Dedicated to Dr. Igor Dvornik on his 85 birthday

Franjo Ranogajec, Marica Mlinac-Mišak, Zvonimir Hell*
Ruđer Bošković Institute, Zagreb, *sada u mirovini

Improvement of the polymer properties by radiation grafting and crosslinking

ISSN 0351-1871
UDK 544.54:678.7
Author's review / Autorski pregled
Received / Primljeno: 10. 2. 2009.
Accepted / Prihvaćeno: 29. 4. 2009.

Abstract

Radiation grafting and crosslinking were applied in collaboration with local industry to demonstrate the possibility of improving the polymer properties. With the aim of preventing the losses of stabilizer due extractability or volatility during the service time the photo-protector 2-hydroxy-4-(3-methacryloxy-2-hydroxy-propoxy) benzophenone has been grafted to low density polyethylene in benzene, tetrahydrofuran and methanol solution, respectively. Direct gamma irradiation method was used. Surface grafting occurs in methanol solution, grafting yield of stabilizer being less than 0.5%. In benzene and tetrahydrofuran grafting proceeds more or less in the inner parts of polymeric film, and the grafting yields are much higher.

To test the improvement of photo-stability by grafting of protector polymer samples with grafted and non-grafted protector were exposed to artificial accelerated aging and to natural weathering, which means exposure to long-term direct action of the sunlight and all climatic factors. Photo-oxidative changes were determined by IR spectroscopy and photo-degradation by measurements of the physical properties. Measurements of the change of carbonyl index, elongation at break and tensile strength in the course of artificial and natural aging of LDPE, with grafted and non-grafted protector, have proven much higher photo-protection achieved by the grafted protector. The surface grafting is the most efficient and the most economical.

It was shown that with the addition of 20phr of polybutadiene waste rubber, grafted with ethylacrylate by direct gamma irradiation method, to polyacrylic rubber compound the properties of rubber worsened but remained within the range of properties characteristic for these types of rubber. The stability of rubber against swelling in hot mineral oil was satisfactory even when 30phr of grafted waste rubber was added to polyacrylic rubber.

Radiation crosslinked PVC pipes were produced. Circumferential stress determined from the pressure at rapture at 80°C, Shore hardness and Vicat softening temperature indicate much higher temperature resistance of radiation crosslinked pipes as compared to unirradiated pipes.

KEY WORDS:
accelerated aging
crosslinked PVC pipes
grafting of waste rubber
natural weathering
photo-protection
surface grafting of stabilizer

KLJUČNE RIJEČI:
cijepljenje otpadne gume
cijevi od umreženog PVC-a
fotozaštita
površinsko cijepljenje stabilizatora
prirodno starenje
ubrzano starenje

Poboljšanje svojstava polimera radijacijskim cijepljenjem i umreživanjem

Sažetak

U suradnji s lokalnom industrijom pokazana je mogućnost poboljšanja svojstava polimera radijacijskim cijepljenjem i umreživanjem. S namjerom da se spriječe gubitci stabilizatora zbog ekstrakcije, migracije ili ishlapljivanja tijekom uporabe proizvoda, ultraljubičasti stabilizator 2-hidroksi-4-(3-metakriloksi-2-hidroksi-propoksi) benzofenon cijepljen je na polietilen niske gustoće iz otopina benzena, tetrahidrofurana i metanola. Za cijepljenje je upotrijebljen postupak izravnog ozračivanja gama-zrakama. Površinsko cijepljenje zbiva se u otopini metanola s prinosom cijepljenog stabilizatora manjim od 0,5 %. U tetrahidrofuranu i benzenu cijepljenje se zbiva manje ili više u unutrašnjim dijelovima polimernog filma i prinosi cijepljenja mogu biti mnogo viši. Da bi se ispitalo poboljšanje fotostabilnosti cijepljenjem stabilizatora, ispitci s cijepljenim i umiješanim stabilizatorom podvrgnuti su ubrzanom umjetnom starenju i dugoročnom prirodnom starenju, djelovanju sunčeva svjetla i svih klimatskih čimbenika. Fotooksidacijske promjene praćene su infra-crvenom spektroskopijom, a fotodegradacija određivanjem fizičkih svojstava. Određivanje promjene karbonilnog indeksa te prekidnog istezanja i rastezne čvrstoće tijekom umjetnoga i prirodnog starenja polietilena potvrdilo je znatno bolju fotozaštitu s cijepljenim stabilizatorom. Površinsko cijepljenje je najučinkovitije i najekonomičnije.

Pokazano je da se dodatkom 20 phr-a polibutadienske otpadne gume, koja je cijepljena s etilakrilatom postupkom izravnog ozračivanja gama-zrakama, poliakrilnoj gumi svojstva pogoršavaju, ali ostaju u granicama svojstava karakterističnih za taj tip gume. Stabilnost gume protiv bubrenja u vrućemu mineralnom ulju zadovoljavala je čak i kada je 30 phr cijepljene otpadne gume dodano poliakrilnoj gumi.

Proizvedene su zračenjem umrežene PVC cijevi koje su pokazale veću otpornost na unutrašnji pritisak i veću toplinsku postojanost od neumreženih cijevi.

Introduction

Radiation crosslinking and radiation grafting are widely used in industrial applications of radiation processing of polymeric materials. In collaboration with the local polymer industry an effort has been made to demonstrate the advantage of the radiation processing as compared with the conventional chemical process. Radiation grafting of photo-stabilizer on low density polyethylene was performed to improve the photo-stability of polyethylene.

The improvement of the polymer stability continues to be an area of active industrial concern and intensive research effort.[1-5] Polyethylene, as well as most organic polymers require protection against the effects of heat, oxygen, light, high energy radiation and so on. Demands for more efficient stabilizers and antioxidants increase. Widely used low molecular weight organic stabilizer molecules which are simply incorporated into the polymer matrix can be lost during the use time by migration to the polymer surface, followed by evaporation. Evaporative loss may be particularly problematic for the uses involving high temperatures or vacuum environment (as in space vehicle applications). By covalently binding stabilizer to the polymer backbone this problem can be eliminated. Radiation grafting or crosslinking could be an efficient method of realizing it when the stabilizer is polymerizable. This new approach was applied in our work. Grafting of 2-hydroxy-4-(3-methacryloxy-2-hydroxy-propoxy) benzophenone onto polyethylene was performed and photo-stability of grafted polyethylene was studied.[6-11]

In collaboration with rubber industry (*Sava*, Kranj) the grafting of ethyl acrylate onto waste polybutadiene rubber was induced by simultaneous gamma irradiation with the aim of investigating the possibility of substituting the part of virgin rubber by grafted waste rubber in some less demanding applications[12,13] and in this way to eliminate waste rubber from the environment.

In collaboration with PVC industry, polyvinylcloride was radiation crosslinked in the presence of triallyl cyannurate as a sensitizer to improve mechanical properties and thermal stability.[14-18]

Photo-stabilization of polyethylene by surface grafting

Low density polyethylene films (LDPE) commercially blown, free of additives (d = 0.919 g/cm^3, melt flow index 2 g/10 mm) were supplied by *INA-Organic Chemical Industry*, Zagreb.

2-hydroxy-4-(3-methacryloxy-2-hydroxy-propoxy) benzophenone (HMB) was chosen as a UV protector for polyethylene. Monomer was used commercial grade as supplied by *National Starch Chemical* Co., USA.

Solvents: benzene, tetrahydrofuran, methanol and hexane were analytical grade supplied by *Merck-Shuchardt*, Darmstadt. The monomer was dissolved in tetrahydrofuran, methanol and benzene respectively and used for grafting as 20wt % solution.

Reaction glass tubes sealed off under vacuum were then subjected to gamma radiation from a ^{60}Co source at a dose rate of 0.15kGy/h and temperature of 50°C. The grafted polymer films were removed from the monomer solution after the irradiation, extracted with boiling tetrahydrofuran and dried to constant weight. The weight increase of polymer films after the grafting reaction was taken as the grafting yield.

The grafting (%) curves vs. irradiation time are shown in Figure 1 for direct grafting of HMB on low density polyethylene in benzene, tetrahydrofuran and methanol solution. Film thickness was 0.05mm and reaction temperature was 50°C.

It is obvious that the nature of the solvent strongly influences the rate and yield of grafting and location of grafted HMB on LDPE.

In the benzene solution the yield of grafting increases linearly with time up to high yields as was found in many grafting systems. The yield of grafting increases as the dose rate increases and a linear dependence of the grafting rate on the square root of dose rate was obtained, which suggests bimolecular termination reaction of growing poly-HMB-chains and non-diffusion controlled propagation reaction in the grafting reaction on LDPE in that case.

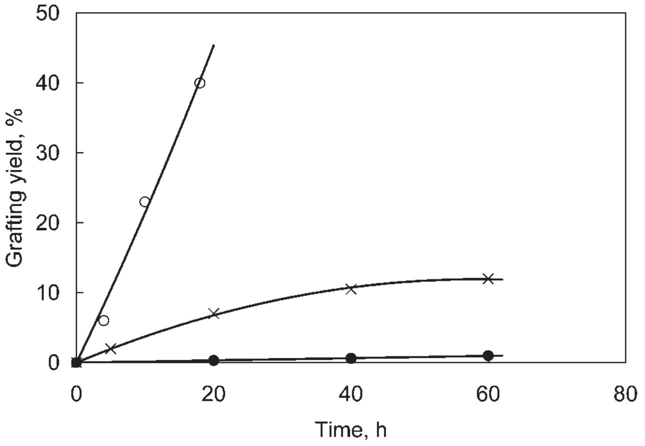


FIGURE 1 - Changes in the grafting yield of poly-HMB in LDPE during gamma irradiation (0.15kGy/h) at 50°C in benzene (○), tetrahydrofuran (×) and methanol (●) solution of HMB (20 % wt)

On the other hand, when LDPE under the same experimental conditions was grafted with HMB in tetrahydrofuran solution, a limiting value of grafting yield was obtained after an initial increase of yield, the limiting value of grafting yield being about 10%. A dose rate effect was observed only during the initial increase of grafting yield[6]. The percent of grafting decreases if the foil thickness and polyethylene density increase.

When LDPE films were immersed in methanol solution of HMB and gamma irradiated under the same conditions as in the case of benzene and tetrahydrofuran, very low weight increase of film was observed but grafted poly-HMB was readily detected by IR-spectroscopy.

On the basis of the obtained results it may be concluded that surface grafting of HMB on LDPE occurs in methanol solution of monomer. The grafting of HMB from tetrahydrofuran occurs primarily close to the surface layer of LDPE, whereas the grafting in benzene occurs more or less homogeneously throughout the film of LDPE.

Direct evidence of surface grafting in tetrahydrofuran was obtained by ATR IR spectroscopic measurement[8]. Tetrahydrofuran swells polyethylene similarly as benzene. The main difference between the two solvents is that tetrahydrofuran dissolves poly-HMB and benzene does not, and it could be the reason for different grafting behaviour. The grafting reaction begins in polyethylene swollen with tetrahydrofuran containing dissolved HMB in a similar way as in benzene. However, while poly-HMB is well dissolved in tetrahydrofuran it is barely dissolved in benzene. During the grafting reaction in tetrahydrofuran the quantity of grafted poly-HMB within the film increases and when the reaction slows down its concentration is several times higher than that of the monomer. A stronger interaction of grafted poly-HMB with tetrahydrofuran as compared to that with benzene means less free solvent for monomer within the film in tetrahydrofuran. Thus the driving force for monomer diffusion into the film decreases as the concentration of grafted poly-HMB increases and reaction slows down.

To test the improvement of photo-stability by grafting of stabilizer grafted and non-grafted polyethylene samples were exposed to artificial accelerated aging using a high pressure mercury lamp at room temperature and to natural weathering which means exposure to long-term direct action of sunlight and all climatic factors. Photo-oxidative changes were determined by IR spectroscopy.

It is well-known that in photochemical oxidation of polymeric materials some oxidized groups are generated, and it is a common practice to determine the change of these groups during the oxidation of polymeric materials. Carbonyl groups are an indication of chemical changes occurring in polyolefin during oxidative degradation. The absorption band in the carbonyl region increases in the course of UV irradiation.

Although the grafted monomer HMB has two different absorption values for carbonyl groups (1620 cm^{-1} and 1720 cm^{-1}), the photoinduced carbonyl groups in LDPE could nevertheless still be detected due to their much broader absorption band; a fact that can be seen after aging.

Experimental results in Figure 2 show that during ultraviolet radiation of grafted LDPE films, the 2-hydroxy-benzophenone absorption band at 1620cm^{-1} slowly disappears, while a new absorption band belonging to carbonyl group appears at 1720cm^{-1}.

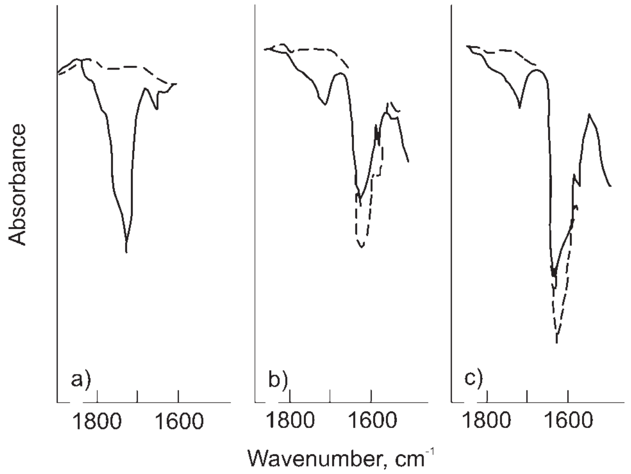


FIGURE 2 - IR absorption band of carbonyl groups in: a - LDPE; b - LDPE + HMB mixture; c - LDPE + HMB grafted, before (------) and after (——) UV irradiation

The grafted LDPE film in methanol and tetrahydrofuran (containing 1 w/w % of grafted HMB), 1 w/w % blended HMB with LDPE and non-grafted LDPE film were all exposed to accelerated aging and their spectral changes expressed by the carbonyl index, which represents the ratio of absorbance at 1720cm^{-1} to that at 1890cm^{-1}, were then compared. These data are shown in Figure 3. In each curve the original values are subtracted to show the change in the quantity of oxidized groups.

The growth of carbonyl in the unprotected film and in film containing added HMB is much higher than in the grafted films, and indicates that a pronounced protective effect is achieved by monomer grafting. From the photo-chemistry of polyolefins it is well-known that photo-oxidation begins at the polymer surface, and the excited chromophores are concentrated close to the film surface. Therefore, surface grafting should be the most efficient for photo-protection.

As expected, the highest increase of carbonyl index was observed in the case of non-protected LDPE. Carbonyl index increased linearly with the time of accelerated aging and after about 600 hours polyethylene was almost completely destroyed. In the case of LDPE with incorporated HMB during the first 800 hours of aging the increase of carbonyl index was much slower than in LDPE without HMB, but a similar increase of carbonyl index was observed after 800 hours of aging. Different behaviour was observed in the case of accelerated aging of LDPE grafted with HMB in THF and methanol solution. After an initial moderate increase the carbonyl index remains approximately constant until about 1600 hours of aging and than again increases like in the case of non-grafted LDPE.

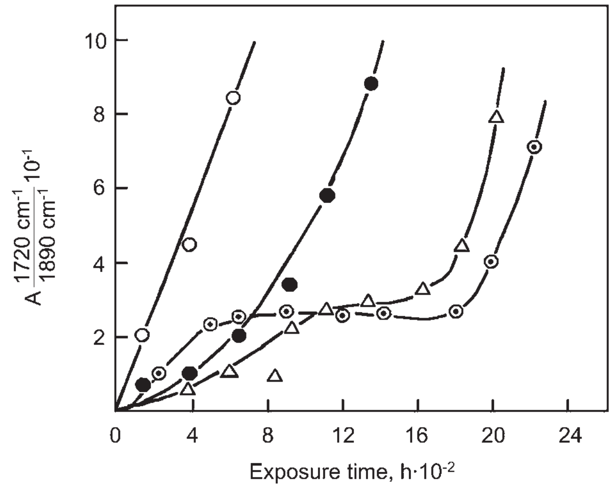


FIGURE 3 - Changes in the carbonyl index during UV irradiation at room temperature: (O) LDPE; (●) LDPE + 1% HMB added; (⦿) LDPE + 1% Poly-HMB grafted in tetrahydrofuran; (△) LDPE + less than 0.5% Poly-HMB grafted in methanol

In order to get evidence about the role of HMB as UV stabilizer in the course of photo-oxidation, the change in the 2-hydroxy-benzophenone absorption band at 1620cm^{-1} was followed by IR spectroscopy in the course of accelerated aging of LDPE. The results are presented in Figure 4. Two experimental facts should be noted. First, in LDPE grafted with HMB a slow, almost linear decrease of 2-hydroxy benzophenone absorption band at 1620cm^{-1} does not indicate dramatic increase of carbonyl index after 2000 hours of aging as observed in Figure 3. Second, in LDPE mixed with HMB, the initial quantity of HMB being much higher than in LDPE grafted with HMB in methanol, the 2-hydroxy benzophenone absorption band at 1620 cm^{-1} is much lower and completely disappears after 1200 hours of aging.

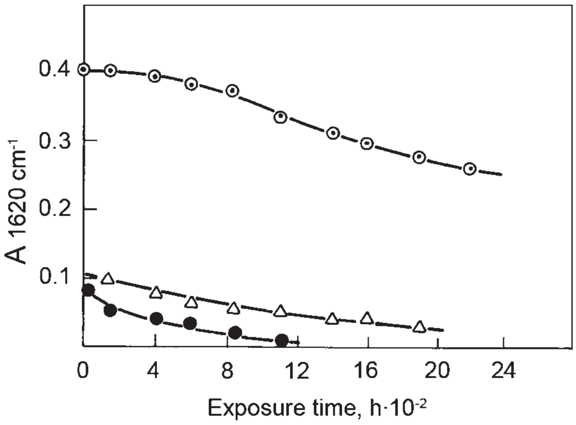


FIGURE 4 - Changes in 2-hydroxy-benzophenone carbonyl absorption during UV aging of LDPE at room temperature: (●) LDPE + 1% HMB added; (⦿) LDPE + more than 1% Poly-HMB grafted in tetrahydrofuran; (△) LDPE + less than 0.5 % Poly-HMB grafted in methanol

It is well known that polyolefins may degrade if they are irradiated with UV radiation for a longer time. In the course of photo-degradation physical properties of the polymers are changed. In practice it has been found that the elongation at break is one of the most sensitive properties. Therefore we investigated the change of elongation at break in the course of accelerated aging of LDPE to describe photo-degradation of non-grafted and grafted LDPE with HMB by comparing it with the change of carbonyl index and

HMB concentration in the polymer. The results are presented in Figure 5.

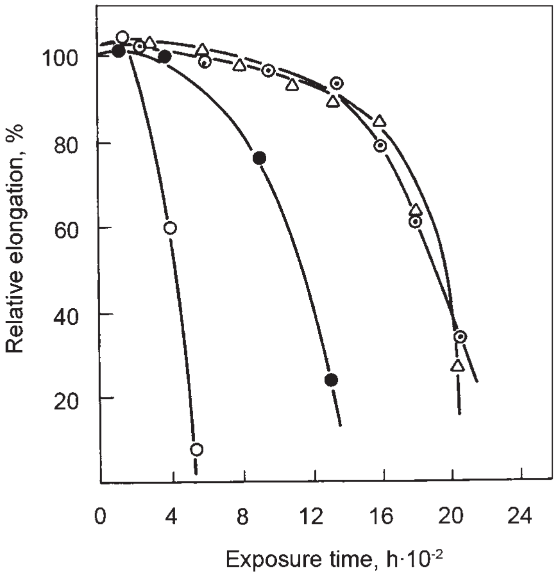


FIGURE 5 - Changes in elongation at break of LDPE during UV aging at room temperature: (O) LDPE; (●) LDPE + 1% HMB added; (⊙) LDPE + 1% Poly-HMB grafted in tetrahydrofuran; (△) LDPE + less than 0.5 % Poly-HMB grafted in methanol.

In an initial period of UV irradiation the elongation at break slightly increased due to crosslinking, then returned to its original value and later decayed more or less rapidly depending on the LDPE sample. To describe the UV radiation induced degradation of LDPE the times of UV irradiation at which the elongation at break reaches half of its original value were compared. These times can represent the lifetime of the polymer in practical use. In investigated conditions the lifetime of unstabilized LDPE was about 400 hours. The lifetime of LDPE with incorporated 1% of HMB was about three times longer, and the lifetime of LDPE grafted with about 1% of HMB was about five times longer than of LDPE without HMB.

Similar results are obtained by measurements of tensile strength in the course of accelerated aging of LDPE samples prepared in the same way. These results are shown in Figure 6. The tensile strength decreases in the course of UV irradiation in a similar way as elongation at break, but it reaches half of its original value at somewhat longer time of irradiation, which shows that the half value for elongation is a more sensitive measure of the degradation than the half value for tensile strength.

Many polymers and especially polyolefins do not strongly absorb the shorter wavelengths of the sun spectrum. However, light-absorbing impurities may be introduced during synthesis or during processing of a polymer (traces of unreacted initiator, breakdown products from initiator, traces of transition metal ions) and they are responsible for photo-oxidative degradation of commercial polymers such as PE and PP. After some controversies during the past two decades in polymer photo-chemistry general consensus was now accepted that hydroperoxides are the most important photo-initiators during the early stages of UV irradiation.

Photo-oxidation is a chain process involving a large number of chemical reactions which are subsequent to the primary event - absorption of a photon, which induces free radical generation. A simplified scheme may be written as follows:

$$\text{Initation}\quad \text{Polymer} \xrightarrow{h\nu} R^{\bullet} \tag{1}$$

In the presence of air addition of oxygen to a free radical is generally a rapid process producing a relatively stable peroxy radical so that

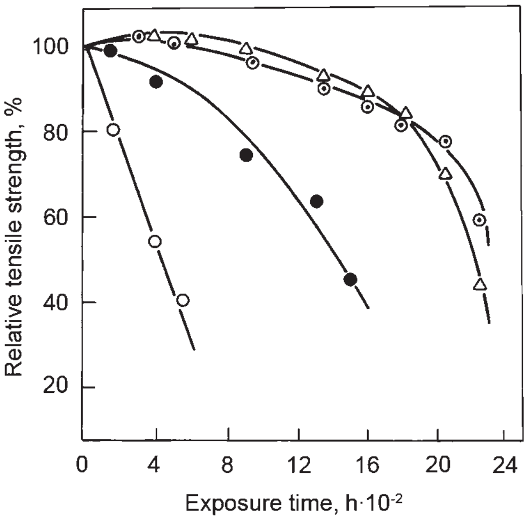


FIGURE 6 - Changes in tensile strenght of LDPE during UV aging at room temperature: (O) LDPE; (●) LDPE + 1% HMB added; (⊙) LDPE + 1% Poly-HMB grafted in tetrahydrofuran; (△) LDPE + less than 0.5 % Poly-HMB grafted in methanol

the second step in the cycle (3) is the rate determining step

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \tag{2}$$

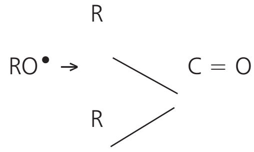
Propagation

$$RO_2^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \tag{3}$$

With a long chain length a single primary initiation reaction will produce a large number of hydroperoxide species, each one capable of initiating further photo-oxidation. A consequence of this fact is that in this stage of photo-oxidation the initiation by photolysis of hydroperoxides is the predominant process. Every molecule of hydroperoxide produced subsequently undergoes photolysis to generate an alkoxy radical which both provides new initiating radicals and at the same time produces carbonyl compounds (predominately ketones):

$$ROOH \xrightarrow{h\nu} RO^{\bullet} + {}^{\bullet}OH \tag{4}$$

$$RO^{\bullet} + RH \rightarrow ROH + R^{\bullet} \tag{5}$$



$$RO^{\bullet} \rightarrow R_2C=O \tag{6}$$

At a later stage these carbonyl-containing products assume the main role in chain scission reactions according to Norrish I and II type processes. Although both of the Norrish photo-cleavage processes can cause backbone scission, only the Norrish I type reaction generated free radicals which can initiate the oxidative process:

$$RCOR \xrightarrow[\text{Norrish I}]{h\nu} RCO^{\bullet} + R^{\bullet} \tag{7}$$

Termination reaction may be as follows:

Termination

$$RO_2^{\bullet} + RO_2^{\bullet} \rightarrow ROOR + O_2 \tag{8}$$

$$RO_2^{\bullet} + R^{\bullet} \rightarrow ROOR \tag{9}$$

$$R^{\bullet} + R^{\bullet} \rightarrow R-R \tag{10}$$

The scheme outlined above is an oversimplification of the real process of photo-oxidation but it gives a good representation of which reactions must be slowed down or stopped for the purposes of stabilization of polymers.

Outdoor use-performance of polymers can be markedly improved by the choice of suitable stabilizers. The basic requirement for an efficient photostabilizer is that the stabilizer itself, its transformation products derived from it during the processing and photo-products of the parent and the derived products, should be stable during the period of exposure to UV light without being destroyed or transformed into sensitizing products. In general, a good UV stabilizer is capable of absorbing UV light and dissipating it harmlessly as heat. HMB belongs to the class of substituted 2-hydroxy benzophenone UV stabilizers which are extremely stable to UV radiation in solution in the absence of oxygen, because they can harmlessly dissipate UV light via keto-enol tautomerism in excited states.

The limitation of this class of UV stabilizers is therefore not their intrinsic instability to photolysis but their instability to hydroperoxides and carbonyl compounds under photo-oxidation conditions. Comparing the results of carbonyl index change with 2-hydroxy benzophenone absorption band change and with mechanical properties change in the course of accelerated aging, it could be concluded that photo-oxidation of LDPE occurs in at least two distinct stages.

In the initial period the photo-initiator is hydroperoxide and the rate of carbonyl formation is proportional to concentration of hydroperoxide. If the change of carbonyl index indicates the rate of photo-oxidation then it is the highest in unprotected LDPE and in LDPE with grafted and non-grafted HMB depends on unprotected surface areas accessible for photolysis. The best photo-protection is achieved in LDPE grafted with HMB from methanol, where the grafted HMB is located mainly at the surface of the PE film. In unprotected LDPE the rate of carbonyl formation is approximately constant to the failure of PE. In LDPE with ungrafted HMB, during the second stage of photo-oxidation the rate of carbonyl formation becomes auto-accelerating.

In the LDPE grafted with HMB at the end of the first stage the rate of carbonyl formation auto-retards to give a plateau. The duration of the plateau depends on the HMB concentration. It lasts longer if the concentration of HMB is higher. In the range of plateau elongation at break and tensile strength decrease very slowly indicating the effective photo-protection of LDPE by grafted HMB. At the same time 2-hydroxy benzophenone absorption decreases slowly and does not indicate dramatic increase in carbonyl index and decrease in mechanical properties at the end of plateau. The above results suggest that HMB does not act by a single mechanism but by a combination of mechanisms. HMB acts primarily by absorbing UV light and dissipating it harmlessly as thermal energy, but also act in part as radical scavenger. The main advantage of radiation grafted LDPE with HMB is that HMB is located mainly at the PE surface and is more homogeneously distributed. HMB cannot be lost during UV exposure because it is chemically bound to the PE. Grafted HMB can be consumed only in reactions occurring during photo-oxidation.

On the other hand, HMB incorporated in LDPE is more inhomogeneously distributed throughout the PE. More unprotected surface area of PE may be available for photo-oxidation from the beginning of UV exposure and unprotected area may increase during exposure due to losses of stabilizer at the polymer surface. This is the reason that several times higher initial quantity of incorporated HMB in LDPE is much less effective in photo-protection of PE than much lower quantity grafted from methanol.

It seems, however, that the accelerated degradation of LDPE takes place when the critical concentration of micro-cracks caused by photo-oxidation is reached although the grafted stabilizer is still present in the polymer.

In the end, it is interesting to compare the results of accelerated aging of grafted and non-grafted LDPE with HMB with the results of natural weathering aging. Natural weathering means long-term combined action of solar radiation, temperature, oxygen, water, ozone and atmospheric impurities like sulphur dioxide and nitrogen oxides. The most important of all climatic factors is the UV component of solar radiation. It is capable of breaking chemical bonds in a polymer molecule and initiating degradation processes, the most important being oxidative degradation.

The test specimens were prepared in the same way as for the accelerated aging and were exposed to natural weathering in free atmospheric conditions. The angle of the specimens to the horizon was 45° and the exposed surface faced south. The change of carbonyl index and change of elongation at break were measured in the course of weathering over a period of 24 months. The results are presented in Figures 7 and 8.

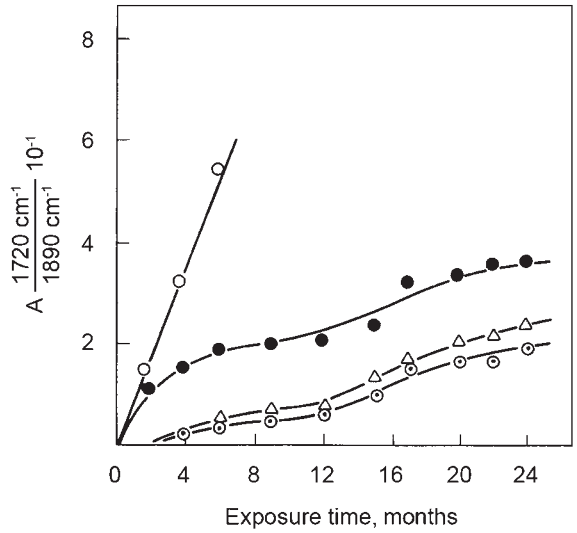


FIGURE 7 - Changes in the carbonyl index during natural weathering aging of LDPE in free atmosphere conditions: (O) LDPE; (●) LDPE + 1% HMB added; (⦿) LDPE + 1% Poly-HMB grafted in tetrahydrofuran; (△) LDPE + less than 0.5% Poly-HMB grafted in methanol

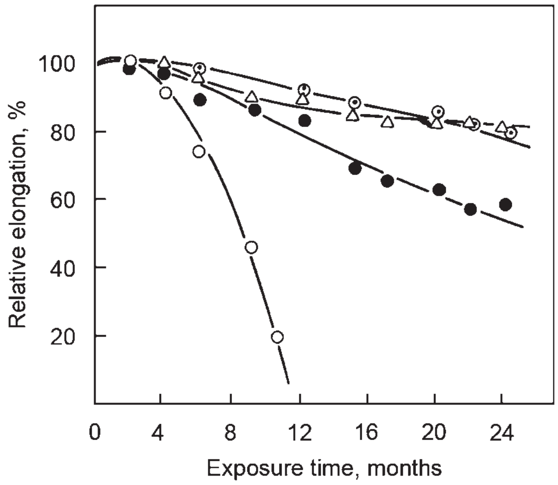


FIGURE 8 - Changes in elongation at break of LDPE during natural weathering aging in free atmospheric conditions: (O) LDPE; (●) LDPE + 1% HMB added; (⦿) LDPE + 1% Poly-HMB grafted in tetrahydrofuran; (△) LDPE + less than 0.5% Poly-HMB grafted in methanol.

Similar behaviour could be observed as in the case of accelerated aging. The best photo-stability was obtained when photo-stabilizer was grafted on LDPE. Although 24 months is a short period of natural weathering aging, it may be concluded that the results obtained in accelerated short time aging provide a good basis for the prediction of long-term behaviour of LDPE under UV irradiation.

Grafting of waste rubber with the aim to reuse it

Waste rubber is one of the big environmental problems. The best way to eliminate waste rubber from the environment is to reuse it. Two approaches are operative in practice. The first is incineration or pyrolytic degradation of waste rubber to basic chemicals; the second is grinding the waste rubber to form granulate or the regenerate, both of which are used in the production of technically less demanding rubber goods. The amount of waste rubber reused in this way is relatively low and new efforts are needed to solve this problem. In collaboration with rubber industry (*Sava*, Kranj) we performed the grafting of ethyl acrylate onto waste polybutadiene rubber (BR) by simultaneous gamma irradiation with the aim of investigating the possibility of substituting the part of virgin rubber by grafted rubber in some less demanding applications.

In our experimental conditions up to 80% of ethyl acrylate on waste rubber granulate was grafted by gamma irradiation.[12]

The grafted granulate prepared by gamma irradiation can be in no case used as substitute material for BR rubber without essential deterioration of the original properties of the BR rubber.

On the other hand with the addition of 20phr of BR granulate grafted with ethyl acrylate by gamma irradiation method to polyacrylic rubber compound, the properties of the rubber worsened, but remained within the range of properties characteristic for these types of rubber. The stability of rubber against swelling in hot mineral oil was satisfactory even when 30phr of grafted granulate was added to polyacrylic rubber. Polybutadiene granulate when grafted with ethyl acrylate gains some properties characteristic for polyacrylic rubber due to the introduction of polar groups into the polymeric chain of the BR rubber. This might be the reason why polybutadiene granulate grafted with ethyl acrylate could be in no case added to polybutadiene rubber.[13]

Radiation crosslinked plasticized PVC pipes

Plastic pipe systems, because of their cost effectiveness, ease of installation and good performance, have successfully penetrated such domestic piping applications as soil and vent, waste, underground drainage and rainwater systems, which were previously the domain of traditional metal or ceramic materials.

PVC is the oldest material used in plastic pipeline construction. The use of PVC may be limited, due to pressure, temperature or flux medium. Crosslinked PVC has improved properties and for this reason it is possible to use it for special applications, especially at higher temperatures and abrasion. A typical formulation for radiation curing includes a base polymer, PVC, poly-functional monomer and a variety of secondary additives such as non reactive plasticizers, stabilizers, fillers, pigments, and so on.

In collaboration with PVC industry (*Jugovinil*, Kaštel Sućurac) the efficiency of various poly-functional monomers in radiation crosslinking of PVC has been investigated. The compound for radiation crosslinked plasticized PVC pipes was prepared and tested.

The basic composition for the crosslinking was 100 parts of PVC suspension type (K-value 70), 30 parts of DOP plasticizer and 2 parts of stabilizer. To this basic mixture 5, 10 and 15 parts (based on PVC) of six poly-functional monomers – triallyl cyanurate (TAC), allyl methacrylate (AM), diallyl phthalate (DAP), 2-ethyl-2(hydroxylmethyl)-propanediol-(1,3)-trimethacrylate (EHPTM), divinyl benzene (DVB) and ethylene glycol dimethycrylate (EGDM) – was added. The mixtures were milled on a two-roll mill at 160°C and pressed into 2 mm sheets at 180°C.

The samples were irradiated in air with Co^{60} gamma source. The dose rate was 1.08×10^4 Gyh^{-1}. Absorbed doses were 50, 100 and 150kGy.

For gel content determination the irradiated samples were cut into small pieces, put in thimble and Soxhlet extracted for 16hr with tetrahydrofuran; then they were dried in vacuum at 60°C to constant weight. These conditions were found to be sufficient for determining "gel"-total amount of insoluble material in the sample. The effect of the radiation dose on gel production is shown in Figure 9.

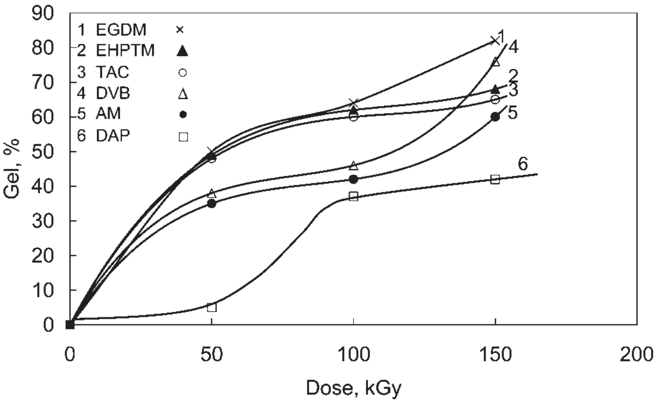


FIGURE 9 - Dependence of gel content on radiation dose for various monomer additives during PVC crosslinking; Monomer content 10 phr. 1 – Ethylene glycol dimethacrylate (EGDM), 2 – 2 ethyl-2(hydroxy-methyl)-propanediol-(1,3)-trimethacrylate (EHPTM), 3 – Triallyl cyannurate (TAC), 4 – Divinyl benzene (DVB), 5 – Allyl methacrylate (AM), 6 – Diallylphtalate (DAP)

In further experiments radiation crosslinking of PVC in the presence of triallyl cyanurate as a sensitizer, dioctyl phthalate as a plasticizer and lead and tin stabilizers was examined. The standard methods of testing PVC materials were used.[19] Direct relations between crosslinking extent, elongation, and Vicat softening temperature changes were found (Figure 10). As expected, solubility and elongation decrease while Vicat softening temperature increases as the radiation dose increases.

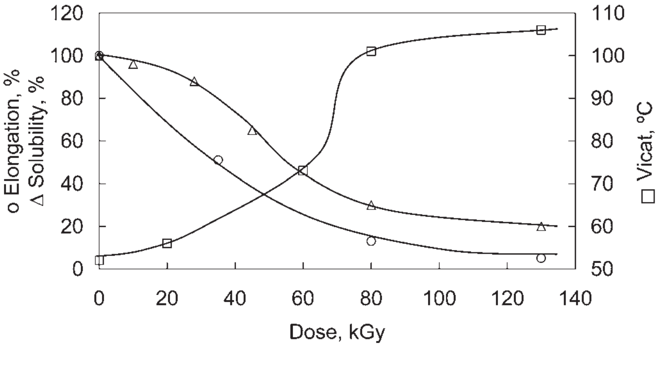


FIGURE 10 - Dependence of solubility (△), elongation (○) and Vicat softening temperature (□) of typical PVC compound on radiation dose.

Elongation at 140°C was measured in an oil bath with temperature of the specimen rising at a constant rate of 120°C per hour and with applied constant load of 10N/cm (ASTM 1637). Vicat softening temperature determination was performed according to ISO/R 306.

PVC does not crosslink to a useful extent when subjected to irradiation by gamma rays or electrons.[20-22] The predominant reaction is dehydrochlorination which leads to undesirable properties of the material. The addition of the radiation sensitizer and a well chosen stabilization system leads to efficient crosslinking reaction with low dehydrochlorination.

On the basis of our earlier experiments, a polyfunctional monomer triallyl cyanurate (TAC) was used in this work as a sensitizer. Two stabilizers, tribasic lead sulphate and tin mercaptide were also used.

Addition of a plasticizer influences rheological properties of the compound which results in higher mobility of the system. For efficient crosslinking the formation of a homogeneous and continuous network within PVC mass is needed. This would be possible by more or less continuous contact between a sensitizer and PVC macromolecules within the PVC mass. During irradiation of a PVC compound free radicals are produced in the TAC and PVC molecules. Non-reactive plasticizer DOP has high stability towards irradiation, which is attributed to energy transfer to the aromatic ring with subsequent non-degradative dissipation of energy. Free radicals initiate homopolymerization of TAC, grafting onto the PVC backbone and PVC crosslinking. DOP affects the competition between homopolymerization, crosslinking and grafting reactions by controlling the mobility of the reacting species. Increasing DOP concentration in the compound may increase the preference for TAC grafting onto the PVC backbone, because of dilution.

Lead stabilizers give very good crosslinking yields. The colour stability was good for doses of up to 150kGy. Tribasic lead sulphate accepts HCl, formed in the dehydrochlorination reaction during the thermal and radiation processing, without inhibiting the crosslinking.

Tin stabilizers give very good colour stability of samples even up to 300kGy doses, but they inhibit more strongly the crosslinking process.

Taking into account the above results two compounds were prepared for pipe production. Both contained 100 parts PVC (K-value 65), 30phr plasticizer (DOP) and 8phr stabilizer (Pb). One was prepared with 25phr crosslinking agent, the other without it.

Pipes of 20mm diameter (d) and 1.1mm wall thickness (s) were extruded on the laboratory single-screw extruder. Zone temperature varied from 155 to 200°C.

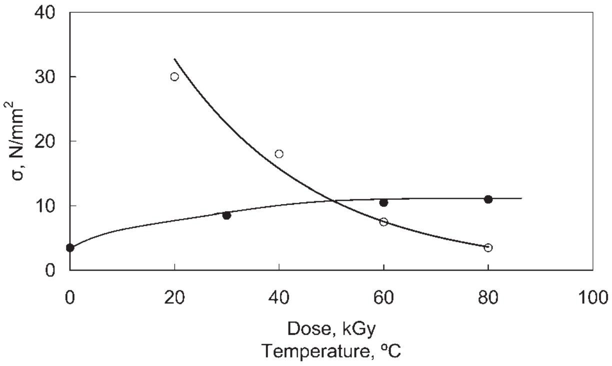


FIGURE 11 - Influence of the temperature on the circumferential stress of normal unirradiated PVC pipe (○). Influence of the dose on circumferential stress of radiation crosslinked PVC pipe at 80°C (●).

Circumferential stress was determined from the pressure at rupture on irradiated PVC-pipes at 80°C. Shore hardness and Vicat softening temperature in dependence on dose were also measured. The results are shown in Figures 11-13. Figure 11 shows the change of the circumferential stress of normal PVC pipe under different temperature conditions compared with radiation crosslinked pipe tested at 80°C. The circumferential stress was calculated by using the following equation:

$$\delta = \frac{d \bullet s}{2s} \, p \; (N/mm^2)$$

where: δ is the circumferential stress, in megapascals, d is the external diameter of the pipe, in millimetres, s is the minimum wall thickness of the pipe, in millimetres, p is the pressure of rupture in megapascals.

The results indicate much higher temperature resistance of radiation crosslinked pipe. Figures 12 and 13 show the dependence of Vicat softening temperature and Shore hardness on dose.

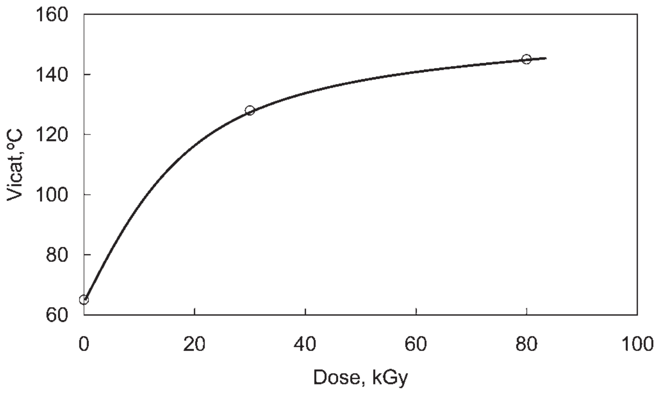


FIGURE 12 - Dependence of the Vicat softening temperature on the dose

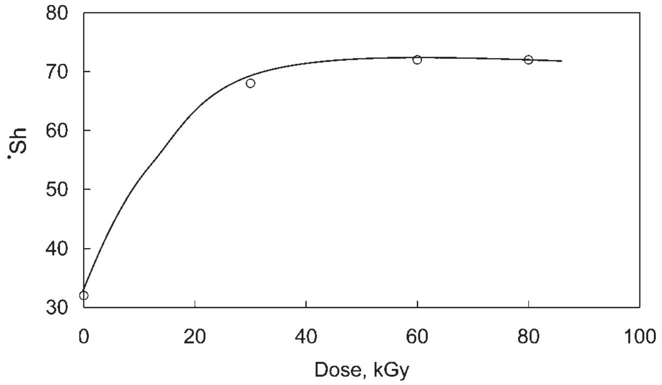


FIGURE 13 - Dependence of the Shore hardness, on the dose

Again the resistance of pipe at higher temperature increases with the dose increase.

The polyfunctional monomers differ in their efficiency in radiation crosslinking of PVC and the choice of monomer for crosslinking will depend on specification of the crosslinked products and on its price. The use properties of plasticized PVC-pipes can be highly improved by radiation crosslinking.

Conclusion

The possibilities of improving the polymer properties by radiation grafting and crosslinking were demonstrated in collaboration with local industry.

Photo-protector 2-hydroxy-4-(-methacryloxy-2-hydroxy-propoxy) benzophenone was grafted onto LDPE with the aim of increasing the persistence of stabilizer in polymer.

Surface grafting occurs in methanol solution of the stabilizer.

Measurements of the change of carbonyl index, elongation at break and tensile strength in the course of artificial and natural aging of LDPE, with grafted and non-grafted stabilizer, have proven much higher photo-protection achieved by grafted stabilizer.

Surface grafting is the most efficient and economical photo-stabilization method.

It was shown that with the addition of 20phr of polybutadiene waste rubber grafted with ethyl acrylate by direct gamma irradiation method, to polyacrylic rubber compound the properties of rubber worsened but remained within the range of properties characteristic for these types of rubber. The stability of rubber against swelling in hot mineral oil was satisfactory even when 30phr of grafted waste rubber was added to polyacrylic rubber.

Radiation crosslinked PVC pipes were produced. Circumferential stress determined from the pressure at rapture at 80°C, Shore hardness and Vicat softening temperature indicate much higher temperature resistance of radiation crosslinked pipes as compared to unirradiated pipes.

Acknowledgement

The author wishes to thank Dr. I.Dvornik, Dr. M. Barić, Mr. M. Ravlić, Mr. sc. G. Adam, Dr. U. Osredkar, Dr. A. Šebenik and Dr. Z. Veksli for their contribution to this research work.

REFERENCES

1. Ramby, B., Rabek, J.F. (Eds.): *Photodegradation, Photo-oxidation and Photo-stabilization of Polymers*, Wiley, New York, 1975.
2. Allen, N.S. (Ed.): *Degradation and Stabilization of Polyolefins*, Applied Science Publishers, London, 1983.
3. Kuckzkowsky, J.A., Gillick, J.G.: *Polymer-Bound Antioxidants*, Rubber Chem. Technol. 57(1984), 621-651.
4. Grassie, N., Scott, G.: *Polymer Degradation and Stabilization*, Cambridge University Press, London, 1985.
5. Scott, G. (Ed.): *Developments in Polymer Stabilization - 8*, Elsevier Applied Science Publishers, London, 1987.
6. Ranogajec, F., Mlinac, M., Dvornik, I.: *Radiation Grafting of UV Screener to Polyethylene and Polypropylene*, Radiat. Phys. Chem. 18(1981), 511-516.
7. Mlinac-Mišak, M.: *Dr. sci. Thesis*, Faculty of Technology, Zagreb, 1983.
8. Mlinac, M., Ranogajec, F., Fleš, D., Jovanović, D.: *Artificial Ageing of LDPE Film Containing Chemically Bound UV Stabilizer*, Angew. Makromol. Chem. 137(1985), 261-268.
9. Mlinac-Mišak, M., Ranogajec, F.: *Polietilen niske gustoće i njegove modifikacije*, Polimeri 20(1999)3, 83-98.
10. Ranogajec, F., Mlinac-Mišak, M.: *Improvement of polymer stability by radiation grafting*, IAEA-TECDOC-1062, 1999, 79-90.
11. Ranogajec, F., Mlinac-Mišak, M.: *Improvement of the polymer stability by radiation grafting,* Radiat. Phys. Chem. 71(2004), 229-233.
12. Adam, G., Šebenik, A., Osredkar, U., Veksli, Z., Ranogajec, F.: *Grafting of waste rubber*, Rubber Chem. Technol. 63(1990), 660-668.
13. Adam, G., Šebenik, A., Osredkar, U., Ranogajec, F., Veksli, Z.: *The possibility of using grafted waste rubber*, Rubber Chem. Technol. 64(1991), 133-138.
14. Hell, Z.,Ravlić, M., Dvornik, I., Ranogajec, F., Ranogajec, M., Tudorić-Ghemo, J.: *Radiation crosslined plasticized PVC-pipes*, Radiat. Phys. Chem. 22(1983), 619-625.
15. Hell, Z.: *Optimization factors of radiation crosslinked PVC products*, *Ph.D. Thesis*, Faculty of Technology, Zagreb, 1984.
16. Hell, Z., Ravlić, M., Bogdanović, Lj., Dvornik, I., Ranogajec, F., Barić, M.: *Postirradiation effects in crosslined PVC*, Polimeri 5(1985)10, 233-234.
17. Hell, Z., Ravlić, M., Bogdanović, Lj., Dvornik, I., Ranogajec, F., Barić, M.: *Effect of stabilizers on radiation grafting of PVC*, Polimeri 5(1985)10, 255-257.
18. Hell, Z., Junaković, Z., Ranogajec, F., Dvornik, I., Barić, M.: *Application problems of PVC materials irradiated with high doses*, Makromol. Chem., Macromol. Symp., 29(1989), 267-275.
19. Ives, C., Mead, J. A., Riley, M. M.: *Handbook of Plastics Test Methods*, The Plastics Institute, London, 1971, 280-283, 299-304.
20. Pinner, S. H.: *Enhancement of radiation-induced cross-linking of polyvinyl chloride,* Nature 183(1959), 1108-1109.
21. Miller, A. A.: *Radiation-cross linking of plasticized poly(vinyl chloride)*, Ind. Eng. Chem. 51(1959), 1271-1274.
22. Loan, L. D.: *Applications of radiation processing in the wire and cable field*, Radiat. Phys. Chem. 9(1977), 253-253.

CONTACT

Dr. sc Franjo Ranogajec
Institut *Ruđer Bošković*
Bijenička cesta 54
HR-10000 Zagreb
Phone: +385 1 456 10 70
Fax: +385 1 468 00 98
E-mail: franjo.ranogajec@irb.hr

Vijesti

Priredila: **Gordana BARIĆ**

Lanxess uvodi skraćeni radni tjedan

U borbi s poslovnim problemima koji su zahvatili i plastičarsku industriju, a kako ne bi došlo do otpuštanja radnika zbog smanjenja potražnje za polimernim materijalima, tvrtka *Lanxess* sa sjedištem u Njemačkoj namjerava sljedećih 12 mjeseci raditi skraćeno. Radni tjedan skraćuje se na 35 sati počevši od ožujka ove godine. Jednako tako, najavljeno je neisplaćivanje stimulacija za svih 5 000 zaposlenika u Njemačkoj, a sve u dogovoru s radničkim predstavnicima i čelnicima njemačkoga *Sindikata rudarstva, energetike i kemijske industrije*. Razlog svemu je recesija, koja je zahvatila u prvom redu automobilsku industriju i građevinarstvo, gdje se osjeti znatno smanjenje narudžbi. Članovima *Upravnoga odbora* snizuju se plaće za 10 %, dok će za ostatak upravljačkih struktura varijabilni dio plaće biti prilagođen poslovnim rezultatima tijekom godine, a povišenje fiksnoga dijela plaće odgođen je za najmanje šest mjeseci. Povišenje plaća u *Lanxessovim* podružnicama također je odgođeno na 6 do 12 mjeseci, a sniženje troškova zaposlenika ovisit će o situaciji u pojedinoj zemlji.

Lanxessovi poslovni rezultati za 2008. godinu nisu odstupili znatno od zacrtanoga, ali se mjere štednje provode zbog velikog pada prihoda u prvim mjesecima 2009.

European Rubber Journal,
ožujak/travanj 2009.

Porast potrošnje plastične ambalaže

Prema istraživanjima *Freedonia Group*, jedne od vodećih svjetskih marketinških tvrtki, potrošnja plastične ambalaže u sljedeće tri godine rast će 2,4 % godišnje. Najveći rast tržišnoga udjela predviđa se u pakiranju hrane za kućne ljubimce i pića na bazi soje. Porast se očekuje i za zaštitnu ambalažu te za ambalažu za voćne sokove i smrznutu hranu. Razlozi koji su doveli do takvih procjena su produljenje trajanja proizvoda, smanjena uporaba materijala te mogućnost ponovnog zatvaranja ambalaže te kuhanja na pari i u mikrovalnim pećnicama.

www.freedoniagroup.com