

Effects of Gasoline Absorption on the Tensile Impact Response of HDPE/SelarTM Laminar Microlayer Composites

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ABSTRACT: The tensile impact performance of polymer/polymer microlayer composites (PPC) was studied before and after storage in unleaded fuel at an ambient temperature (RT) and at -40°C , respectively. The PPCs were produced by extrusion blow molding of high-density polyethylene (HDPE), $d = 0.945 \text{ g/cm}^3$, blended with a modified polyamide (SelarTM RB 901 of DuPont) in 4, 7, and 14 wt %, respectively. It was shown that the fuel absorption obeys the Fickian law of diffusion. With increasing Selar content the sorption was reduced, whereas diffusion (D) and permeability (P) coefficients of the PPCs did not appear to change. The Selar microlayers worked as reinforcements, so that the strength and stiffness of the PPCs were increased, however, at the cost of the ductility and toughness. The exact opposite trends were observed due to fuel absorption. Gasoline, acting as plasticizer, resulted in reduced stiffness and strength with simultaneously increased ductility and toughness of the PPCs. All of the above-mentioned properties were similar for all blends after storage in gasoline. The failure mechanism of the PPCs was studied by fractography and is discussed in relation to the composite structure. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 561–569, 1998

Key words: barrier resin; gasoline absorption; HDPE; microlayer composites; plastication; SelarTM; strain–stress behavior; tensile impact

INTRODUCTION

In recent years a new type of polymeric/polymeric composite (PPC) material is gaining acceptance in manufacturing of bottles, hollow bodies, and various containers for liquids. This PPC, having a discontinuous laminar microlayer structure developed during processing, was launched by DuPont and termed “Selar technology.”¹ Due to the analogy in advance composite laminates, this microlayer composite is also referred to as stratified PPCs. The

overall barrier performance to low molecular-weight penetrants, including gasoline, and the impact properties are of crucial importance for those polymeric materials, which should meet the stringent application criteria for fuel tanks.^{1,2} The former requirement is achieved by the labyrinth principle in SelarTM barrier (modified amorphous polyamide) resin-modified polymers.¹

The high impact resistance provided by the HDPE matrix ensures that the fuel tank will not be damaged after a crash, thus preventing the fuel from exploding. The driving forces for using high-density polyethylene (HDPE) for the production of fuel tanks is the design freedom given by the advanced blow-molding technology and the low density of this polymer (yielding considerable weight reduction). Furthermore, the use of HDPE is favored due to its outstanding toughness over a broad temperature range. Because HDPE exhib-

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its poor barrier performance to penetrants, the inner surface of HDPE tanks is always treated (fluorination and sulphochlorination) to meet this requirement. Due to environmental issues, the latter method is declining. Instead of surface treatment the barrier performance required is set by coextrusion (resulting in continuous laminar polymer/polymer composites) or extrusion blow molding from a HDPE/SelarTM blend (where the SelarTM barrier resin is dispersed discontinuously in form of microlayers *in situ*, i.e., during the blow-molding process). By employing the latter technique, SelarTM layers are finely dispersed (in the order of few μm thickness) in the HDPE matrix.

In previous works,³⁻⁵ it has been stated that the stratified microstructure of the SelarTM resin strongly influences the impact response. An attempt was also made to predict the tensile after impact behavior of HDPE/Selar microlayer composites.⁶ Because no results are available in the open literature on how fuel absorption affects the impact performance of this particular PPC, this work was devoted to this issue by investigating the effect of gasoline absorption on the tensile impact behavior.

EXPERIMENTAL

Specimen Preparation

Specimens were cut from the circumferential section of extrusion blow-molded bottles (nominal volumetric capacity of 1 L and an average wall thickness of 1 mm), provided by DuPont Automotive (Wilmington, DE). The bottles were blow molded from blends of HDPE (Lupolen 4261A, BASF AG, Ludwigshafen, Germany) with 0, 4, 7, and 14 wt % SelarTM RB 901 resin, respectively.

Dumbbell specimens (type S3A, according to DIN 53504; cf. Fig. 1) subjected to tensile impact were punched by a Ceast (Torino, Italy) hydro-pneumatic press.

Storage in Gasoline

The weight gain in gasoline of the blends was studied, employing a gravimetric technique. Three specimens from each HDPE/Selar blend were weighed in the dry stage and immersed in unleaded commercial gasoline of 95 octane number (EN 228) at room temperature ($RT = 20^\circ\text{C}$). Each of the specimens was frequently taken out

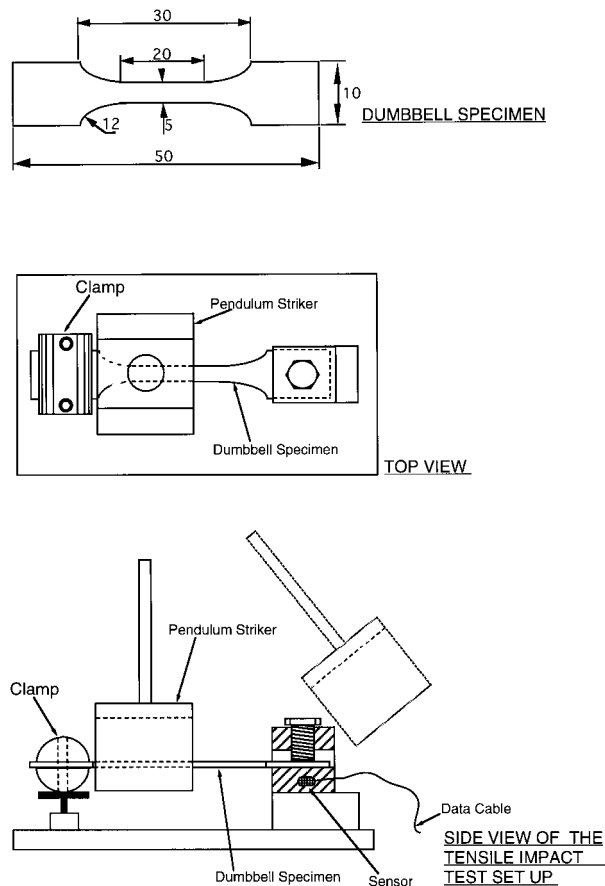


Figure 1 Specimen and test setup of the tensile impact test.

of the gasoline and weighed. Weight gain was determined on a high-precision laboratory electronic balance. During the first 4 days, time intervals between weight sampling were short in order to capture the high initial absorption rates, whereas they were prolonged afterwards, while specimens reached saturation. The overall immersion time was 120 days. The results reported in this article are mean values for the three parallel specimens.

The relative gasoline uptake (M_t) was calculated using eq. (1):

$$M_t = \frac{W_w - W_d}{W_d} \quad (1)$$

where W_w is the specimen weight after an exposure time, t , and W_d is the weight in the dry stage, respectively. M_t is plotted as a function of the immersion time t .

The common approach to describe molecular diffusion is application of Fick's law assuming a single-phase diffusion process. Fick's law predicts

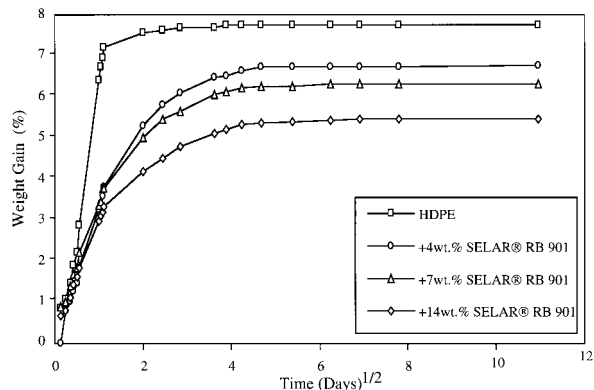


Figure 2 Relative weight gain (wt %) versus $t^{1/2}$ for the PPCs, composed of HDPE and Selar, exposed to unleaded fuel.

that the relative mass of the absorbed phase increases linearly with the square root of time ($t^{1/2}$) and then gradually declines until it reaches an equilibrium plateau. However, the diffusion coefficient (D) is calculated for the initial stages of sorption via⁷

$$\frac{M_t}{M_m} = \frac{4}{\sqrt{\pi}} \sqrt{\frac{Dt}{h^2}} \quad (2)$$

where h is the specimen thickness and M_m is the saturation or equilibrium fuel content.

The relative gasoline uptake (M_t) as a function of \sqrt{t} is shown for the HDPE/Selar blends in Figure 2. Diffusion coefficient D was calculated from the initial slope of the curves (up to $t = 1.245$ days) in Figure 2 using eq. (2). The related M_m values were read from the equilibrium plateau of the corresponding curves.

Tensile Impact Testing

The testing geometry is shown in Figure 1. Tensile impacting of the specimens was carried out using a Ceast, AFS_MK4 (Torino, Italy) impact pendulum machine, according to the DIN 53504 testing standard. The impact velocity was $v = 3.7$ m/s. The impact energy was 7.50 J, and the test time was set at ≤ 32 ms. Testing was carried out at -40°C and at RT. Force data was obtained using a PC supported data acquisition system featuring specialized software. From the fractograms obtained (force over time curves), the following data were read or calculated: dynamic Young's modulus (E), yield stress (σ_y), fracture stress (σ_b), ultimate strain (ϵ_b), and total energy re-

quired to fracture. Furthermore, the fracture response was characterized by the specific tensile impact energy (W_f) values, representing total energy normalized at specimen cross section area.

Tensile impact tests performed at -40°C (set by a refrigerator cooled with liquid nitrogen), because drop tests of toluene-filled fuel tanks²⁻⁴ are carried out at this specific temperature.

Microstructure and Failure Assessment

A JEOL, JSM 5400 (Tokyo, Japan) scanning electron microscope was employed to investigate the fracture surfaces of the impacted specimens. Specimens were sputtered with gold.

RESULTS AND DISCUSSION

Gasoline Absorption

The relative gasoline uptake versus \sqrt{t} for all HDPE/Selar™ blends is shown in Figure 2. It is evident that HDPE is most sensitive to fuel sorption. The gasoline uptake decreases with increasing Selar content, and high resistance to fuel sorption is already observed at only 4% wt Selar, a fact also stated by other workers.¹ The lowest equilibrium plateau value is, however, obtained, for the PPC with 14 by wt % of Selar™ RB 901 resin. Figure 2 shows the change in the sorption kinetics as a function of the Selar content. In order to magnify the sorption differences between the PPCs, values of M_t/M_m were plotted versus \sqrt{t} for the initial stage (cf. Fig. 3). Linear regression lines could be easily fitted. This confirms the initial assumption that Fick's law can be applied to this

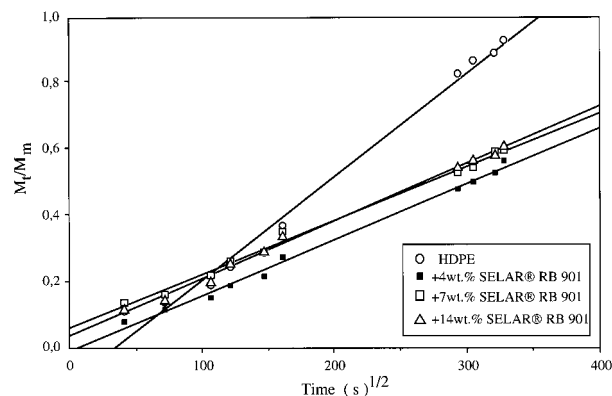


Figure 3 Determination of the diffusion coefficients (D) for the HDPE/Selar blends from the initial stage (up to $t \approx 1$ day) of liquid gasoline absorption.

Table I Sorption (*S*), Diffusion (*D*), and Permeability (*P*) Coefficient of the PPCs Toward Unleaded Super Gasoline

PPC Systems	<i>D</i> 10 ¹³ (m ² s ⁻¹)	<i>S</i> (g/g)	<i>P</i> 10 ¹⁴ (m ² s ⁻¹)
HDPE	19.0	0.077	14.63
HDPE + 4 wt % SELAR® RB 901	5.62	0.065	3.62
HDPE + 7 wt % SELAR® RB 901	5.19	0.060	3.13
HDPE + 14 wt % SELAR® RB 901	5.93	0.051	3.05

type of permeation process. From the slopes of the regression lines the diffusion coefficient (*D*) was calculated using eq. (2) and the results are shown in Table I. Table I also shows the values of the sorption coefficient *S* (taken from the equilibrium plateau of the sorption curves), and the related permeability coefficient *P*, as calculated via

$$P = DS \quad (3)$$

Examination of the *D* and *P* values shows that the improvement in the resistance to gasoline permeation by addition of Sellar is obvious. Gasoline diffusion through pure HDPE lies about a half an order of magnitude higher than in the Sellar-modified PPCs. It is interesting to note that neither diffusion nor permeability coefficient changes significantly when the Sellar content is increased. On the other hand, great differences can be seen in respect to their sorption characteristics. This implies that tensile impact response, due to exposure to gasoline, highly depends on their sorption characteristics. Based on analogies with other low molecular weight compounds⁸ gasoline can also be regarded as a plasticizing agent in PPCs composed of HDPE and Sellar barrier resin.

Fracture Response

Effects of Temperature and Composition

Stress-strain fractograms for pure (as supplied) HDPE and PPC with 7 wt % Sellar, are shown as a function of testing temperature in Figures 4 and 5, respectively. Figure 4 shows that both σ_y and σ_b increase, whereas ϵ_b is reduced with decreasing temperature. Similar results are obtained for the

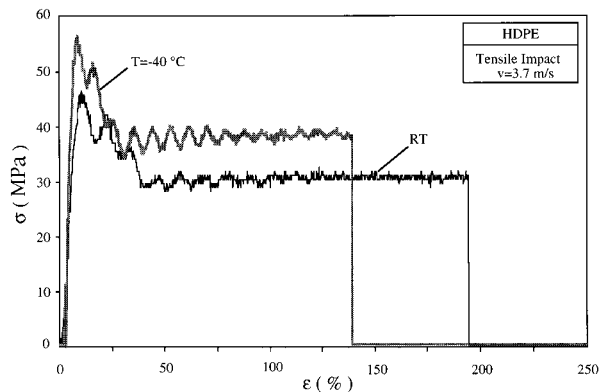


Figure 4 Stress-strain (σ - ϵ) traces in function of temperature for plain HDPE due to instrumented tensile impact.

PPC with 7 wt %. This finding is consistent with the usual effect of reduced testing temperature on the mechanical response of thermoplastics known as “low temperature embrittlement.” Comparing the σ - ϵ curves of Figures 4 and 5, it becomes evident that the Sellar layers act as reinforcements in the HDPE matrix. As a consequence, the strength is increased, however, impairing the ductility of the materials (i.e., reduced elongation accompanied with decreased W_f values). It is worth noting that the σ - ϵ trace of the PPC with 7 wt % Sellar is less influenced by the testing temperature than the related response of the HDPE. In the necking stage of the HDPE, stress oscillations can be resolved. The authors are, however, not aware as to why this phenomenon becomes more pronounced at lower testing temperature.

The most important tensile impact properties are summarized in Table II. The strong influence

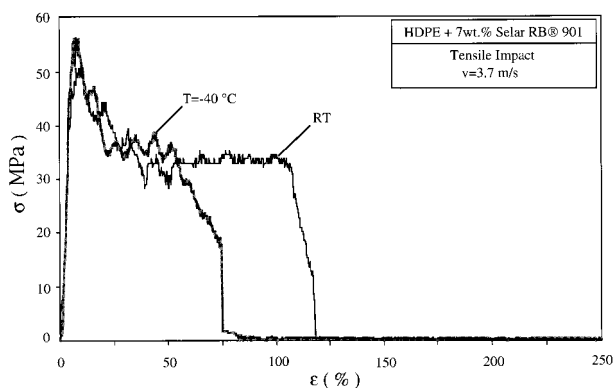


Figure 5 Tensile impact response in form of σ - ϵ curves for a PPC with 7 wt % Sellar™ RB 901 in function of testing temperature.

Table II Tensile Impact Data of HDPE and PPCs Consisting of HDPE and Selar® RB 901 Prior and After Storage in Gasoline for 3 Months in Function of the Testing Temperature

PPC Systems	State	W_f (mJ/mm ⁻²)		E Modulus (MPa)		σ_y (MPa)		ϵ_b (%)	
		RT	-40°C	RT	-40°C	RT	-40°C	RT	-40°C
HDPE	dry	989	803	594	881	40	48	191	122
	stored	1271	1115	481	567	35	38	237	218
HDPE + 4 wt % SELAR® RB 901	dry	650	552	656	904	43	49	122	100
	stored	919	752	502	604	33	43	192	137
HDPE + 7 wt % SELAR® RB 901	dry	711	630	811	975	53	51	119	86
	stored	1060	749	504	537	37	41	190	101
HDPE + 14 wt % SELAR® RB 901	dry	676	717	702	1084	48	53	109	104
	stored	1012	769	489	544	36	43	183	117

This table includes mean values of eight specimens. Scatter is in the range of ca. $\pm 6\%$.

of the testing temperature, along with the reinforcing effect of the Selar discontinuous layers, is demonstrated. It can be seen that, with increasing Selar content, properties such as E modulus and yield strength increase, whereas the ultimate strain and tensile impact energy are reduced. The above tendency is not monotonous as a function of the Selar content (cf. Table II). This indicates that an optimum balance between stiffness and toughness is linked to a given Selar amount. Recall that for the production of the actual fuel tanks usually 7 wt % Selar™ RB 901 is added to the HDPE.^{3,4}

Effects of Gasoline Absorption

As expected, gasoline absorption was accompanied by plastification of the HDPE matrix. This was manifested in reduced stress and increased strain values after storage in gasoline. Typical fractograms for the plain HDPE (Fig. 6) and PPC with 7 wt % Selar™ RB 901 (Fig. 7) clearly demonstrate the plasticizing effect. The stiffness and strength values are clearly lower, while the ϵ_b and W_f values are increased by the gasoline uptake.

The mechanism behind this behavior is plastification of the HDPE by gasoline. Gasoline molecules penetrate the amorphous phase and in-

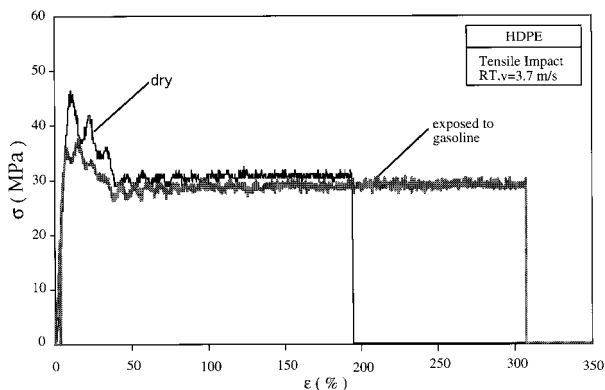


Figure 6 Comparison of the tensile impact σ - ϵ traces of plain HDPE at RT prior and after storage in gasoline.

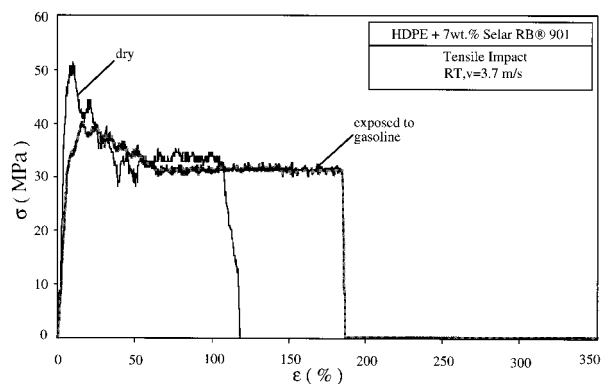


Figure 7 Comparison of the tensile impact σ - ϵ traces of PPC with 7 wt % Selar™ RB 901 at RT prior and after storage in gasoline.

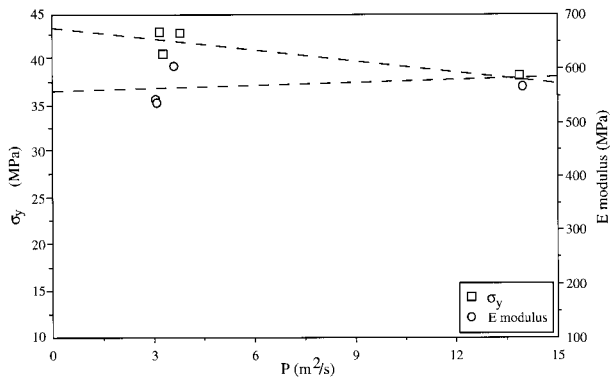


Figure 8 E modulus and σ_y plotted against the sorption coefficient (P) values for PPCs composed of HDPE and SelarTM RB 901 resin.

crease the molecular mobility, so that gasoline acts as an internal lubricant for HDPE. Beside this bulk diffusion process, diffusion along and across the interface also takes place. Insufficient adhesion between HDPE and Selar (where a non-disclosed polymeric couplant is present, referred to as the compatibilizer) offers numerous sites for the gasoline molecules to penetrate. In addition, the diffusion and sorption characteristics of this compatibilizer may differ from those of the HDPE and amorphous polyamide (aPA). The interfacial sorption may further reduce the adhesion and allow the Selar layers to detach more easily from the HDPE matrix. This effect is analogous to hydrolysis, observed in filler and fiber-reinforced composites when exposed to humid environments.⁹ The tensile impact properties after immersion in gasoline are also included in Table II. Due to the matrix plastification, the E moduli and yield stress are significantly lower than those established for dry specimens. This statement is true for all PPCs at both test temperatures. On the other hand, the ductility related terms: ϵ_b and W_f were improved, as expected.

The experimental data derived for this series of tests seem to confirm the effect of interfacial diffusion mechanism in these PPCs. The tensile impact properties for all exposed PPCs at a given test temperature differ very little from one another irrespective of changes in the Selar concentration. The impact characteristics of the plain HDPE, on the other hand, differ considerably from those of the PPCs after exposure to gasoline. The reason for this is the absence of protection against gasoline penetration provided by the Selar microlayer system.

To demonstrate the actual changes in stiffness and toughness for all blends due to gasoline diffusion, mechanical properties were plotted versus the sorption coefficient (P). Figure 8 shows the course of σ_y and E modulus for all PPCs as a function of P : clearly, an increase in the sorption coefficient P results in lower σ_y .

Surprisingly, the E modulus practically did not change due to gasoline absorption. This can be attributed to the high loading frequency of the tensile impact test (dynamic impact conditions). The test frequency can be estimated by dividing the impact speed ($v = 3.7$ m/s) with the ligament length of the specimens (ca. 20 mm) yielding ≈ 2 kHz. The plasticising effect of the gasoline is well reflected by the increase of both ductility (i.e., ϵ_b) and specific tensile impact energy W_f when plotted against the sorption (cf. Fig. 9). As displayed, increasing sorption equates with decreasing Selar content. For Figures 8 and 9 the linear regression lines drawn show the trend in the experimental data.

Fracture Surface Analysis

In this section SEM pictures taken from fracture surfaces of nonexposed PPC specimens tested at $T = -40^\circ\text{C}$ are displayed. The reason for this selection is that the effects of the Selar structuring are most pronounced at -40°C . At ambient temperature, or after storage in gasoline, the predominant ductile tearing failure mode does not allow us to make distinctions in the failure processes. PPC with 4 wt % Selar failed by a multiple delamination splitting mechanism [Fig. 10(a)] favored by weak adhesion between HDPE and Selar (con-

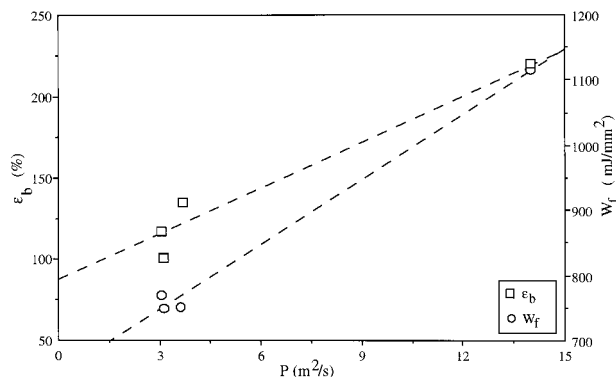


Figure 9 Specific tensile impact energy (W_f) and ultimate tensile impact strain (ϵ_b) plotted against the sorption coefficient (P) values for the PPCs.

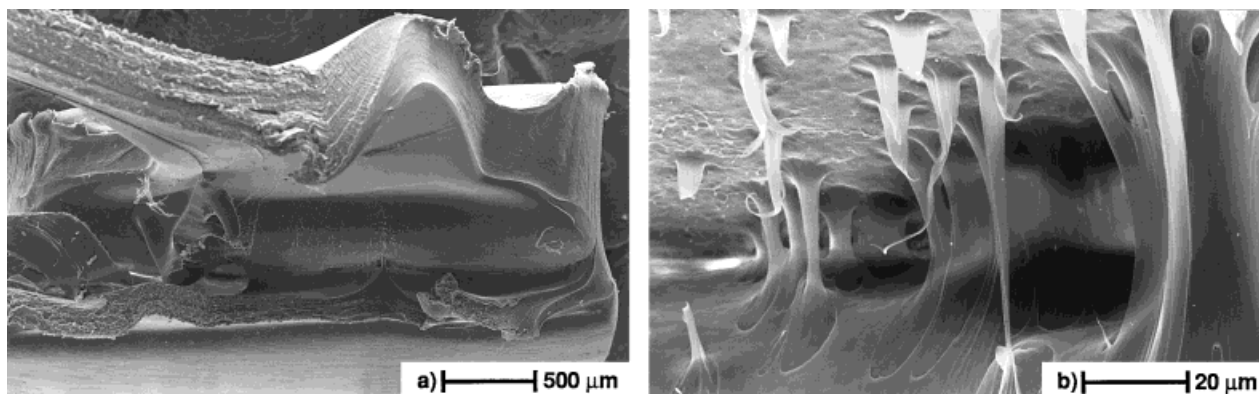


Figure 10 SEM pictures on the fracture surface of a dry PPC specimen with 4 wt % Selar content.

taining in this case less compatibilizer than usual). Magnification of the delamination site [Fig. 10(b)] shows the presence of fibrillae protruding from the Selar layer and anchored sites in the HDPE matrix. These fibrillae, generated during failure, are believed to develop due to the presence of the compatibilizer located in the interphase region between HDPE and the aPA. The interphase itself can be considered as an interpenetrating network structure (IPN), at least locally. This was confirmed by fractography performed on PPC samples cut from a fuel tank that was exposed to diesel fuel (EN 590) for 2 months (Fig. 11). The SEM picture in Figure 11, taken from a Charpy specimen after fracture transverse to the wall of the tank, demonstrates how the compatibilizer is dispersed. From this edge-on view of a nonbroken Selar platelet the compatibilizer can

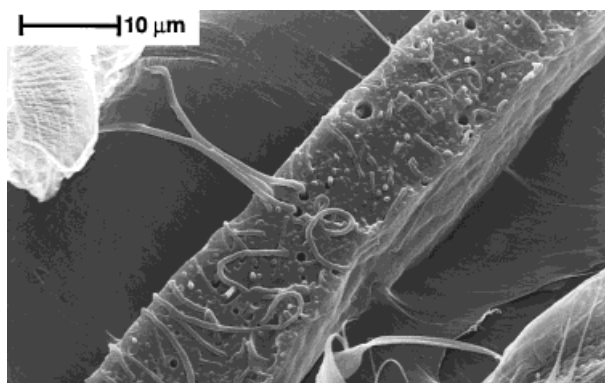


Figure 11 Edge view on a Selar microlayer in a PPC with 7 wt % Selar after storage in diesel fuel for 2 months. (Note: fracture surface was produced by out-of-plane-type loading of a Charpy specimen.)

be seen as inclusions that underwent a large plastic deformation during failure. Viewing the failure of PPC with 7 wt % Selar, a very complex failure mode was observed in the necked region of the impacted specimen. In Figure 12(a) delaminations between the Selar and HDPE, as well as sites with considerable ductile tearing, are discernible [arrow indicates in Fig. 12(b)]. This tearing behavior can be understood based on the analogy with impact-modified plastics. In the latter systems the modifier is finely dispersed in the matrix so that between the modifier particles small matrix ligaments are built up. This microstructure triggers the deformation under plane stress conditions, which imparts higher ductility to the material. Recall that this analogy holds for the interphase between HDPE and aPA in which the the compatibilizer is finely dispersed, and locally even an IPN structure may be present. The ductile failure mode in microscopic scale is also favored by the presence of thin ($\leq 10 \mu\text{m}$ thickness) Selar microlayers.³⁻⁵ The result of this failure scenario is a strongly elongated fibrillated structure, as shown in Figure 12(b). It should be noted here that, in case of thicker Selar layers, the failure path alters in the PPCs [see in Fig. 13(b)].

Figure 13 shows a peculiarity of the failure of laminar PPCs with 14 wt % Selar. The overall fracture surface is again very complex: beside ductile tearing, sites of brittle fracture with delaminations can also be found. The higher magnification SEM picture in Figure 13(b) shows that thicker Selar layers tend to fail brittlely. This observation is consistent with our previous findings.³⁻⁵ The above-discussed failure scenario underlines the

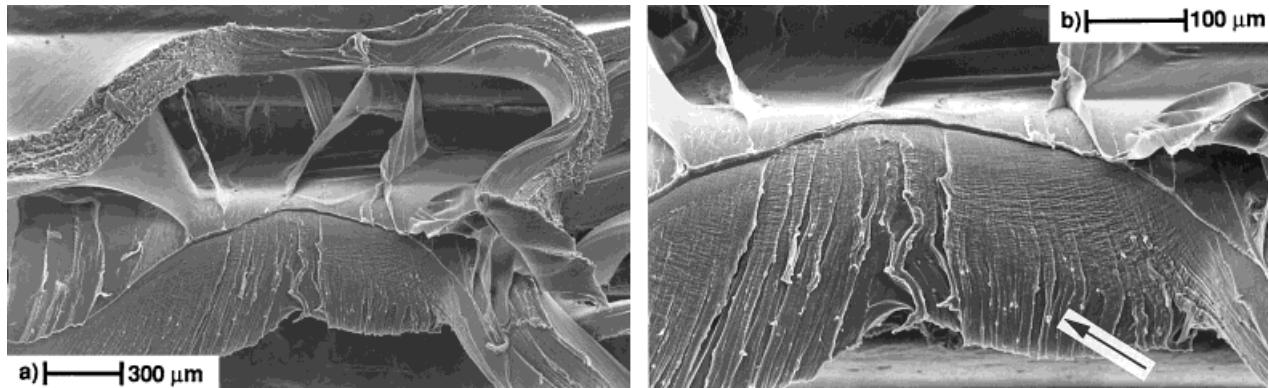


Figure 12 SEM pictures on the fracture surface of a dry specimen of PPC with 7 wt % Selar.

crucial importance of both composition and layering of the Selar barrier resin. Because the the Selar structuring (distribution of layer thickness and interlayer distance) depends on the processing conditions (i.e., extrusion blow molding), hardly any uniform Selar distribution can be achieved. This is the rationale for the sophisticated failure mode described above. Furthermore, the scatter within the tensile impact data is a direct manifestation of the local variation in the microstructure of PPCs.

CONCLUSIONS

Based on this study devoted to the effects of gasoline absorption and temperature change on the tensile impact properties of polymer–polymer microlayer composites (PPC) composed of HDPE and Selar™ RB 901 with various Selar content, the following conclusions can be drawn:

1. The presence of *in situ*-formed Selar layers in a HDPE matrix reduces the diffusion coefficient (D) of the HDPE considerably. The gasoline sorption (S) of the PPCs decreases, whereas D , determined by the Fickian approach, is marginally influenced by an increase of the Selar content.
2. The Selar microlayers act as platelet-type reinforcements in HDPE. This reinforcing effect is manifested in increased stiffness and strength at simultaneously reduced ductility and tensile impact energy values for the PPCs. Exactly the opposite tendency is observed for the PPC systems after storage in gasoline, which is attributed to the plasticizing effect of the gasoline.
3. Fractographic investigations show a very complex failure mode in these PPCs, even in the dry state. The failure seems to be controlled by the complex microstructure of the Selar compound itself (consisting of an amor-

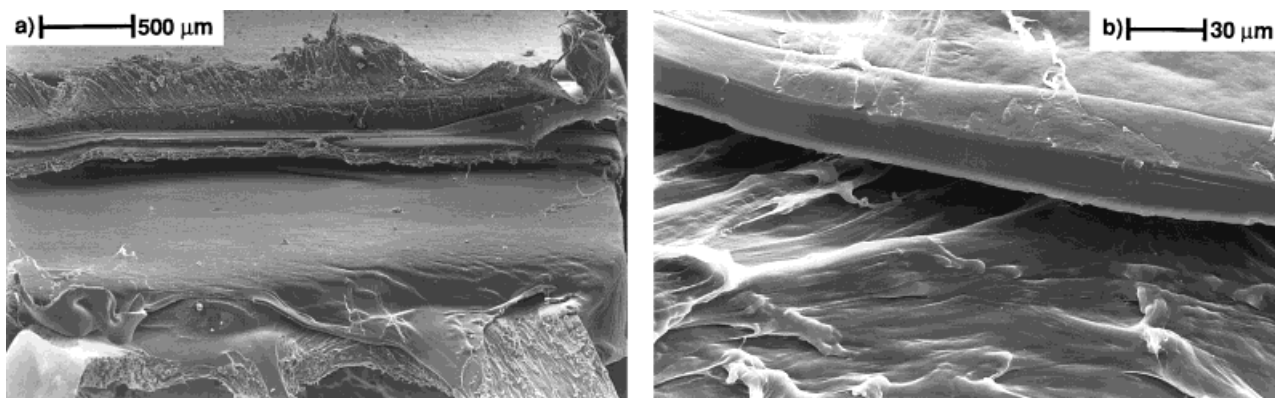


Figure 13 SEM pictures on the fracture surface of a dry specimen of PPC with 14 wt % Selar.

phous PA and a polymeric compatibilizer), by the selective plastification of the PPC constituents due to storage in gasoline (bulk and interphase) and by the processing-induced laminar structuring of the Selar platelets. It is supposed that the compatibilizer promotes the formation of an interphase with interpenetrating network feature.

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