

The Influence of EB-Crosslinking on Barrier Properties of HDPE–Mica Composites

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SYNOPSIS

High-density polyethylene (HDPE) was compounded with untreated and surface-treated mica (10, 20, 40 wt %) and composites were injection-molded. The composites were radiation crosslinked (100, 300, 700 kGy) and hydrocarbon permeability, tensile impact strength, and tensile strength at 25 and 80°C of the composites were examined. The permeability of HDPE decreased from 7 to 3.6 g/(d × m²) by compounding the polymer with 20 wt % mica, and the permeability was additionally reduced to 1.3 g/(d × m²) by irradiation of the compounds (700 kGy). When surface-treated mica was used, the permeability of the composite furthermore decreased to about 1.0 g/(d × m²). Upon irradiation, the *E* modulus measured at 25°C increased 5% when the dose was 300 kGy. At 80°C, the corresponding increase was 40%. The tensile impact strength of an unfilled polymer increased more than three times by an irradiation dose of 700 kGy, and for a polymer with 10 wt % mica, the tensile impact strength was twice the level of an unirradiated composite. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Due to a high degree of inertness to chemicals, high-density polyethylene is an appropriate material for containers and automobile tanks. A low rate of diffusion is an important requirement of polymers used for liquid storage. The diffusion of a penetrant is a very complex process and depends on different factors. Physical conditions as density, molar mass, crystallinity, and cohesive energy density of the polymer affect the rate of diffusion.^{1–4} Any factor which tends to make the polymer chain segments less mobile, or pack more closely, decreases the permeability.⁵ If symmetry and cohesive energy density increase, permeability can be expected to decrease as well.

Chemical properties such as polarity and degree of branching, of both the polymer and the penetrant, strongly influence the permeability.⁶ The branching of the penetrant has a greater effect on the diffusion coefficient than has molecular size.⁵ External conditions affecting the permeability are pressure and

temperature according to Arrhenius relationships.⁶ Different methods may be applied to improve the barrier properties of polyethylene.⁷ Permeability may be decreased by using inert flaky fillers as barriers.⁸ Furthermore, polymeric material can be modified by crosslinking⁹ or by grafting functional groups onto the polymer chains.¹⁰ Introduction of barrier layers on the surface of polyethylene also reduces the permeability of organic vapors. Barrier properties can also be obtained by means of chemical modification, such as sulfonation or fluoridation,¹¹ or by means of processes like coating, painting, coextrusion, galvanizing, and Al lining.⁷ This study investigates the effects of irradiation of HDPE–mica composites on the hydrocarbon permeability of the material.

EXPERIMENTAL

Materials

Unstabilized high-density polyethylene (Lupolen 4261 A, MFI 5.4 g/10 min) was supplied as a powder by Suomen BASF Oy, Helsinki, Finland. Phlogopite mica (40 S), with an average size of 40 μm, was sup-

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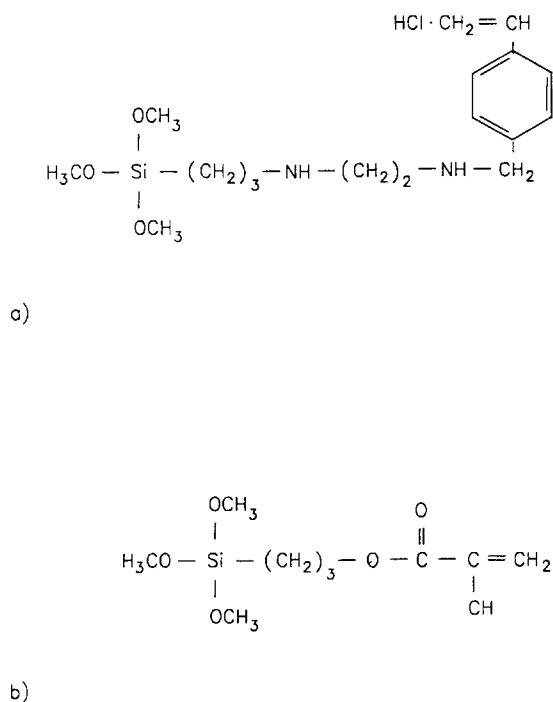


Figure 1 Silane coupling agents: (a) *N*-(*N*-vinylbenzyl-2-aminoethyl)-3-aminopropyltrimethoxysilane hydrochloride, Z6032, Dow Corning; (b) metacryloxypropyltrimethoxysilane, A 174, Dow Corning.

plied by Kemira Ltd, Pori, Finland. Polymer composites of both surface-treated and untreated mica were studied. Surface treatment was carried out by deposition of the coating agent from an aqueous alcohol solution¹² at Kemira Ltd, Pori, Finland. Coupling agents used in this study were a cationic vinylbenzyl silane [*N*-(*N*-vinylbenzyl-2-aminoethyl)-3-aminopropyltrimethoxysilane hydrochloride, Z 6032, Dow Corning] and a trimethoxy silane (metacryloxypropyltrimethoxysilane, A 174, Dow Corning). The chemical structure of both silanes are presented in Figure 1.

Preparation of Composites

Polymer and filler were compounded in a single-screw extruder (Axon BX 22, $D = 22$ mm, $L = 30$ d) at 60 rpm. The temperature profile of the extruder was 240–235–230–225–210°C. The theoretical concentrations of mica in the composites were 0, 10, 20, and 40 wt %. Untreated mica, mica treated with A 174, and mica treated with Z 6032 were used in the composites of 20 wt % filler. The mica used in the 10 and 40 wt % composites was treated only with Z 6032. Specimens for permeability testing, tensile impact strength, and tensile properties were pre-

pared by injection molding (Engel 50//75 AS). Round plaques with a radius of 30 mm and thickness of 2 mm ($S_x = 0.9\%$) were used for permeability tests. Test specimens for tensile impact were prepared according to DIN 53 448 were prepared and those for tensile properties according to the ASTM standard D 638M (Type M-I). Electron-beam processing was carried out by Beta Tech, Jönköping, Sweden, using a 10 MeV linear accelerator (Model EB10) developed by Scanditronix AB. The accelerator is equipped with a 90° bending magnet as a spectrometer and a parallel beam at the exit. The radiation dose varied between 100 and 700 kGy.

Testing Procedure

For testing the permeability of the composites, a gravimetric method was used. A measuring cell was filled with FAM (Fachausschuss Mineralöl- und Brennstoffnormung) testing fluid for polymer materials (DIN 51 604), which corresponds to petrol. The measuring cell was covered with a plaque of the material to be tested and sealed by a ring, which was tightened with four screws, according to Figure 2(a). When the measurement was started, the cell was turned upside down to allow the fluid to permeate through the plaque (2b). The weight loss of the cells was concluded to depend solely on the permeability of the testing fluid through the test specimens, since the standard deviation of three parallel tests were less than 5% and it took 10–14 days before any weight loss could be registered. The equipment and the specimens were conditioned before the

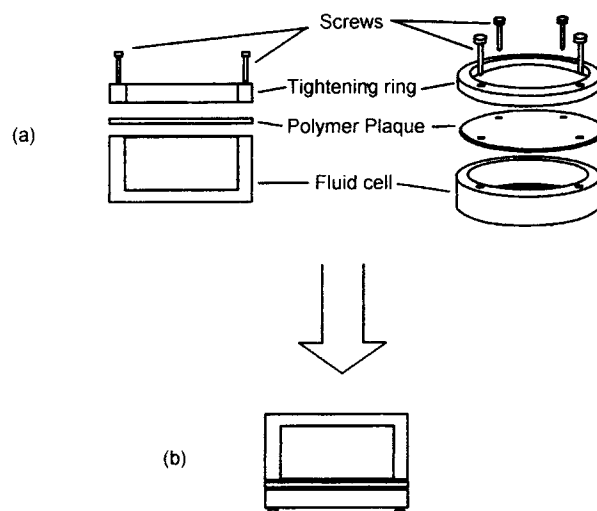


Figure 2 Measuring cell for the determination of diffusion rate of hydrocarbons.

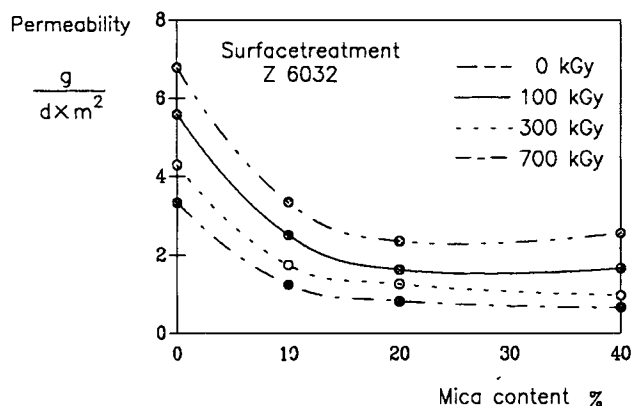


Figure 3 Effect of irradiation on diffusion for composites containing 0–40 wt % mica. The diffusion given as gram penetrated fluid through a square meter of the polymer per 24 h.

measurement, and the cells were stored in a conditioned room (23°C, 50% RH).

The weights of the cells were recorded at least every second day, and the weight loss was registered as a function of time. The results are given as gram hydrocarbons permeated per square meter and 24 h for the given specimen thickness [$\text{g}/(\text{d} \times \text{m}^2)$]. As an indication of the degree of crosslinking, gel content was determined according to ASTM D 2765.

Crystallinity was determined with a Perkin-Elmer differential scanning calorimeter (System 4). The temperature was increased from 50 to 160°C at 10°C/min. After rapid cooling, a second run was performed. For the calculation of crystallinity of the samples, a heat of fusion of 293 J/g (Ref. 13) was used and the value was corrected in accordance with the actual mica content.

Tensile property data were collected using an Instron 4202 tensile tester at room temperature and at 80°C. A minimum of five samples were tested in each series. The speed of testing was 25 mm/min and an extensometer was not used. The results were calculated using a Hewlett-Packard computing system including an Instron Series IX automated materials testing system, Version 4.03. Tensile properties are reported as the E modulus, which was calculated from the stress-strain curve. The coefficient of variation was less than 12%.

Tensile impact tests were performed at room temperature on a Zwick Pendulum impact tester 5101 according to the DIN-standard no. 53 448. The coefficient of variation was less than 8%.

RESULTS AND DISCUSSION

Diffusion Properties

As stated in the Introduction, the diffusion rate in a polymer material is related to the mobility of the polymer chains. The chain mobility can, for instance, be reduced by crosslinking. Introducing filler particles into a polymer matrix is also another established method to reduce the permeability. In this study, both approaches were tested separately and together. Figure 3 shows the combined influence of the filler and irradiation. The diffusion rate was close to $7 \text{ g}/(\text{d} \times \text{m}^2)$ of the original HDPE polymer and already a content of 10% mica reduced the permeability below $4 \text{ g}/(\text{d} \times \text{m}^2)$, and it stabilized at about $3 \text{ g}/(\text{d} \times \text{m}^2)$ with increased mica content. Furthermore, this figure shows that the reducing influence of the filler on the diffusion rate is further increased by means of radiation. Using a dose of 300 kGy, the permeability of the unfilled HDPE polymer decreased about 30%, the decrease being about 50% in the presence of 20 wt % mica. Using an addition of a 20 wt % filler and a radiation dose of 300 kGy, the permeability was only $\frac{1}{5}$ of that of the original polymer. As far as permeability is concerned, surface treatment of mica is considered to be important. It is, however, well known that dispersion of a flaky filler, like mica, in a highly viscous high molecular weight polyethylene is difficult. Surface treatment may facilitate better dispersion and, in favorable cases, create chemical bonds between the filler surface and the polymer matrix.

The influence of the coupling agent was studied by treating mica with two different types of silane

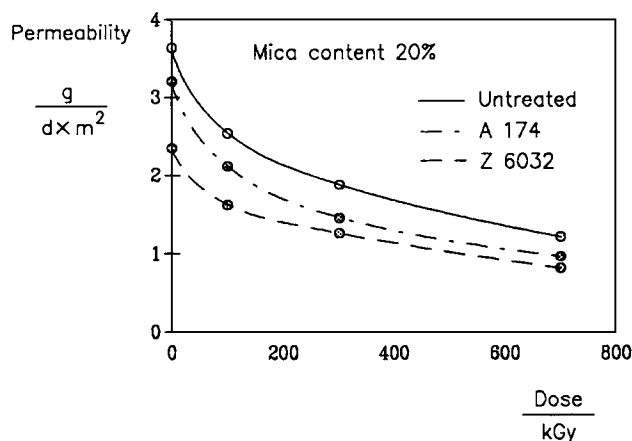


Figure 4 Effect of irradiation on diffusion for composites containing untreated mica and mica surface-treated with Z 6032 and A 174.

Table I Effect of Radiation and Mica Content on Crystallinity

| Dose (kGy) | Degree of Crystallinity (%) | | | |
|------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| | 0 Wt % Mica | 10 Wt % Mica | 20 Wt % Mica | 40 Wt % Mica |
| 0 | 49 ^a (46) ^b | 41 ^a (40) ^b | 32 ^a (31) ^b | 18 ^a (16) ^b |
| 100 | 43 ^a (45) ^b | 35 ^a (38) ^b | 28 ^a (31) ^b | 16 ^a (17) ^b |
| 300 | 41 ^a (50) ^b | 28 ^a (32) ^b | 26 ^a (30) ^b | 13 ^a (16) ^b |
| 700 | 40 ^a (50) ^b | 24 ^a (31) ^b | 24 ^a (30) ^b | 13 ^a (16) ^b |

^a From the second run.^b From the first run.

coupling agents before being dispersed into the polymer matrix. The results obtained are plotted in Figure 4 as a function of radiation dose. As expected, permeability decreased with increasing dose. An obvious dependence of permeability on the presence and type of surface treatment is, however, also observed. The permeability of the unirradiated polymer decreased to $\frac{1}{3}$ of the permeability of the original polymer when 20 wt % mica was added using Z 6032 as the surface-treatment compound. The permeability was 3.2 g/(d × m²) for a composite containing mica treated with A 174 and 2.4 g/(d × m²) when Z 6032 was used for the surface treatment. The effect of coupling agents on permeability decreased when the radiation dose was increased. This means that the degree of crosslinking is of greater importance on the permeability than is the type of coupling agent. However, it has been reported that vinylsilane treatment of fillers cause improved mechanical properties of the composite.¹⁴ This phenomenon is probably due to covalent coupling of the silanes to the polymer matrix or a result of improved filler dispersion which decreases filler agglomerates that would act as weak points in the composite.¹⁵⁻¹⁷ This coupling tends to decrease the mobility of the polymer chains by tying the chain to the filler. This, in turn, will lead to reduced permeability.

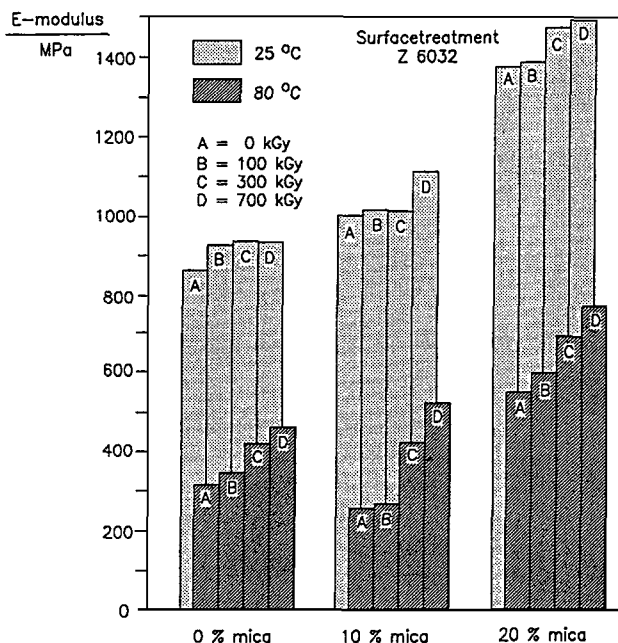
Second, radiation reduces the mobility of the polymer chains by covalently bonding the chains together. A reduced mobility will, in turn, result in reduced permeability. The reduction of permeability as a function of irradiation dose was about 15% less for composites containing Z 6032 surface-treated mica than for the composites containing untreated mica and mica treated with A 174. Since the permeability of unirradiated composites containing Z 6032 surface-treated mica was about 30% lower than that of unirradiated composites containing untreated or A 174-treated mica, one can assume that

there is a difference in the chain mobility of the composites, i.e., the chain mobility is more restricted in the composite containing Z 6032 surface-treated mica. The effect of irradiation on the chain mobility is therefore less for this composite.

As can be seen from Table I, the crystallinity decreased with increased mica content. The crystallinity, based on data from the second run, also decreased when the radiation dose was increased. This indicates that the improved barrier properties are a result of the crosslinking of the polymer. The reduced crystallinity is a result of the increased amount of chain defects produced by the irradiation.

Mechanical Properties

The influence of radiation on tensile properties at 25 and at 80°C are presented as the *E* modulus in Figure 5. As radiation produces crosslinks between polymer chains, some influence on the *E* modulus might be anticipated, especially at elevated temperature as the crosslinks prevent chains from flowing. Tensile properties were, therefore, tested at ambient and elevated temperatures. As revealed by Figure 5, the radiation dose does not significantly influence the *E* modulus of the pure polymer at ambient temperature. However, a clear dependence of the *E* modulus on the irradiation dose is observed at elevated temperature. These results indicate that fairly long flexible segments still exist between points of

**Figure 5** *E* modulus at 25 and 80°C as a function of mica content and radiation dose.

crosslinking. The increased E modulus at elevated temperature is a consequence of prevented chain flow. Furthermore, the figure shows that a significant influence of the filler on the E modulus is fairly independent on the testing temperature. At a dose of 300 kGy, an addition of 20 wt % mica increases the E modulus 62% at ambient temperature and 67% at 85°C compared to the E modulus of the pure polymer. This indicates that interface properties are fairly independent of temperature. The E modulus of the pure polymer at 25°C increased from 876 to 918 MPa (5%) when the irradiation dose was 300 kGy. The corresponding increase, caused by crosslinking, at 80°C was from 305 to 420 MPa (40%).

The gel content of unfilled and filled polymer at different radiation doses are presented in Table II. As can be seen, there is no remarkable difference between the gel content of unfilled and filled HDPE, which indicates that the presence of the filler does not significantly influence the penetration of the radiation or the behavior of the radicals.

It is well known that crosslinking influences the impact behavior of polymers. In case of the pure polymer, this influence was very significant. As can be seen from Figure 6, the tensile impact strength of unfilled HDPE was improved from 23 to 86 J/m² upon irradiation, and a composite with 10 wt % mica reached twice the original strength of the unirradiated composite. This dramatic increase is primarily a function of an optimal combination of hard segments due to adsorption to filler surfaces, soft flexible segments, and prevented molecular flow. It is evident that mica concentration at a given point, in the interval 10–20 wt %, makes the material less flexible and thus the irradiation has no influence on tensile impact strength.

CONCLUSIONS

This study shows that introduction of mica into HDPE combined with radiation processing pro-

Table II Gel Content at Different Radiation Doses

| Dose (kGy) | Mica Content | | |
|------------|--------------|---------|---------|
| | 0 Wt % | 10 Wt % | 20 Wt % |
| 0 | 1.4 | 3.2 | 3.9 |
| 100 | 65.2 | 66.0 | 63.9 |
| 300 | 83.8 | 86.5 | 83.9 |
| 700 | 90.8 | 93.0 | 91.9 |

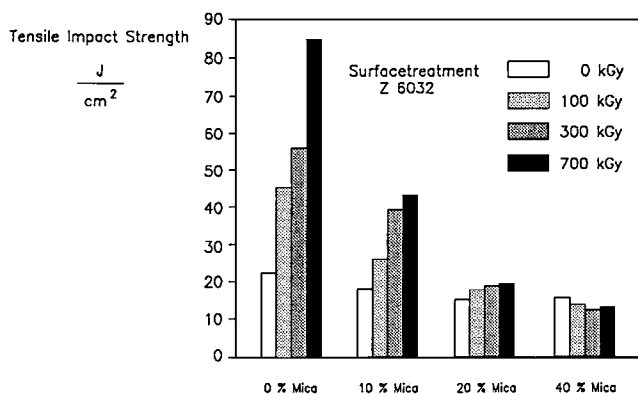


Figure 6 Effect of irradiation on impact tensile strength at various mica contents.

duces quite interesting new properties. Due to an extended restriction of chain movement, permeability is reduced to $\frac{1}{5}$ of the original value. However, radiation as such not only gives a fair reduction in permeability, but it also facilitates a most significant increase in tensile impact strength. Both effects should be of considerable interest for many technical applications. Crosslinking obviously introduces good shock-absorbing properties which still prevail at a low filler content. This study is not especially devoted to interface properties but it may, however, be concluded that the type of silane has some influence on material properties, especially in the case of barrier properties. As the introduction of the coupling agent clearly reduces permeability, it is obvious that it also increases the interaction between filler particles and polymer chains. Further, the interaction is somewhat stronger with the vinylbenzyl silane than with the aminosilane.

As regards the influence of radiation, 300 kGy may be regarded as a fairly high dose. A dose of 700 kGy may already be considered to cause some damage to the polymer material. Based on experimental results, it may be stated that an electron beam-irradiated HDPE composite containing surface-treated mica will be applicable to different kinds of storage utensils where high tensile impact strength and a low diffusion rate are required.

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