values of hydrodynamic expansion factor,  $\alpha_h$ , ideal intrinsic viscosity  $[\eta]_o$ , ideal root-mean-square end-to-end distance ( $\langle r^2 \rangle_0^{1/2}$ ), and ideal root-mean-square radius of gyration ( $\langle S^2 \rangle_0^{1/2}$ ) of CA in acetone were calculated according to the following expression (Kulicke, 2004), the subscript zero is used to indicate unperturbed dimensions.

$$a_h^3 = \frac{1 + B \langle M_v \rangle_r^{1/2}}{K_o} \quad (11)$$

$$a_h^3 = \frac{[\eta]}{[\eta]_o} \quad (12)$$

$$\langle r^2 \rangle^{1/2} = a_h \langle r^2 \rangle_0^{1/2} \quad (13)$$

$$\langle S^2 \rangle_0^{1/2} = \frac{\langle r^2 \rangle_0^{1/2}}{(6)^{1/2}} \quad (14)$$



**Figure 5** Stockmayer–Fixman plot for  $\gamma$ -irradiated CA in acetone at 25 °C.

The relation between hydrodynamic expansion factor and  $\gamma$ -exposure time for CA, in acetone at 25 °C, demonstrates the reduction in the hydrodynamic expansion factor with increasing  $\gamma$ -irradiation time, due to the marked scission on polymer chains (O'Donnell, 1991). This is in accordance with the average number of bond,  $n$ , characteristic ratio,  $C_\infty$  calculated from the following expression (Kulicke, 2004).

$$C_\infty = \frac{\langle r_o^2 \rangle}{nl^2} \quad (15)$$

$l$  is the bond length =  $1.43 \times 10^{-8} \text{ cm}$ .

Table 3 illustrated the decrease in the characteristic ratio by increasing  $\gamma$ -irradiation due to the decrease in the short-range interactions.

### 3.3. Cohesion parameters and their kinetic behavior

Refractive index, dielectric constant, solubility and cohesive energy density parameters are related with each other as follows (Sun, 1994):

$$\varepsilon_r = n_r^2 \quad (16)$$

$$\delta = (30.3) \frac{(\varepsilon_r - 1)}{(\varepsilon_r + 2)} \quad (17)$$

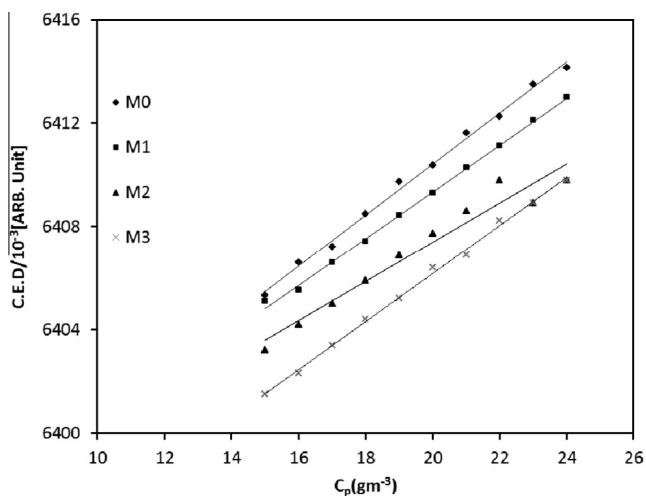
$$\delta = (C.E.D.)^{1/2} \quad (18)$$

where,  $n_r$ ,  $\varepsilon_r$ , is the refractive index, dielectric constant,  $\delta$ , is the solubility parameter,  $C.E.D.$ , is cohesive energy density of native and irradiated CA in acetone.

Fig. 6 shows linear increase in the values of cohesive energy density with increasing concentration at 25 °C. However, further consideration of the plots in Fig. 6 indicates that the  $\gamma$ -irradiation has a reduction effect on such values due to scission effect on the CA chain. This is in accordance with the values of viscosity parameters described above.

## 4. Conclusion

From the obtained data, one can notice that cellulose acetate undergoes random chain scission due to the effect of  $\gamma$ -irradiation. The periods of exposure time have considerable



**Figure 6** Cohesive energy density vs. concentration for native and different degradable CA in acetone at 25 °C.

influence on the amount of scission and consequently on the intrinsic properties and their parameters. The intrinsic properties play a major role in the kinetics of cellulose acetate degradation.

## References

- Aliste, A.J., Vieira, F.F., Del mastro, N.L., 2000. Radiation effects on agar, alginates and carrageenan to be used as food additives. *Radiat. Phys. Chem.* 57, 305–308.
- Alwan, T.J., 2012. Gamma irradiation effect on the optical properties and refractive index dispersion of dye doped polystyrene films. *Turk. J. Phys.* 36, 377–384.
- American Society for Testing and Materials, 1989. Standard specifications and operating instructions for glass capillary kinematic viscometers. In: *Annual Book of ASTM Standards*, (vol. 05.01, D 446). West Conshohocken, PA, USA.
- Byun, E.H., Kim, J.H., Sung, N.Y., Choi, J.I., Lim, S.T., Kim, K.H., Yook, H.S., Byun, M.W., Lee, J.W., 2008. Effects of gamma irradiation on the physical and structural properties of  $\beta$ -glucan. *Radiat. Phys. Chem.* 77, 781–786.
- Cao, Y., Wu, J., Meng, T., Zhang, J., He, J., Li, H.Q., 2007. Acetone-soluble cellulose acetates prepared by one-step homogeneous acetylation of cornhusk cellulose in an ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl). *Carbohydr. Polym.* 69, 665–672.
- Cerqueira, D.A., Rodrigues Filho, G., Meireles, C.S., 2007. Optimization of sugarcane bagasse cellulose acetylation. *Carbohydr. Polym.* 69, 579–582.
- Charlesby, A., 1981. Crosslinking and degradation of polymers. *Radiat. Phys. Chem.* 18, 59–66.
- Debye, P., 1946. The intrinsic viscosity of polymer solutions. *J. Chem. Phys.* 14, 336–339.
- Ershov, B.G., 1998. Radiation-chemical degradation of cellulose and other polysaccharides. *Russ. Chem. Rev.* 67, 315–334.
- Flory, P.J., 1949. The configuration of real polymer chains. *J. Chem. Sci.* 17, 303–310.
- Fujita, H., 1997. *Polymer Solutions*, Studies in Polymer Science 9. Elsevier Science Publishers B.V., Amsterdam.
- Gladius, L., 2001. Properties of crosslinked ultra-high-molecular-weight polyethylene. *Biomaterials* 22, 371–401.
- Graham, J.A., Panozzo, J.F., Lim, P.C., Brouwer, J.B., 2002. Effect of gamma irradiation on physical and chemical properties of chickpeas (*Cicer arietinum*). *J. Sci. Food Agric.* 82, 1599–1605.
- Hoenich, N., 2006. Cellulose for medical applications: past, present, and future. *Bioresources* 1, 270–280.
- Hon, D.N.S., Chan, H.C., 1982. Photoinduced grafting reactions in cellulose and cellulose derivatives. *ACS Symp. Ser.* 187, 101–118.
- Hugo, W.B., 1995. A brief history of heat, chemical and radiation preservation and disinfection. *Int. Biodeterior. Biodegrad.* 36, 197–217.
- Johnston, H.K., Sourirajan, S., 1973. Viscosity–Temperature Relationships for Cellulose acetate-acetone Solution. *J. Appl. Polym. Sci.*, 317–319, John Wiley & Sons Inc., New York.
- Kratohvil, P., 1987. Classical light scattering from polymer solutions. In: Genkins, A.D. (Ed.), *Polymer Science Library*. Elsevier, Amsterdam, pp. 77–92.
- Kulicke, W.M., 2004. *Viscosimetry of Polymers and Polyelectrolytes*. Springer, Berlin.
- Kurata, M., Tsunashima, Y., 1999. Viscosity–molecular weight relationship and unperturbed dimension of linear chain molecules. In: Brandrup, J., Immergut, E.H., Grulke, E.A. (Eds.), *Polymer Handbook*. John Wiley & Sons Inc., New York, pp. 1–83.
- Leung, M.Y.K., Liu, C., Koon, J.C.M., Fung, K.P., 2006. Polysaccharide biological response modifiers. *Immunol. Lett.* 105, 101–114.
- Moradali, M.F., Mostafavi, H., Ghods, S., Hedjaroude, G.A., 2007. Immunomodulation and anticancer agents in the realm of macrofungi (macrofungi). *Int. Immunopharmacol.* 7, 701–724.
- Mowery, D.M., Assink, R.A., Derzon, D.K., Klamo, S.B., Clough, R.L., Bernstein, R., 2005. Solid-state <sup>13</sup>C NMR investigation of the oxidative degradation of selectively labeled polypropylene by thermal aging and gamma-irradiation. *Macromolecules* 38, 5035–5046.
- O'Donnell, J.H., 1991. Chemistry of radiation degradation of polymers. In: Clough, R.L., Shalaby S.W. (Eds.), *Radiation Effects on Polymers*, Washington: American Chemical Society Symposium Series 475, pp. 412–413.
- Reichmanis, E., Frank, C.W., O'Donnell, J.H., Hill, D.J.T. 1993. Radiation effect on polymeric materials: a brief overview. In: Reichmanis, E., Frank, C.W., O'Donnell, J.H., (Eds.), *Irradiation of polymeric materials*. Washington: American Chemical Society Symposium Series 527, pp. 1–8.
- Rimdisit, S., Jingjid, S., Damrongsakkul, S., Tiptipakorn, S., Takeichi, T., 2008. Biodegradability and property characterizations of methyl cellulose: effect of nanocompositing and chemical cross-linking. *Carbohydr. Polym.* 72, 444–455.
- Risch, S.J., 2009. Food packaging history and innovations. *J. Agric. Food Chem.* 57, 8089–8092.
- Sandula, J., Kogan, G., Kacurakova, M., Machova, E., 1999. Microbial (1–3)- $\beta$ -D-glucans, their preparation, physico-chemical characterization and immunomodulatory activity. *Carbohydr. Polym.* 3, 247–253.
- Schoff, C.K., 1999. Concentration dependence of the viscosity of dilute polymer solution: Huggins & Schulz–Blaschke constants. In: Brandrup, J., Immergut, E.H., Grulke, E.A. (Eds.), *Polymer Handbook*. John Wiley & Sons Inc., New York, pp. 265–289.
- Sharma, T., Aggarwal, S., Kumar, S., Mittal, V.K., Kalsi, P.C., Manchanda, V.K., 2007. Effect of gamma irradiation on the optical properties of CR-39 polymer. *J. Mater. Sci.* 42, 1127–1130.
- Shin, H.J., Lee, D.C., 2003. Study on the process to decrease the molecular weight of beta-(1,6)-branched beta-(1,3)-D-glucans. *Korean J. Biotechnol. Bioeng.* 18, 352–355.
- Sun, S.F., 1994. *Physical Chemistry of Macromolecules: Basic Principles Issues*. John Wiley & Sons Inc., New York.
- Van Krevelen, D.W., 1997. *Properties of Polymers*. Elsevier, Berlin.