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High impact polystyrene modified by ionizing γ-radiation

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Abstract

The purpose of applying the high-energy γ-ionizing radiation with doses up to 100 kGy was to enable controllable change of mechanical properties of high impact polystyrene (PS-HI) and, at the same time, to investigate the possibility of using reprocessed irradiated polymeric material. Dielectric relaxation of radiation modified high impact polystyrene (PS-HI) has been investigated below the polystyrene glass transition temperature (T_g) by the direct current (dc) charging/discharging transient method. Time dependence of charging/discharging current for the PS-HI has been well described by the power function of the logarithm of time. The relationship between the dc conductivity and the dielectric relaxation time (τ) has been approximated by the fractal dimension. The dc transient current method is considered to be a practical tool for analyzing the dielectric relaxation process of the radiation modified PS-HI. It was also shown that yield strength and tensile strength increase while elongation at break decreases with increasing radiation dose. The specimen prepared by a post-irradiation moulding gave higher melt flow rate than those of specimens formed before irradiation. These results indicate that after radiation the system of PS-HI is reprocessable. It is concluded that an oxygen environment at the beginning of irradiation leads to enhanced chain scission at the expense of crosslinks via peroxide formation and causes oxidative degradation of the main polymer chain of irradiated PS-HI at a low dose. However, at higher absorbed doses the quasi-inert environment has been established and crosslinking, due to recombination of macroradicals, is dominant.

KEY WORDS:
charging/discharging current
fractal
high impact polystyrene (PS-HI)
ionization γ-radiation
tensile properties

KLJUČNE RIJEČI:
fraktal
ionizirajuće γ-zračenje
polistiren visoke žilavosti (PS-HI)
rastezna svojstva
struja nabijanja/izbijanja

Polistiren visoke žilavosti modificiran γ-ionizirajućim zračenjem

Sažetak

Primjena γ-ionizirajućeg zračenja visoke energije do doza od 100 kGy omogućuje nadziranu promjenu mehaničkih svojstava polistirena visoke žilavosti (PS-HI) te istodobno pruža mogućnost oporabe ozračenih polimernih materijala. Dielektrična relaksacija zračenjem modificiranog PS-HI-ja praćena je ispod stakljišta (T_g) postupkom nabijanja/izbijanja istosmjerne (dc) struje. Vremenska ovisnost struje nabijanja/izbijanja za PS-HI dobro je opisana logaritamskim oblikom potencijalne funkcije. Veza dc provodnosti i dielektričnoga relaksacijskog vremena (τ) prikazana je fraktalnom dimenzijom. Postupak nabijanja/izbijanja istosmjerne struje praktično je sredstvo za analizu dielektričnoga relaksacijskog procesa radijacijski modificiranog PS-HI-ja. Također, pokazano je kako granica razvlačenja i rastezna čvrstoća rastu, dok prekidno istezanje opada s porastom radijacijske doze. Ispitci pripravljeni injekcijskim prešanjem nakon ozračivanja pokazuju višu rasteznu tecivost (nižu viskoznost) od ispitaka pripravljenih prije ozračivanja. Ti rezultati pokazuju kako polistiren visoke žilavosti i nakon ozračivanja može sačuvati korisna preradbena svojstva. Pri niskim dozama zračenja prisutnost kisika uzrokuje porast cijepanja lanaca u odnosu na umreživanje zbog nastajanja peroksida, što dovodi do oksidativne razgradnje "glavnoga" polimernog lanca u ozračenom PS-HI-ju. Ipak, pri većim apsorbiranim dozama, kada se uspostavi kvaziinertna atmosfera, umreživanje prevladava u ozračenom PS-HI-ju.

Introduction

Amorphous polystyrene is well-known for its well balanced dynamical feature and ease of processing, and application for various purposes. The general purpose polystyrene (PS-GP), which is made by polymerizing the styrene monomer, is transparent, colourless, with high reflex index and it is good for high frequency insulation. However, it is rather easy to break. The brittleness of PS-GP is well improved in high impact polystyrene (PS-HI), which is a copolymer of poly-butadiene rubber and PS-GP. This improvement in the durability is due to the absorption of the impact energy by generation and growth of crazes, which are defects consisting of highly oriented fibres and micro-voids, in the polystyrene matrix.[1] High impact polystyrene is the first commercial polymer that has been toughened by the addition of second-phase particles. The toughness of PS-HI is increased at least by a factor of two, as compared to the toughness of the PS homopolymer. The PS-HI, an elastomeric - modified thermoplastic, provides good balance between rigidity and elasticity that is not found in the unmodified PS-GP. PS-HI is produced by bulk polymerization of a solution of poly-butadiene in styrene. The resulting material can be structurally defined as a multiphase system in which poly (1,4-butadiene) (PB) rubber granules are dispersed in a continuous rigid polystyrene matrix. The high impact polystyrene exhibits grain/ micro-domains or a salami structure. These micro-domains might be understood as dense zones (typically of 5–30nm in diameter) of polystyrene chains, embedded in low-density grafted butadiene material with randomly arranged chains.[2] Manufacturing of PS-HI requires the addition of 6-8.5wt.% of butadiene rubber which ends up being 15-30vol.% due to polystyrene occlusions.[3] Bucknall and Smith[4] gave the first successful explanation of the mechanism of rubber toughening in PS-HI. By stretching thin PS-HI films, they found that macroscopic yielding was accompanied by the formation of multiple crazes around the rubber particles.

The modification of polymers using ionizing radiation is now a well established area of material science research. Ionizing radiation affects the performance of some of the polymers used in various applications. The changes in macro-properties generally observed in terms of chemical, optical, thermal and electrical modifications can be traced to transformations taking place at micro-level in the chemical structure due to bond-breaking, main chain-scissoring, cross-linking, carbon cluster formation, volatile species liberation and formation of new chemical bonds.[5] The use of radiation in the processing of polymers is gaining more and more interest because it can be suggested as an alternative to the traditional chemical methods to modify the molecular structure of polymers. The possibility of processing the final shape of the polymeric material in the solid state opens up new opportunities to obtain materials with well-tailored properties.

Our study of the mechanical, rheological and electrical behaviour of the PS-HI irradiated with gamma rays from a ^{60}Co source and at high integral doses – up to 1MGy, in the presence of air and at room temperature, was performed to get information related to the radiation stability of polymeric moulded articles and the possibility of reprocessing of radiation-treated PS-HI. In the present paper we report results of irradiating polymer test samples under commercial processing conditions at ^{60}Co gamma irradiator.

General part

Effect of γ-ionizing radiation

Gamma radiation is a powerful tool for crosslinking elastomers; however, exposure to its higher dosage degrades the polymer.[6] The extent of crosslinking and the degradation undergone by a polymer depends on its structural characteristics and the presence of initiators/sensitizers. Intermolecular crosslinking of polystyrene and polybutadiene upon γ-irradiation results in the formation of a three-dimensional network and, consequently, causes partial in-solubilisation of the polymer. Apart from crosslinking PS and PB undergo additional chemical alterations. In the case of PS unsaturations are formed (conjugated C=C bonds in the main chain) and pendant benzene groups are converted into cyclohexadiene groups. In the case of PB, unsaturations are destroyed. Upon irradiation in the presence of oxygen (O_2) peroxide, hydro-peroxide and carbonyl groups are incorporated into the polymers. Crosslinking increases the molecular weight of the polymers. However, oxygen retards crosslinking. The results prove that crosslinking prevails up to a dose of 4-5MGy.[7] Irradiation of 3mm polystyrene sheet in the air at 30°C with γ-rays caused rapid decrease in the tensile and flexural strengths and strains to fracture. These properties decreased to 50% of their initial values after ca. 800kGy and to 25% after ca. 2MGy, beyond which dose the rate of change was relatively small.[8] In addition, studies conducted by Vishwa Prasas and Singh[9] indicate that phase separation (styrene and butadiene) takes places in styrene-butadiene-styrene (SBS) and PS-HI due to degradation, forming micro-cracks that result in deterioration of mechanical behaviour. The property deterioration was explained in terms of scission reactions in the PS-HI two-phase matrix. Schnabel et al.[10] demonstrated that at high irradiation doses (>1MGy) in SBS intermolecular crosslinks were generated, whereas at low doses, unsaturations are produced in the butadiene part of the copolymer. Dole,[11] in turn, reported that at very high irradiation doses, styrene–butadiene based copolymers showed crosslinking, hardening and embrittlement of the rubber phase, thus resulting in sudden decrease in mechanical properties.

Fractal approach

The polymeric materials may reach the electrets state after charging by appropriate methods.[12] The initial and residual (after ionizing irradiation and after electrical charging) film surface charge densities may be measured with appropriate devices.[13,14] A certain approach to the explanation of the temporal effects during electrochemical reactions is a Nernst diffusion layer theory. The current is the ions movement to an electrode on which these ions are reduced or oxidized. As consequence, an iso-surface ion concentration differs from volume concentration. Nernst conception is based on the assumption that an ion concentration is under the linear dependence within the diffusion layer. Under potentiostatic mode, a diffusion layer thickness is increased continuously in the course of time, as result of the current reduction. According to the Cottrell equation, the *current density* (j) vs. *time* (t) dependence is linear when plotted as j *vs.* $t^{1/2}$. However, the diffusion layer theory is restricted and does not describe many experimental facts. One of the restrictions is that an electrode surface is supposed to be energetically homogeneous. But an electrode surface is usually heterogeneous; therefore, the current–time dependence takes a more complicated form. In particular, over time the area of the so-called autocatalytic effect can precede the ordinary current reduction period: after short-term reduction, the current increase is spontaneous. The reason for this phenomenon, apparently, is energy heterogeneity of the metal surface and the formation of surface adsorption complexes with opposite functions (stimulating and inhibiting) as consequence. Parts with different electrochemical activity yield uncertainty of experimentally determined kinetic parameters and complicate essentially the theoretical description of diffusion transfer. Some approach can be based on the assumption that the energy heterogeneity of a metal surface is of fractal kind. There are results generalizing some known expressions of diffusion transfer (Cottrell, Levich, etc.) for the electrode fractal surface.[15,16] In these papers the correlation between the experimental parameters of electrical process and the fractal dimension D_F are established. From the fractal type analysis and the Cottrell type dependence follows that the electrical process rate is reduced slower to the electrode fractal surface, than to homogeneous surface. The reason of such slowing-down is because of the tangential diffusion streams, which compensate partly the temporary change of perpendicular concentration gradients.

Experimental part

Preparation of samples and irradiation procedures

The polymer selected for testing was high-impact polystyrene (PS-HI) type PS 485 from *DIOKI,* Zagreb, Croatia. The two procedures (A and B) were used for the specimen preparation. In the first set of experiments (procedure A), the PS-HI polymer granulated was irradiated and then formed into plaques or specimens for mechanical tests. In the second example (procedure B), the already formed plaques and specimens were irradiated to pre-set radiation dose (Figure 1). As consequence, solely the impact of the different irradiation modalities on the polymer properties has been investigated.

Methods

Such a way of preparing specimens, including additional operation of injection moulding of the pre-irradiated granulate, reflects the basic mechanical and heat load, occurring during re-processing of (irradiated) plastic wastes. The main objective in testing the non-irradiated and irradiated PS-HI using injection moulding was to prove that irradiated PS-HI can be reprocessed easily. Replicate samples of PS-HI polymer (in granulate form (procedure A) and as pre-moulded specimens (as processed plaques and ISO test specimens, procedure B) are exposed to nominal doses from 20kGy up to 1MGy using γ-ionizing radiation ^{60}Co source (at a dose rate of 3.6kGy/h). All irradiations were performed in air with a PE bag surrounding the polymer samples. Routine dosimeters were placed to measure the absorbed dose during the irradiation process. After irradiation half of the exposed specimens as well as half of the accompanying controls were kept at room temperature during 8 weeks. Following storage, all specimens were tested for determination of mechanical and rheological properties. The error bars reported below were determined as the 95% confidence limit from the scatter in the measurements of the replicates. The melt mass-flow ratio (MFR) and melt-volume ratio (MVR) of PS-HI was measured using a *Melt Indexer* (*Zwick,* Germany) according to *ISO 1133:1997* standard. The test temperature was set at 200°C and the nominal load was 5kg. The measurements of each sample were repeated six times and the average was taken as the representative value. The tensile properties were measured at room temperature using an Instron 1185 universal testing machine (*Instron,* UK) at a test speed of 50mm/min according to *ASTM D638.* The tensile strength (σ_B) and elongation at break (e_B) were determined from stress–strain curves. The electrical conductivity studies were carried out using standard two electrode methods by *High Voltage Source Measuring Unit (SMU 237)* with *Model 6107* steel electrode adapter (Keithley, UK). Ohmic contacts were made through silver paste applied to the irradiated surface of the polymeric plaque samples. The measurements were carried out nearly two months after the irradiation of the foils, hence the reported results represent the stationary state of the irradiated foils where the meta-stable defects are expected to have got annealed and the radiation enhanced oxidation would have got completed.

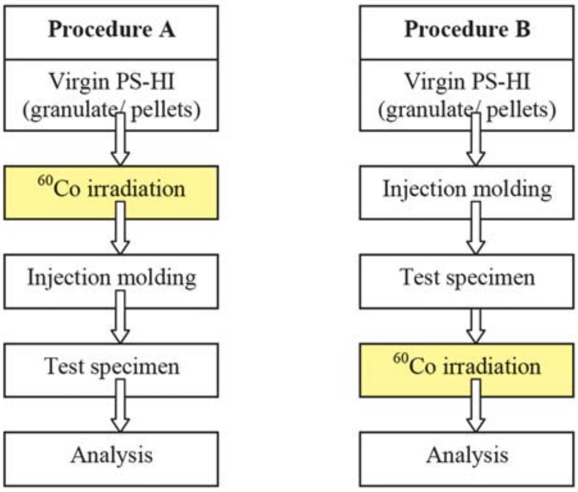

FIGURE 1 - Processing and γ-irradiation procedures; procedure A: injection moulding of specimen forms (plaques of 1.5mm thickness and as *ISO* mechanical test specimens) from pre-irradiated PS-HI granulate; procedure B: γ-irradiation of PS-HI injection moulded specimen forms (as plaques of 1.5mm thickness and as *ISO* mechanical test specimens)

Results and discussion

Rheological and mechanical properties

Degradation and crosslinking due to ionizing radiation cause alterations in the internal structure of the exposed polymer. These changes give rise to a variation in rheological and mechanical behaviour. Because the processing parameters of injection moulding/ or extrusion are related to the viscosity of polymer, it is necessary to study the effect of radiation on the viscosity of butadiene-grafted-polystyrene (PS-HI). The apparent viscosity (the melt volume rate, MVR) of PS-HI after irradiation is shown in Figure 1. It can be seen that the viscosity increases with the increasing absorbed dose. It is known that the viscosity of polymer is related to the interaction between molecules. The crosslinking of molecular chains and the entanglement interactions between molecules increase, and consequently, the flowing resistance and viscosity of PS-HI increase by radiation-induced crosslinking. High impact polystyrene (PS-HI), a binary component polymer system, thus mainly crosslinks by a recombination of free radicals, which is in competition with their reactions with molecular oxygen. The density of intermolecular crosslinking bridges formed during irradiation determines the degree of miscibility of the two components. The mechanical properties of irradiated PS-HI are presented in Figure 2, Figure 3, and Figure 4. For both procedures applied, the determination of the tensile strength showed comparable results between granulate samples exposed to ionizing radiation (and moulded afterwards) (procedure A) and those prepared moulded samples irradiated with ^{60}Co gamma rays (procedure B). After initial drop PS-HI exhibits almost near-linear increase of the tensile strength with radiation dose increase (Figure 3). Figure 4 presents the tensile elongation at break e_B as function of the absorbed dose. The most affected mechanical property by irradiation was elongation at break. This is in agreement with data of Wilski[17] who reported that the elongation at break is the most radiation sensitive property, and recommended this parameter to be used to assess the radiation stability of polymers. Elongation at break decreases with dose increase (Figure 4). In materials exposed to radiation it is common to find surface cracks or micro-cracks, which act as stress concentrators and which greatly reduce the ductility of the polymer. Radiation causes significant changes in the materials surface, in such a way that the external layers of PS-HI specimens are altered, thereby modifying the surface topography. These variations cause an increase in roughness, which results in the appearance of micro-cracks over long exposure periods. The presence of free radicals generated during radiation exposure accelerates the cross-linking process and consequently increases the structural rigidity. Crosslinking increases the molecular weight of the polymers. The results prove that crosslinking prevails up to a dose of 1MGy. Unlike tensile behaviour of pure, homo-polymeric polystyrene (PS-GP), the PS-HI exhibits a distinct yield point and a considerably greater elongation (Figure 5). The difference between the modulus of non-irradiated PS-HI and irradiated PS-HI is not very large so that γ-irradiation results in the comparable modules to commercial, non-irradiated PS-HI. Simple kinetic indicative adjustments could be done out by means of mathematical equations to the mechanical properties analyzed: tensile strength (σ_B) and elongation at break (e_B). The mathematical expressions corresponding to the kinetic behaviour of the blends show coefficient of determination of $R^2 > 0.8$; however, due to a small number of data points, these approximations could be only indicative.[18,19] At higher doses a dominant mechanism of crosslinking appears with an apparent decrease of the properties in the break point (σ_B and e_B). The stress and elongation at break are clearly influenced by the increase in radiation dose, with a progressive diminution of elongation at break (e_B) and an increase of tensile strength at break (σ_B). The radiation may introduce alterations in the chemical structure of PS-HI, resulting in a slightly more brittle material. The tensile stress at break σ_B shows, on the contrary, a slight decrease during initial irradiation times, but after 20kGy the σ_B values increase. This complex behaviour suggests a combination of different physical and chemical effects in the radiation oxidative degradation of PS-HI. Chemical attack appears to govern the crosslinking for shorter irradiation times due to the presence of oxygen in the beginning, whereas physical ageing seems to predominate for longer irradiation times in quasi-inert environment due to the exhaustion of oxygen.

The γ-radiation dose of 600kGy raises the yield stress, while reducing the elongation at break of high-impact polystyrene (PS-HI). Similar reductions in fracture resistance are observed in notched Izod impact specimens. The Izod impact strength of irradiated PS-HI decreases with the prolonged irradiation time (i.e. larger dose). This could be explained by the fact that the rubber will be more crosslinked by γ-radiation and hence stiffen and decrease the Izod-type impact strength. It is concluded that the observed changes in mechanical properties are due almost entirely to crosslinking of the polybutadiene. This not only inhibits cavitations and fibrillation in the rubbery membranes of the salami particle, thereby delaying yield, but also makes the fibrillated membranes more resistant to further dilatation, so that craze thickening rates in the polystyrene matrix are reduced.[20]

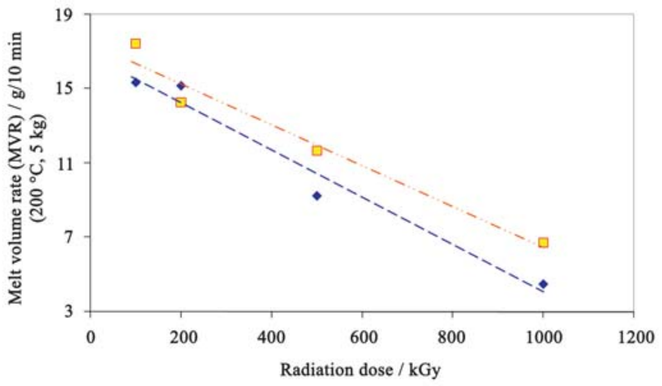

FIGURE 2 - Melt volume rate (MVR) (200°C, 5kg) of (■) injection moulded specimens from pre-irradiated PS-HI granulate (procedure A); and of (♦) irradiated PS-HI injection moulded specimens (procedure B) as function of radiation dose

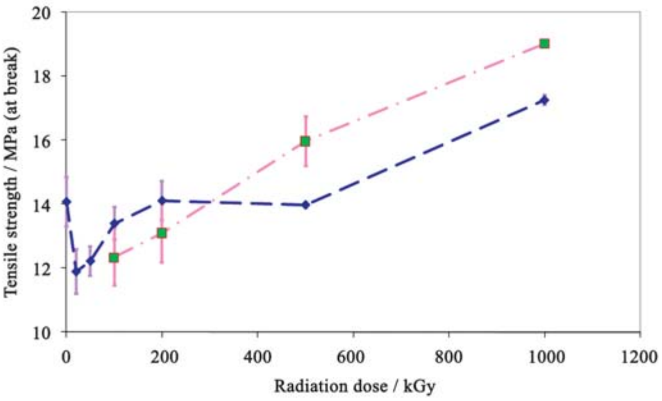

FIGURE 3 - Tensile strength (at break) of (■) injection moulded specimens from pre-irradiated PS-HI granulate (procedure A); and of (♦) irradiated PS-HI injection moulded specimens (procedure B) as function of radiation dose

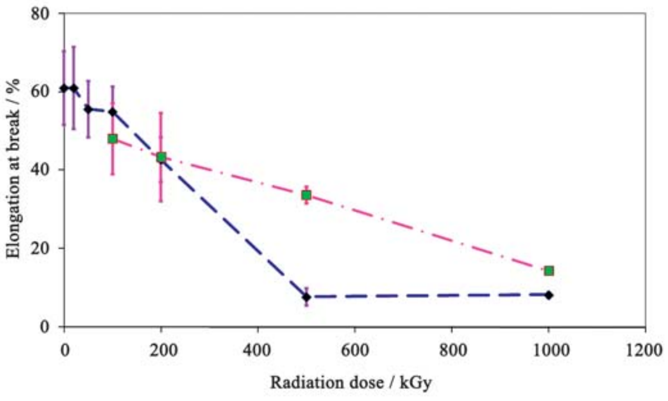

FIGURE 4 - Elongation at break, e_B, of (■) injection moulded specimens from pre-irradiated PS-HI granulate (procedure A); and of (♦) irradiated PS-HI injection moulded specimens (procedure B) as function of radiation dose

Charging/discharging current temporal dependence

Charge/discharge curves as well as potential step techniques were used to interpret radiation-induced changes and to study the dynamics of these reactions. Figure 6 gives a representative plot of electrical charging current density, ($j_{pol}/(E\varepsilon_o)$), reduced by electrical field, *E*, and vacuum permittivity, ε_o, of PS-HI injection moulded specimens (plaques) from the pre-irradiated granulate (procedure A) as function of absorbed dose (in kGy) and charging time. However, the discharging characteristics are almost identical; the reduced discharging current does not change much with the increase in the radiation dose (Figure 7). Figure 8 is a representative plot of electrical charging current density, ($j_{pol}/(E\varepsilon_o)$), reduced by electrical field, *E*, and vacuum permittivity, ε_o, of irradiated PS-HI injection moulded specimens (plaques; procedure B) as function of absorbed dose (in kGy) and charging time. It is observed that the irradiated PS-HI injection moulded specimens had decreasing electrical characteristic of reduced charging current with the increase in dose (Figure 8). However, the discharging characteristics are almost identical; the reduced discharging current practically does not change with the increase in radiation dose (Figure 9). The influence of irradiation on the electrical conductivity is more pronounced in the case of moulded plaques from the pre-irradiated PS-HI granulate than in the case of the irradiated PS-HI injection moulded specimens (plaques). The pre-irradiated PS-HI granulate (procedure A) dramatically changed the electric response of the materials compared to the moulded-irradiated PS-HI sample (procedure B). The reason could be much larger surface of PS-HI granulates in contact with air and thus higher quantity of created oxidative groups which increase the polarity and charge transfer. The volume resistivity of injection moulded-pre-irradiated PS-HI granulates (procedure A) is lower than that of the moulded-irradiated PS-HI sample (procedure B). The relaxation process related to the trapped free charge carriers at the interface is still observed after the heating of the samples (procedure A).

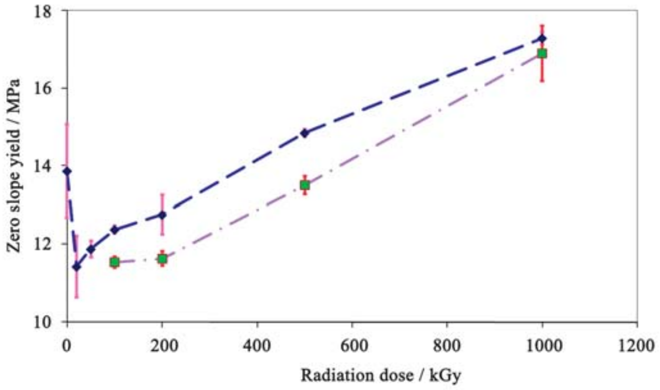

FIGURE 5 - Zero slope yield of (■) injection moulded specimens from pre-irradiated PS-HI granulate (procedure A); and of (♦) irradiated PS-HI injection moulded specimens (procedure B) as function of radiation dose

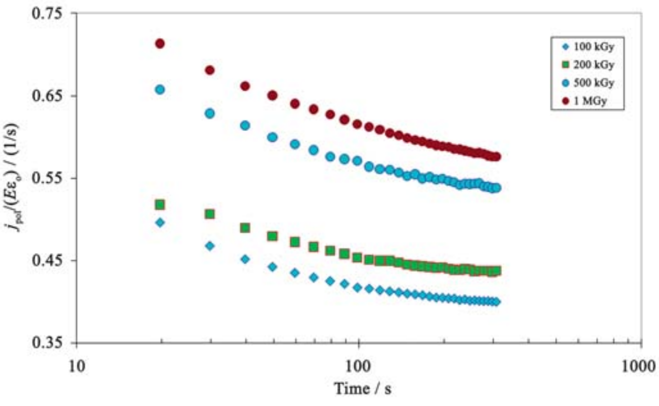

FIGURE 6 - The reduced charging current density, $j_{pol}/(E\varepsilon_o)$, reduced by electrical field and vacuum permittivity, of PS-HI injection moulded specimens (plaques) from the pre-irradiated granulate (procedure A) as function of charging time and radiation dose: (♦) 100kGy; (■) 200kGy; (●) 500kGy; (●) 1MGy

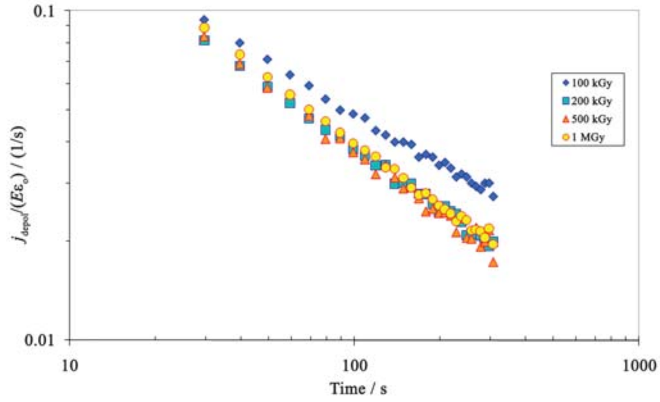

FIGURE 7 - The reduced discharging current density, $j_{depol}/(E\varepsilon_o)$, reduced by electrical field and vacuum permittivity, of PS-HI injection moulded specimens (plaques) from the pre-irradiated granulate (procedure A) as function of discharging time and radiation dose: (♦) 100kGy; (■) 200kGy; (▲) 500kGy; (○) 1MGy

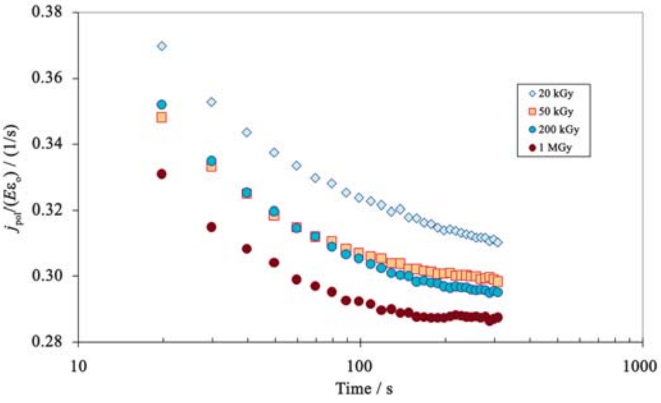

FIGURE 8 - The reduced charging current density, $j_{pol}/(E\varepsilon_o)$, reduced by electrical field and vacuum permittivity, of γ-irradiated PS-HI injection moulded specimens (plaques) (procedure B) as function of charging time and radiation dose: (♦) 20kGy; (■) 50kGy; (●) 200kGy; (●) 1MGy

It is well known that the diffusion-limited current, $I(t)$ in charging/discharging (chrono-amperometric) measurements is proportional to the fractal-like parameter α.[15,16].

$$I(t) \propto t^{-a} \tag{1}$$

The fractal-like parameter α can be simply transformed to the fractal dimension D_F by equation

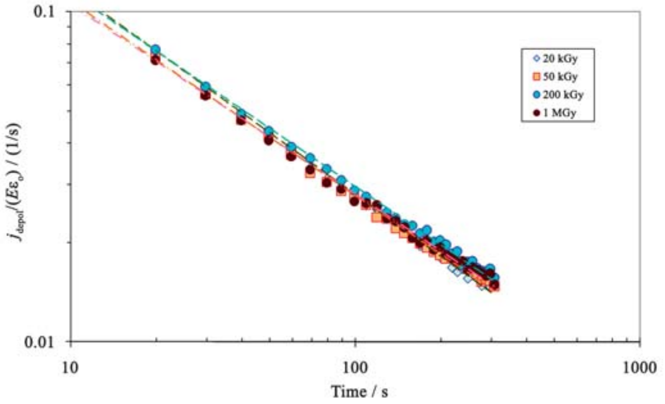

FIGURE 9 - The reduced discharging current density, $j_{depol}/(E\varepsilon_o)$, reduced by electrical field and vacuum permittivity, of irradiated PS-HI injection moulded specimens (plaques) (procedure B) as function of charging time and radiation dose: (♦) 20KGy; (■) 50kGy; (●) 200kGy; (●) 1MGy

$$\alpha = \frac{D_F - 1}{2} \tag{2}$$

Thus, the fractal dimension D_F can be calculated by plotting the diffusion-limited current versus time in logarithmic scales. In other words, slopes of such logarithmic plots are equal to the fractal parameter α. A comparison of the fractal dimensions derived from the slopes (Equation 2) is shown in Table 1 and Figure 10.

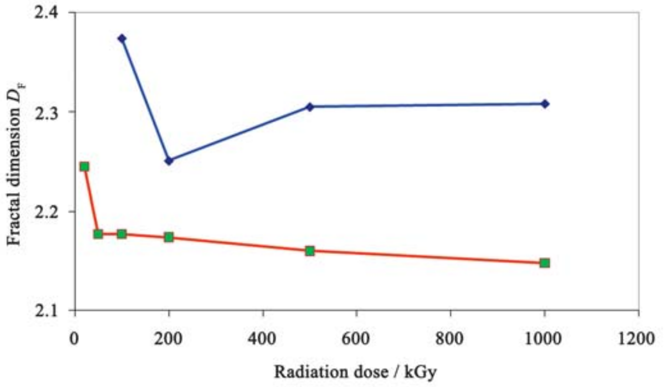

FIGURE 10 - Fractal dimension D_F (derived by equation 2) from the discharging currents of PS-HI moulded specimens (plaques) from the pre-irradiated granulate (procedure A) (♦), and of irradiated PS-HI injection moulded specimens (plaques) (procedure B) (■) as function of radiation dose.

TABLE 1 - Power function (intercept and exponent α) parameters and fractal dimension D_F (according to Equation 2) of discharging current (after 5-minute 100V charging at room temperature) for γ-irradiated PS-HI specimens.

Dose (kGy)	Power function		Coefficient of determination R^2	Fractal dimension D_F
	intercept	exponent α		
Procedure A: Moulded plaque from pre-irradiated granulate				
100	0.809	-0.687	0.998	2.374
200	0.688	-0.625	0.996	2.250
500	0.771	-0.652	0.991	2.305
1000	0.822	-0.654	0.996	2.308
Procedure B: irradiated moulded plaque				
20	0.490	-0.622	0.996	2.244
50	0.416	-0.588	0.994	2.177
100	0.421	-0.588	0.995	2.177
200	0.440	-0.586	0.995	2.173
500	0.452	-0.580	0.994	2.160
1000	0.394	-0.573	0.993	2.147

The dielectric relaxation process is due to percolation of the apparent dipole moment excitation within the developed fractal structure of the connected channels.[21] This excitation is associated with the self-diffusion of the charge carriers through the fractal structure of the porous medium. A model was proposed[22] which enabled the non-Debye dielectric response associated with percolation to be characterized through the net of connected channels. The movement of charge carriers results in a transfer of the electric excitation within the channels along random paths. A detailed description of the relaxation mechanism associated with an excitation transfer based on regular and statistical fractal models has been introduced[23] where it was applied to the cooperative relaxation at percolation in terms of the dipole correlation function (DCF) $\Phi(t)$. DCF is defined as:

$$\Phi(t) = \frac{< M(0) \cdot M(t) >}{< M(0) \cdot M(0) >} \tag{3}$$

where $M(t)$ is the time-dependent fluctuation dipole moment of a sample; symbols < > denote the ensemble averaging. For both foregoing fractal models the time dependence behaviour of $\Phi(t)$ may be written in the form of an asymptotic stretched exponential term:

$$\Phi(t) = \exp\left[-\left(\frac{t}{\tau_p} \right)^{D_p/3} \right] \tag{4}$$

where τ_p is an effective relaxation time. This result reflects the general ideas previously developed[24] that the transfer of electric excitation in various condensed media occurs by the transport from a donor unit to an acceptor unit through many parallel channels. In order to determine the value of the fractal dimension D_p of the paths of excitation transfer within the porous medium, the relaxation law can be further fitted to the experimental correlation functions. In general, the fractal dimension of these paths should coincide with the fractal dimension of the matrix space.

Macro-radicals that are formed in PS-HI by radiation in the initial processes react with atmospheric oxygen, consequently leading to the formation of different oxidation products according to the mechanisms described in relevant literature. These products are macromolecules with carbonyl, hydroxyl, and peroxide groups of different type (inside the chain or at its ends). Increase in the oxidation of the surface layer of polymeric materials causes increase in both its wettability and surface free energy and, at the same time, improvement of their adhesion, gluing and printing properties. However, due to the large volume of irradiated specimens and small amount of oxygen present inside the specimen body, the oxidative degradation is limited mainly to the surface and to the initial irradiation until the oxygen present is exhausted.[25]

Conclusion

Change in mechanical properties of the irradiated PS-HI that has incorporated butadiene grafted phase is due to the chain scission and crosslinking reactions procuring in both the styrene and butadiene phases. The tensile strength for PS-HI increases with radiation dose while elongation at break decreases. The flowability of irradiated granules and that from the irradiated PS-HI moulded specimen decrease with the radiation dose. The electrical conductivity of both plaque samples from the pre-irradiated granulated and that from the post-moulding irradiated PS-HI do not change much. However, the relaxation rate properties, as defined by the discharging rates, increase with the absorbed dose. Fractal dimensions D_F from the discharging currents of irradiated PS-HI decrease by radiation. Early degradation of the pre-irradiated (granule) sample (procedure A) compared to the pre-processed (injection moulded) irradiated sample (procedure B) indicates the effect of oxygen. Inter-chain crosslinking reaction occurs in the elastomeric phase. This extent of crosslinking increases when the PS-HI is subjected to heat treatment before irradiation (procedure B). Thus, the rheological stability of the pre-irradiated PS-HI granule sample (procedure A) is increased compared to the processed and irradiated PS-HI sample (procedure B). Oxidation of the PS-HI may occur as consequence of irradiation. The procedure by which the PS-HI granulate is first pre-irradiated and then moulded (procedure A) increases the surface layer oxidation yield because this procedure gives additional radicals per surface area that form under the influence of radiation and react with oxygen present in the air and in the material surface layer. It is concluded that oxygen environment leads to enhanced scission at the expense of crosslinks via peroxide formation and causes oxidative degradation of the main polymer chain of irradiated PS-HI only at a very low dose. However, at higher absorbed doses in the quasi-inert environment the crosslinking, due to recombination of macroradicals is dominant.

REFERENCES

1. Beahan, P., Thomas, A. and Bevis, M.: *Some observation on the micromorphology of deformed ABS and HIPS rubber-modified materials*, J. Mater. Sci., 11(1976), 1207.
2. Rek, V., Holjevac-Grgurić. T., Jelčić, Ž.: *Effect of Styrene-Butadiene-Styrene Block Copolymer on Dynamic-Mechanical Properties of High-Impact Polystyrene*, J. Macromol. Sci.: Pure Appl. Chem., A35(1998)7-8, 1385-1402.
3. Jelčić, Ž.: *Polystyrene and Styrene-Butadiene Copolymers, Mixtures, Blends*, Alloys, Conference Records *Styrenic Polymers*, SPRE, Zagreb, 1991, 31-35.
4. Bucknall, C. B., Smith, R. R.: *Stress-whitening in high- impact polystyrenes*, Polymer, 6(1965), 437-446.
5. Czvikovszky, T.: *Expected and unexpected achievements and trends in radiation processing of polymers*, Rad. Phys. Chem., 67(2003)3-4, 437-440.
6. Thomas, S., Gupta, B. R., De, S. K.: *Mechanical properties, surface morphology and failure mode of γ-ray irradiated blends of polypropylene and ethylene-vinyl acetate rubber*, Polym. Degr. Stab., 18(1987)3, 189-212.
7. Ziaie, F., Noori, A., Anvari, F., Ghaffari, M., Ahmadian, V., Durrani, S. A.: *Effect of high-dose electron irradiation on specific heat capacity of high-impact polystyrene*, Proc. 22nd Int. Conf. Nuclear Tracks in Solids, Radiation Measurements, 40(2005)2-6, 758-761.
8. Bowmer, T. N., Cowen, L. K., O'Donnell, J. H., Winzor, D. J.: *Degradation of polystyrene by gamma irradiation: Effect of air on the radiation-induced changes in mechanical and molecular properties*, J. Appl. Polym. Sci., 24(1979)2, 425-439.
9. Vishwa Prasad, A., Sing, R.: *Photooxidative degradation of styrenic polymers: 13C-NMR and morphological changes upon irradiation*, J. Appl. Polym. Sci., 70(1998), 637.
10. Schnabel, W., Levchik, G., Wilkie, C., Jiang, D., Levchik, S.: *Thermal degradation of polystyrene, poly(1,4-butadiene) and copolymers of styrene and 1,4-butadiene irradiated under air or argon with 60Co-γ-rays*, Polym. Deg. Stab.. 63(1999), 365-375.
11. Dole, M.: *The radiation chemistry of polymer composites*, Int. J. Rad. Appl. Instr. Part C. Rad. Phys. Chem., 37(1991)1, 65-70.
12. Sessler, G. M.: *Introduction and physical principles of electrets*, G. M. Sessler (Ed.), Electrets, Springer-Verlag, Springer-Verlag, New York, USA, 1980.
13. da Silva, N. C., de Almeida, A., Campos, J. S. C.: *X-ray image produced on an electret film*, 9th International Symposium on Electrets (ISE9), IEEE, China, 1996, 1067-1072.
14. Parada, M. A., de Almeida, A.: *Teflon electret radiation dosimeter*, Nucl. Inst. Meth. Phys. Res. B: Beam Interact Matls. Atoms, 191(2002)1-4, 820-824.
15. Nyikos, L., Pajkossy, T.: *Diffusion to fractal surfaces*, Electrochim. Acta, 31(1986), 1347-1350.
16. Pajkossy, T., Nyikos, L.: *Diffusion to fractal surfaces: II. Verification of theory*, Electrochim. Acta, 34(1989)2, 171-179.
17. Wilski, H.: *The radiation induced degradation of polymers*, Radiat. Phys. Chem., 29(1987), 1-14.
18. Albano, C., Reyes, J., Ichazo, M. N., Gonzalez, J., Rodriguez, M.: *Effects of the high doses of irradiation on the mechanical properties of PS/PP blends*, Nucl. Instrum. Meth. Phys. Res. Sect. B: Beam Interact. Mat. Atoms, Ionizing Rad. Polym., 208(2003), 485-488.
19. Chipara, M. I.: *On an anomalous kinetic in irradiated polymers around the glass transition temperature*, Nucl. Instrum. Meth. Phys. Res. Sect. B: Beam Interact. Mat. Atoms, Ionizing Rad. Polym., 131(1997)1-4, 180-187.

20. Bucknall, C. B., Soares, V. L. P.: *Cavitation of rubber particles in high-impact polystyrene: Effects of crosslinking by g-irradiation*, J. Polym. Sci. Part B: Polym. Phys. Ed., 42(2004), 2168-2180.
21. Ryabov, Ya., Gutina, A., Arkhipov, V., Feldman, Yu.: *Dielectric Relaxation of Water Absorbed in Porous Glass*, J. Phys. Chem., B105(2001)9, 1845–1850.
22. Gutina, A., Axelrod, E., Puzenko, A., Rysiakiewicz-Pasek, E., Kozlovich, N., Feldman, Yu.: *Dielectric relaxation of porous glasses*, J. Non-Cryst. Sol., 235-237(1998), 302-307.
23. Feldman, Yu., Puzenko, A., Ryabov, Y.: *Non-Debye dielectric relaxation in complex materials*, Chem. Phys., 284(2002), 139-168.
24. Klafter, J., Blumen, A.: *Models for dynamically controlled relaxation*, Chem. Phys. Lett., 119(1985), 377-382.
25. Misović, V., Šegudović, N., Jelčić, Ž.: *Promjene u strukturnim, reološkim i mehaničkim svojstvima pri oporabi polistirena injekcijskim prešanjem*, Polimeri, 21(2001)5, 145-152.

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OBLJETNICE

Uspješan inženjer i gospodarstvenik – 80. rođendan Petra Tomičića

Petar TOMIČIĆ, dipl. ing.

Poznati i vrsni stručnjak Petar Tomičić ove godine navršava 80. godina. Cijeli je radni vijek radio na izgradnji, unapređenju i razvoju petrokemijske industrije u nas, posebno polistirena. Rođen je 1930. u Ričicama, u općini Lovinac, a diplomirao na Kemijskom odjelu *Tehnološkog fakulteta* u Zagrebu. Kraće je vrijeme radio u *Tvornici olovaka Zagreb*, a zatim od 1961. godine do umirovljenja proveo u *Organsko-kemijskoj industriji* – OKI, Zagreb.

Nakon specijalizacije u poznatom naftno-petrokemijskom kompleksu *ARCO* u SAD-u vodio je izgradnju tvornice polistirena na lokaciji Žitnjak, koja je u početku proizvodila uži asortiman polistirena nazvanoga *OKIROL*, no poslije je, njegovim velikim doprinosom, uvedena proizvodnja cijele palete proizvoda: od normalnoga, modificirajućega do pjenećeg *OKIROLA*.

Iz istog vremena datira, kao rezultat njegove suradnje sa zaposlenicima *Instituta za makromolekularnu kemiju*, i patentiranje proizvodnje samogasivoga pjenećeg polistirena, odnosno PS-E-a.

Osim stručnih aktivnosti Petar Tomičić bio je uspješan i kao gospodarstvenik te je od šefa pogona polistirena u razdoblju od 1967. izabran za direktora bazne proizvodnje *INA-OKI* za razdoblje 1971. – 1975.

U to vrijeme dolazi do prvih rekonstrukcija i izgradnje novih postrojenja *INA-OKI*-ja te Tomičić vodi ekipu koja je realizirala proširenje kapaciteta i proizvodnog asortimana polistirena.

Usporedno s tim poslovima član je ekipe koja je realizirala prvi *Ugovor o zajedničkom ulaganju sa stranim partnerima* u nas na tom području. Realizacijom ulaganja izgrađeno je postrojenje za proizvodnju polistirena toplinskim postupkom kapaciteta 33 000 t/god. P. Tomičić imenovan je direktorom toga zajedničkog pothvata i tu dužnost obavlja do 1980. godine, kada je imenovan glavnim direktorom *INA-OKI*-ja.

Tijekom njegova mandata (1980. – 1984.) pušteno je u rad nekoliko važnijih petrokemijskih proizvodnih kapaciteta, od kojih treba spomenuti proizvodnju etilena na lokaciji Žitnjak u sklopu tvrtke *Naftaplin*, prvu fazu petrokemijskoga kompleksa na Krku u sklopu *Ine* i izgradnju novog pogona za proizvodnju polietilena niske gustoće na lokaciji Žitnjak kapaciteta 50 000 t/god. Sva su ta postrojenja i danas u radu te čine okosnicu proizvodnje tvrtke *Dioki*, koja je od 2004. u privatnom vlasništvu.

U realizaciji svih tih projekata P. Tomičić dao je zapažen doprinos kao gospodarstvenik i stručnjak.

To doba, unatoč znatnim teškoćama u poslovanju, može se smatrati jednim od najuspješnijih razdoblja organsko-kemijske/petrokemijske proizvodnje u nas, a Petar Tomičić pionirom u izgradnji i razvoju polistirenske proizvodnje. Kao vrlo uspješan gospodarstvenik, nakon završetka mandata imenovan je na odgovornu dužnost u *INA Tradeu* Ltd., Lugano, Švicarska, te je nakon toga bio savjetnik generalnog direktora.

Od samih početaka Petar Tomičić radio je i na izobrazbi zaposlenika neposredno u proizvodnji, kao i tehničke poslove povezane s preradom i primjenom polistirena.

Također je bio djelatan u suradnji sa strukovnim organizacijama te je obavljao odgovorne dužnosti u *Društvu plastičara i gumaraca* od samog početka, kao i *Sekciji za petrokemiju Znanstvenog vijeća za naftu HAZU*, za što je dobio priznanja. Zbog svojih zasluga za *Društvo* izabran je za njegovoga zaslužnoga člana 1983. U povodu 50. obljetnice *Organsko-kemijske industrije Zagreb* primio je *Zahvalnicu* za velik doprinos u izgradnji, radu i razvoju toga petrokemijskog kompleksa (2009.).

Čestitajući 80. obljetnicu života Petru Tomičiću, očekujemo i nadalje njegov kritički doprinos u radu ove važne industrijske grane te njegov stručni doprinos u radu spomenutih udruga.

Stanislav JURJAŠEVIĆ