

# Influence of Small Rubber Particles on the Environmental Stress Cracking of High Impact Polystyrene

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**ABSTRACT:** This article exploits the influence of rubber particle size (RPS) and rubber crosslinking on environmental stress cracking resistance (ESCR) of high impact polystyrene (HIPS), with special interest on the influence of small rubber particles fraction. Three commercial HIPS of high ESCR were selected and four batches of HIPS were prepared in-house, including samples based on high *cis* and very high viscosity polybutadiene (PB). Their morphologies were analyzed by low angle laser light scattering, optical microscopy, and transmission electron microscopy, and the samples were submitted to flexural ESCR tests with fatty agents. The ESCR to sunflower oil was found to increase with the reduction of the rubber particles fraction smaller than 1–2 micron. Results have also confirmed that an increase

in RPS is the key parameter to promote ESCR, although there is limit for RPS to be effective on ESCR improvement. The reduction of small rubber particles fraction in HIPS was achieved by using a high *cis* PB, that promotes low grafting efficiency of polystyrene onto PB backbone because of the low content of 1,2 vinyl isomer. Besides the ESCR improvements, HIPS with high *cis* PB showed higher elastic modulus and impact resistance than HIPS containing medium *cis* PB, which is desired for thickness reduction in food packaging and refrigeration cabinets. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1697–1706, 2011

**Key words:** environmental stress cracking; polystyrene; particle size distribution; failure; high *cis* polybutadiene

## INTRODUCTION

Polystyrene (PS) toughness may be greatly improved by incorporating a dispersed rubber phase, usually polybutadiene (PB), via *in-situ* polymerization, yielding the so-called high impact PS (HIPS). This modification has led to a considerable growth in the range of applications for this polymer,<sup>1,2</sup> including refrigeration cabinets, general packaging, electronics, toys, household appliances, and disposables. With the rubber modification, the originally brittle polymer shows a great increase in impact strength and environmental stress cracking resistance (ESCR).<sup>3–5</sup> The ESCR improvement of HIPS has allowed its use in refrigeration cabinets replacing ABS and HIPS/polyethylene blends.<sup>6,7</sup> In this application, the polymer may come into contact with a variety of agents throughout the product life cycle, such as detergent, fat, and mainly cyclopentane or Freon<sup>®</sup>, which are commonly employed as foaming agents for polyurethanes used for thermal insulation.<sup>8</sup>

However, standard HIPS and even some ESCR grades of HIPS are prone to undergo environmental stress cracking (ESC), when used in fatty food packaging, because chemical attack on the stressed material may result in polymer embrittlement.<sup>9</sup> The ESCR is basically related to the retention of the original mechanical properties when the stressed material or package is in contact with a specific aggressive chemical agent, bearing in mind that these agents would show no effect on nonstressed material. There are various ways of evaluating ESCR, as reported in.<sup>10,11</sup>

Stress is typically originated during manufacturing and/or handling, and the level of stress plays a key role in the ESC process. Accordingly, three stress ranges were identified:<sup>12</sup> (i) higher than 15 MPa, where dry crazes are formed regardless of the presence of a chemical agent; (ii) in the 5–15 MPa range, where time to failure is dependent on the penetration rate of the chemical agent through the dry crazes; and (iii) lower than 5 MPa, where there is a preliminary incubation period for the development of dry crazes and a subsequent period for crack growth.

In addition, three main aspects related to the chemical agent have been identified: (i) chemical nature (i.e., composition); (ii) solubility parameter, i.e., the closer the solubility parameters of the agent and the polymer, the higher the chemical similarity and consequently the expected ESC; and (iii) viscosity, which

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TABLE I  
Main Characteristics of the HIPS Samples

Sample	$\overline{M}_w \times 10^{-3}$ (g/mol)	PB content (wt %)	RPS, D <sub>10</sub> ( $\mu\text{m}$ )	RPS, D <sub>50</sub> ( $\mu\text{m}$ )	RPS < 1 $\mu\text{m}$ (%)	RPS < 2 $\mu\text{m}$ (%)	M <sub>p</sub> ( $\mu\text{m}$ )	Gel phase content (wt %)	Swelling index (%)
A	165	8.7	1.2	4.3	9.3	17.8	5.6	26.6	15.8
B	176	8.2	1.4	4.3	7.5	17.1	5.0	27.2	15.1
C	160	8.4	1.4	5.2	7.0	16.2	7.3	23.2	19.0
D	213	7.4	1.3	3.3	7.0	22.0	3.8	24.9	16.4
E	205	5.2	1.5	5.5	6.7	12.8	8.0	14.2	22.7
F	195	7.0	2.0	8.7	5.8	10.0	8.0	12.7	26.5
G	199	7.6	1.9	10.0	6.6	10.4	9.7	17.0	23.8

$\overline{M}_w$ , weight-average molecular weight; RPS, rubber particle size; M<sub>p</sub>, median of the rubber particle distribution.

will dictate, to some extent, the growth rate at the crack tip.<sup>9</sup>

Commercial HIPS classified as ESCR grades usually contains high PB content and large rubber particles, although these characteristics tend to decrease polymer stiffness and may even decrease its impact resistance.<sup>13</sup> Furthermore, being PB more expensive than styrene, a higher PB content increases the final cost of HIPS. A common strategy to attain these ESCR HIPS is to produce low molecular weight PS until phase inversion takes place, aiming to decrease the viscosity of the PS in the styrene phase, resulting in large rubber particles dispersed in low molecular weight PS. However, high molecular weight PS is also required to improve ESCR.<sup>14</sup> Also, in the final stages of HIPS production, aiming to remove nonreacted styrene and oligomers in the so-called devolatilization, PB is partially crosslinked as a consequence of the high temperature.<sup>3</sup>

In this work, HIPS samples based on high *cis* and very high viscosity PB were obtained, and their ESCR characteristics toward fatty agents were evaluated and compared with available ESC resistant commercial HIPS. This article exploits the influence of rubber particle size (RPS) and rubber crosslinking on ESCR to fat, with a special interest on the influence of small rubber particles fraction (<1 and 2  $\mu\text{m}$ ).

## EXPERIMENTAL

This study was performed in seven HIPS samples, being three commercially available HIPS classified as ESC resistant grades (samples A, B, and C) and four HIPS obtained in-house with varying PB content, viscosity, and microstructure (samples D, E, F, and G). The selected commercial HIPS were produced using different technologies and represent the state-of-art for ESC resistant grades, being largely employed in thermoformed refrigeration cabinets.

Samples D–G were obtained through polymerization of different PB solutions in styrene (provided by Innova S.A. Triunfo, Brazil) in a 1.8-L batch reac-

tor at 112°C under stirring. The reaction was peroxide initiated (450 ppm of 1,1-di-(*t*-butylperoxy)cyclohexane, provided by Akzo Nobel, Itupeva, Brazil) in the presence of a chain transfer agent (*t*-dodecyl mercaptan, provided by Arkema, Rio Claro, Brazil), to control PS molecular weight, and 2% mineral oil (provided by Sonneborn, Petrolia, Pennsylvania, United States), commonly used as an internal lubricant for HIPS. When styrene conversion was completed, the polymer was devolatilized at 230°C to remove nonreacted monomer and also to promote controlled rubber crosslinking. Further details of the polymerization conditions to obtain the HIPS samples may be found elsewhere.<sup>15</sup>

A commercial high-viscosity PB grade (260 mPa s in a 5.43 wt % toluene solution at 25°C—ISO 3105, provided by Lanxess, Germany) with a medium *cis* isomer content (38%) obtained via anionic catalysis with butyl-lithium was used in composition D, representing the common PB for ESC resistant HIPS. A very high-viscosity PB grade (300 mPa s—ISO 3105, provided by Petroflex S.A. Cabo de Santo Agostinho, Brazil) was used for samples E–G. This PB shows an essentially linear chain configuration with a high 1,4-*cis* isomer content (96% min.), obtained with a neodymium (Nd) based catalyst, being the high *cis* and medium viscosity PB grade used to obtain HIPS with optimized balance between stiffness and impact resistance.<sup>16</sup> A detailed description of the processes to obtain such high *cis* rubbers may be found in the literature.<sup>17,18</sup>

The main characteristics of all samples used are summarized in Table I. Considering the data presented, it can be added that samples E–G contain particles dispersed in a high molecular weight PS matrix and they show low rubber crosslinking (high swelling index), nevertheless they differ in PB content and RPS.

Weight-average molecular weight ( $\overline{M}_w$ ) was measured by gel permeation chromatography on a Waters chromatograph pump 515 with a Waters refractive index detector 2410, with four Styrogel HR 5E

columns, using THF (tetrahydrofuran) as eluent (1 mL/min). PS standards were employed for calibration. PB content was evaluated based on the reaction of PB double bonds with iodine (Wijs reagent). The nonreacted iodine is titrated with a 0.1-N sodium thiosulfate factor solution, using a starch aqueous solution for the indication of the titration end point.<sup>19</sup>

Further characterization of PB in HIPS can be carried out by determining gel content, i.e., the insoluble fraction of HIPS in toluene/methyl ethyl ketone (MEK), according to the Ruffing phase separation technique.<sup>20</sup> Rubber crosslinking was evaluated by swelling of the gel phase in toluene. The gel phase basically represents a mixture of PS-grafted PB, partially crosslinked PB and PS occluded within rubber particles, which is determined after removal of the PS matrix by solubilization. The swelling index is used here as an indirect measurement of the rubber crosslinking density, i.e., the higher the swelling, the lower the PB crosslinking.

RPS was measured by low-angle laser-light scattering (LALLS) using a Mastersizer Micro Particle Analyzer, from Malvern Instruments. For the analysis, 0.03 g of dry gel obtained with the Ruffing method<sup>20</sup> was dispersed in 25 mL of MEK and kept in ultrasound for  $\sim 20$  s for gel dispersion. The dispersed sample was inserted in the analyzer cell containing 150 mL of ethanol. The results are expressed in terms of  $D_{10}$ ,  $D_{50}$ ,  $M_p$ ,  $RPS < 1 \mu\text{m}$ , and  $RPS < 2 \mu\text{m}$ .  $D_{10}$  means that 10% of the rubber particles are smaller than the indicated size and  $D_{50}$  means 50%, in this case ignoring very large rubber particles that could have been formed by gel agglomeration.  $M_p$  is the maximum point (median) in the particle size distribution curve obtained with LALLS.  $RPS < 1 \mu\text{m}$  to  $RPS < 2 \mu\text{m}$  indicate the percentage, in volume, of rubber particles with a diameter smaller than 1 or 2  $\mu\text{m}$ , respectively—also obtained with LALLS.

RPS distribution was qualitatively observed via optical microscopy using a Leica microscope (model DM 2500). Although optical micrographs are not capable of revealing the internal structure of the rubber particles, they are particularly useful for fast monitoring of the morphology evolution during HIPS polymerization. Rubber particle morphology was assessed via transmission electron microscopy (TEM) using a Philips electron microscope model EM208S operating at 80 kV.<sup>21,22</sup> The samples were prepared by staining with osmium tetroxide after slicing (thickness: 150 nm) in a Leica ultramicrotome model UCT Ultracut. When LALLS is used in combination with TEM, the reliability of the laser scattering technique is improved, as discussed in Ref.<sup>23</sup>

HIPS specimens (type I in ASTM-American Society for Testing and Materials-standard D 638) for tensile and ESCR tests were injection molded under the following conditions: injection pressure = 120

bar, temperature profile = 210/215/215/220°C, and mold temperature = 50°C. The fixture to submit the specimens to a constant flexural strain throughout the duration of the test was built based on ISO 22088-3 (Determination of resistance to environmental stress cracking (ESC)—Part 3: Bent strip method). A napkin was embedded with sunflower oil or with a mixture of oleic acid and cottonseed oil (1 : 1, called here oleic mixture), and maintained in contact with the central region of the bent specimen for 24 h at 23°C. These fats are the most common fatty chemical agents applied in ESCR tests by the refrigeration sector and are considered very aggressive to HIPS. The ESC resistant grades of HIPS generally resist to polyurethane expansion agents (Freon<sup>®</sup>, usually 141b, and cyclopentane), but are prone to failure on thermal cycling tests when in contact with fat.

The initial stress level ( $\sigma$ ) to which the bent specimen is submitted depends on the curvature radius ( $R$ ), the specimen thickness ( $B$ ), and the Young's Modulus of the polymer ( $E$ ), and can be estimated with  $\sigma = E \times B / (2 \times R + B)$ .<sup>24</sup> Under the experimental conditions used in this work, the specimens were found to be less than 13–14 MPa of stress, this means that, according to the Bubeck's classification,<sup>12</sup> the time to fracture is dependent on the penetration rate of the chemical agent through the pre-established dry crazes.

After 24 h, the specimens were removed from the fixture and the chemical agent was completely wiped up from the specimen surface. Then, after a relaxation period of 30 min, tensile tests were carried out and the results were compared with those of the original samples. Tensile testing was carried out in a Zwick Z010 equipment with a constant cross-head speed of 5 mm/min under controlled temperature (23°C) and humidity (50%), according to ASTM standard D-638. Eight specimens were tested for each condition and the results are presented in relation to the result found for a virgin specimen (i.e., before any chemical attack).

The samples were further characterized regarding their impact properties. Izod impact tests were carried out in notched specimens in a CEAST Resil Impactor, following ISO 180 standard.

## RESULTS AND DISCUSSION

Table I presents the main characteristics expected to determine ESCR of HIPS samples, especially  $\bar{M}_w$  of the PS matrix, RPS, rubber content, and crosslinking. Samples A–C, typical commercial ESC resistant HIPS grades, present a balance of relatively low  $\bar{M}_w$  (from 160,000 to 176,000 g/mol),  $D_{50}$  greater than 4.0  $\mu\text{m}$  and medium *cis* PB content (higher than 8 wt%). Sample C shows high swelling, suggesting that it was obtained with a mild devolatilization process,

which resulted in a lower rubber crosslinking, despite presenting the lowest PS molecular weight among the commercial samples.

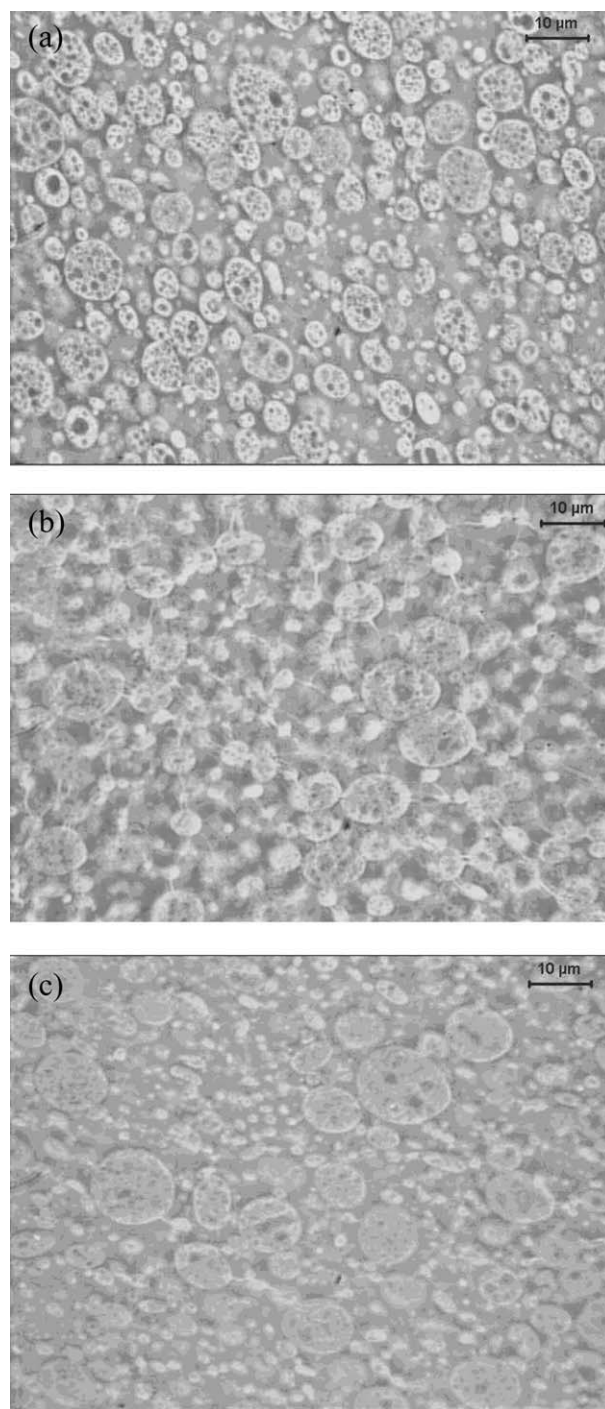
On the other hand, samples D–G were produced in the lab aiming at a  $\overline{M}_w$  approximately 200,000 g/mol. Sample D contains 7.4 wt % of usual medium *cis* and high viscosity PB used for ESC resistant HIPS, possibly the same PB found in samples A–C. However, due to the high  $\overline{M}_w$  of the PS in this sample, particle growth was hindered during phase inversion ( $D_{50} = 3.3 \mu\text{m}$ ).

Samples E–G present  $\overline{M}_w$  approximately 200,000 g/mol with increasing high *cis* and very high viscosity PB content (5.2, 7.0, and 7.6 wt %) that led to a  $D_{50}$  of 5.5, 8.7, and 10  $\mu\text{m}$ , respectively. An important characteristic of HIPS with high *cis* PB is the low rubber crosslinking during devolatilization, as shown by the high swelling index. This in turn leads to a low gel phase content estimated with the Ruffing method. However, it is important to bear in mind that this method may misjudge the overall gel content. In fact, the low PB crosslinking allows the partial extraction of occluded PS during the separation of the PS matrix by solubilization, which leads to an underestimation of the gel content.<sup>25</sup> Furthermore, LALLS could overestimate the RPS because of gel swelling during dispersion in ethanol. This is an important issue for samples E–G, which present low rubber crosslinking. Nevertheless, LALLS was the analytical technique chosen in this study because it is widely applied to determine RPS in HIPS. Only by applying complex stereological methods to TEM micrographs, RPS could be precisely determined.<sup>21,22</sup>

In addition to LALLS measurements, qualitative RPS and particle size distribution of the HIPS samples were observed in the optical micrographs (Figs. 1 and 2) and in the TEM micrographs (Figs. 3 and 4) revealing the *salami* cell structure of the particles.<sup>22</sup> These figures confirm the heterogeneous distribution of RPS, which had been observed with LALLS when comparing  $D_{10}$ ,  $\text{RPS} < 1 \mu\text{m}$ , and  $\text{RPS} < 2 \mu\text{m}$  values.

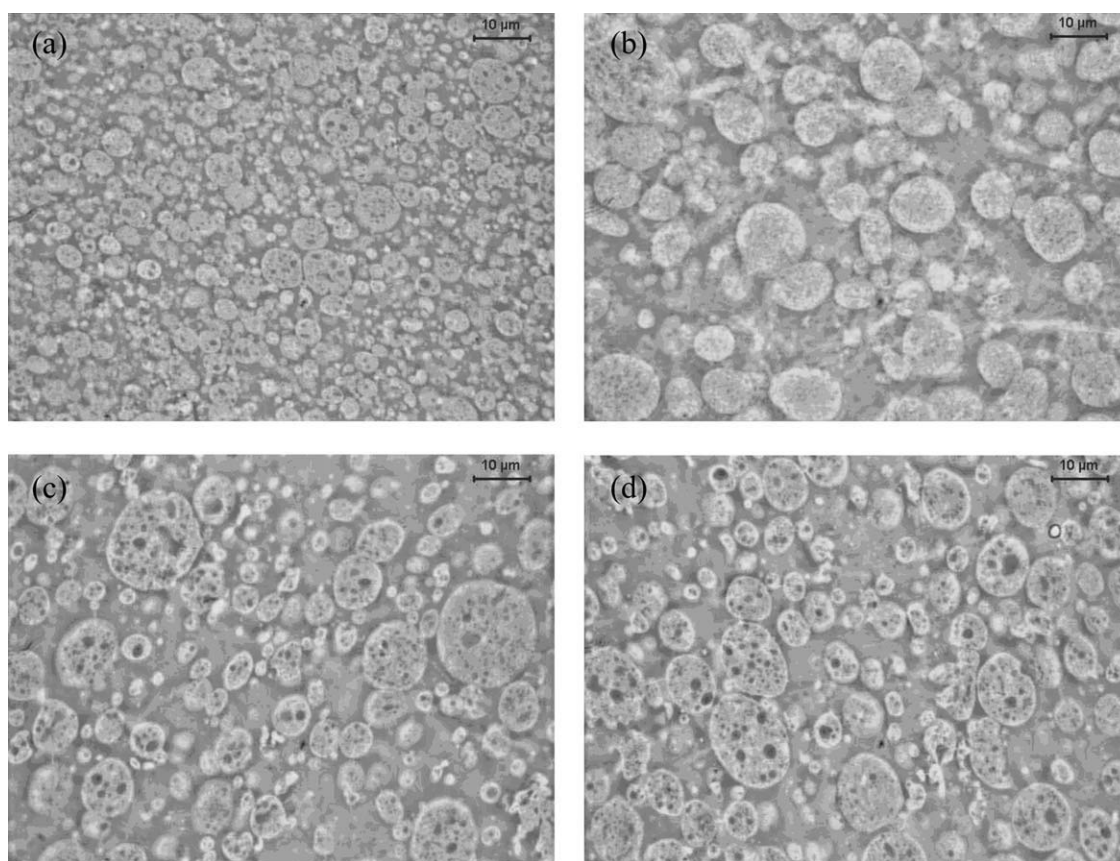
Table II shows the main mechanical properties results obtained for the various samples. Samples A–D show typical properties for ESC resistant HIPS, such as impact strength in the 9.7–11.5  $\text{kJ}/\text{m}^2$  range and elastic modulus around 1460 MPa. The low stiffness is a consequence of the high PB content and microstructure, along with the large RPS. In samples E–G, produced in-house with high *cis* and very high viscosity PB, the elastic modulus is around 2000 MPa, indicating that PB microstructure is determinant for this property even if the material shows large RPS. Samples F and G also show the highest impact strength among all studied samples.

Table III shows the main residual properties of the various HIPS samples after ESCR tests. The yield strength and elastic modulus were not significantly



**Figure 1** Optical microscopy images of HIPS samples A (a), B (b), and C (c); magnification:  $\times 1000$ .

altered because of chemical attack, the opposite was found for tensile strength and strain at failure, which are listed in this table. The decrease in tensile strength is directly related to the decrease in strain at failure. After the yield point, HIPS samples with large RPS show an increase in tensile strength, which can be related to stress hardening of the rubber. So, the decrease in the strain at failure causes the decrease in tensile strength.

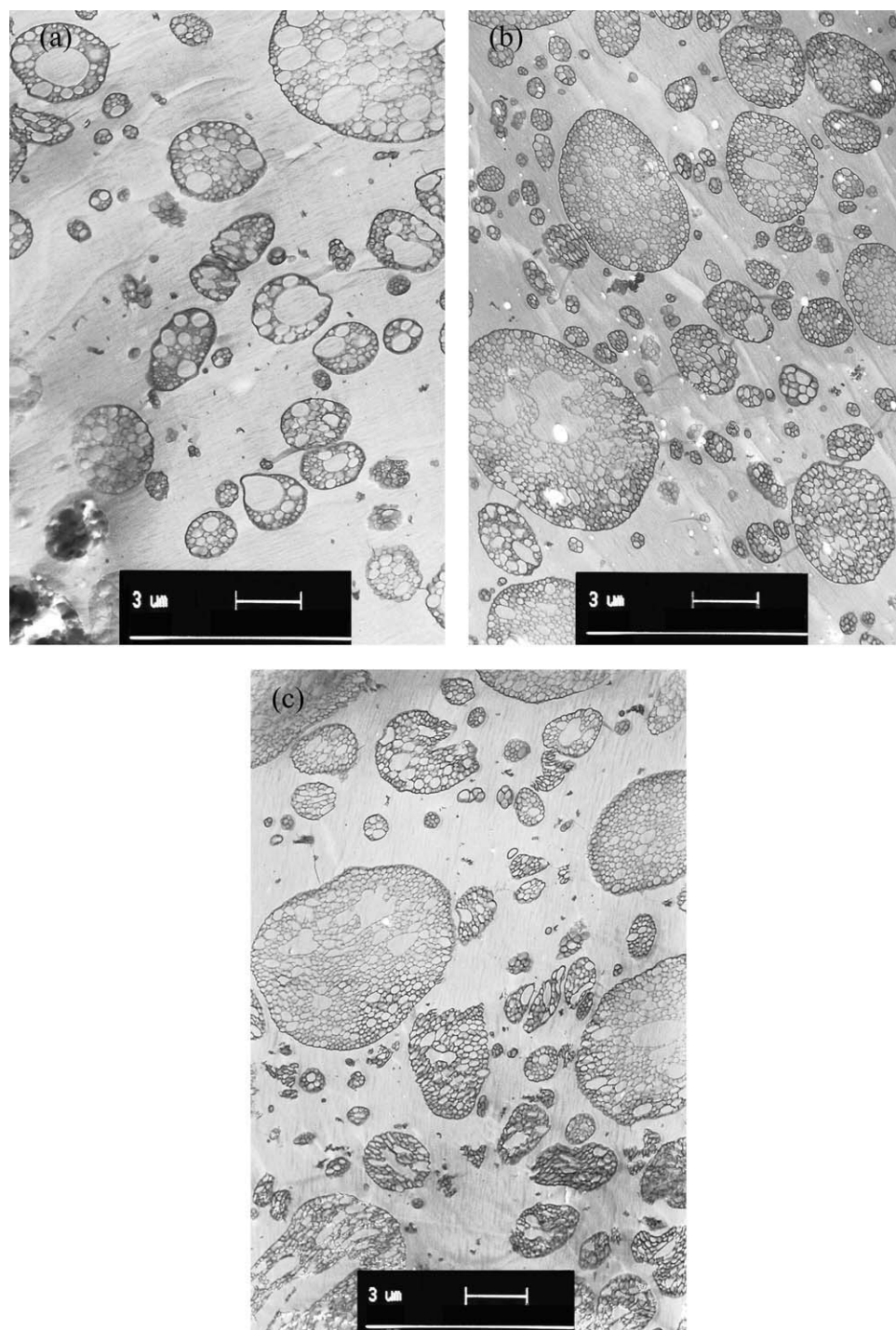


**Figure 2** Optical microscopy images of HIPS samples D (a), E (b), F (c), and G (d); magnification:  $\times 1000$ .

The maximum scatter in the strain at failure results was 5% and 10%, for the oleic mixture and the sunflower oil, respectively, in accordance with ASTM D638 standard for common tensile tests (5% maximum scatter in 5 specimens). As the sunflower oil is more aggressive than the oleic mixture, a higher scatter in tensile results was detected. For the same HIPS sample, the same crazing pattern would be expected. However, the difference may reside in the oil transport from the surface to the craze tip. Flow is a dynamic process and probably not constant, resulting in higher scatter in the results with sunflower oil. All samples are very resistant to the oleic mixture, maintaining their tensile properties nearly unaffected after oil contact. On the other hand, the sunflower oil seems to be a more aggressive chemical agent, allowing a more detailed discussion regarding the differences between the samples. The difference in the behavior of two aggressive media could also be studied based on the difference in viscosity, solubility parameters, and composition, especially for the content of saturated and unsaturated oil. However, this topic will not be discussed in this article, keeping the focus on HIPS composition and RPS.

In Figure 5, a good correlation between RPS and strain at failure after attack with sunflower oil can

be seen. It appears that even though the other parameters ( $\bar{M}_w$ , PB content, gel content and swelling index) are not constant, RPS shows a vital role in the determination of ESCR of the samples. The ESC phenomenon starts with nucleation and formation of crazes, which is dependent on the rubber particles. If there is no crazing, stress will cause rupture, as can be observed for PS (homopolymer). The PB content is also very important, but plays an indirect role. RPS can be controlled by monitoring PB viscosity, and large RPS is obtained when using a high content PB of high viscosity. So, the PB content is indirectly related to RPS. A good example to illustrate this would be the physical blend of PB and PS: even with high PB content, ESCR can not be achieved because discrete rubber particles are not obtained. There are some commercial grades of PS (e.g., for yoghurt packaging) with the same PB content of ESCR grades of PS, but with small rubber particles. The former shows a very low ESCR to fat. Based on our current understanding of the ESC phenomenon (nucleation of crazes), we believe that RPS is more relevant to determine the ESCR characteristics of HIPS than the molecular weight of the PS. The latter is commonly used as a "fine tuning" to improve ESCR in HIPS. Besides, a PS of high molecular weight is required for better performance in



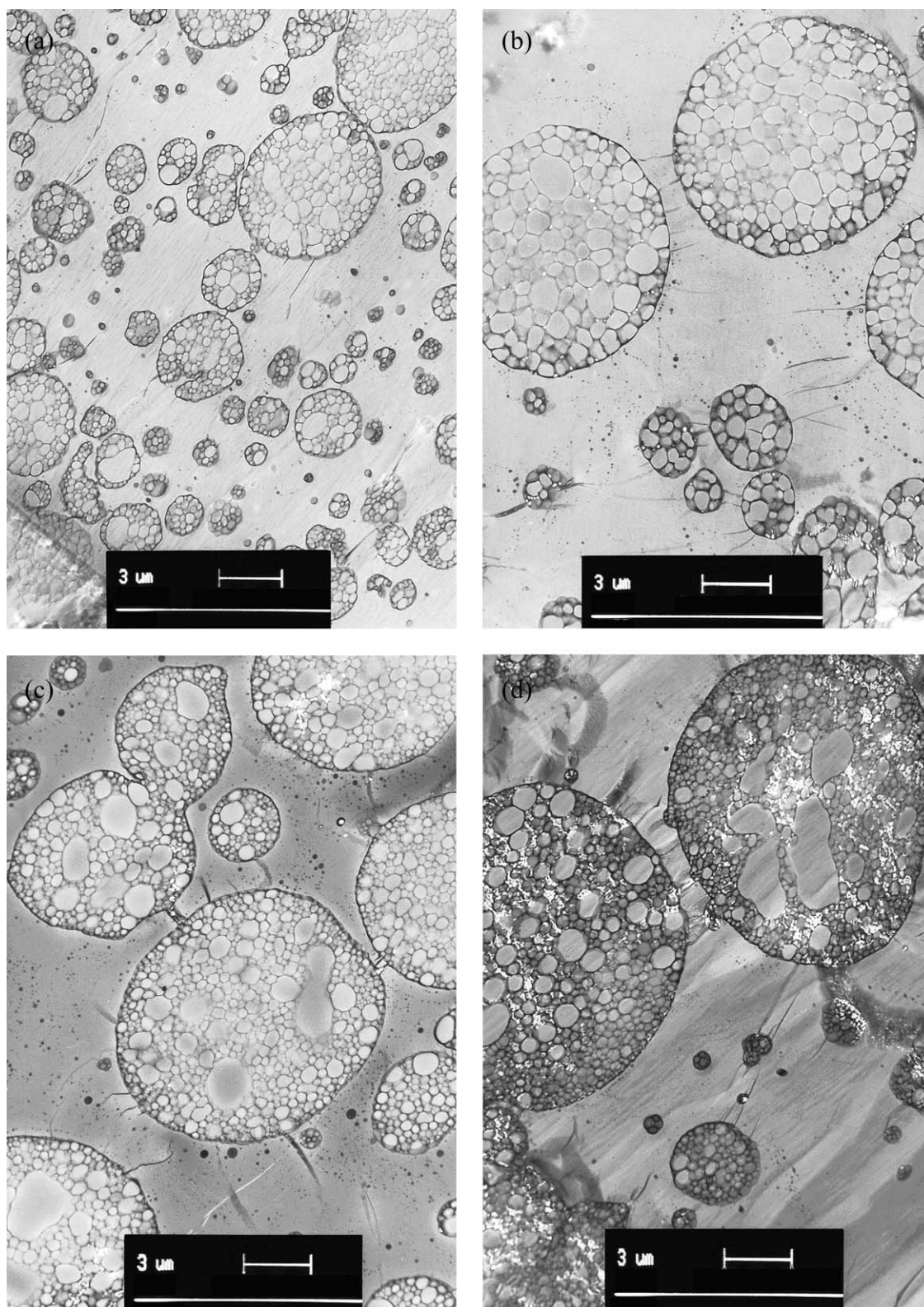
**Figure 3** TEM micrograph of HIPS samples A (a), B (b), and C (c); magnification:  $\times 3200$ .

extrusion (higher extrusion pressure and stability) and, especially, in deep thermoforming.

The importance of the  $M_p$  and  $D_{50}$  parameters toward ESCR are similar. In addition, it is interesting to notice that the correlation between  $D_{50}$  and ESCR does not apply when  $D_{50}$  is  $>6 \mu\text{m}$ , i.e., an increase in the amount of particles larger than  $6 \mu\text{m}$  does not affect ESCR so markedly. Besides, sample D does not follow this correlation as well as the other samples, maybe due

to the fact that the high  $\overline{M}_w$  of the PS matrix (213,000 g/mol) partially compensates the  $D_{50}$  of  $3.3 \mu\text{m}$ .

The steeper slope of the fitting curve found in Figure 5 for  $D_{10}$  indicates a more pronounced effect of this parameter than  $D_{50}$ . Considering the  $D_{10}$  curve, one can infer that not only the large particles influence ESCR but also the small ones. As shown in Figure 6, samples with lower fraction of small particles (i.e., with lower RPS



**Figure 4** TEM micrograph of HIPS samples D (a), E (b), F (c), and G (d); magnification:  $\times 3200$ .

values) display higher ESCR to sunflower oil. Similarly to what was found for  $D_{50}$ , this effect seems determinant even when comparing samples with distinct composition.

It is worth mentioning that even for HIPS samples with large RPS, small particles seem to be produced as a result of the polymerization process and the type of PB. In this work, small particles were found in all

TABLE II  
Main Mechanical Properties of the HIPS Samples

Sample	Izod impact strength (kJ/m <sup>2</sup> )	Young's modulus (MPa)	Strength at yield (MPa)	Tensile strength (MPa)	Strain at failure (%)
A	9.9	1460	20	26	67
B	9.7	1460	21	28	73
C	11.5	1480	18	23	64
D	11.4	1460	19	24	56
E	10.6	2077	23	26	52
F	17.2	2050	23	23	57
G	16.9	1940	21	23	53

studied samples, regardless of the production process, large-scale or lab-scale, or even the type of PB.

The swelling index also showed good correlation with strain at failure after attack with sunflower oil as shown in Figure 7. However, one must consider that the samples showing higher swelling are also those with higher  $D_{50}$ , and therefore, some superposition of effects may be present, which is a common problem when studying HIPS. As the samples with higher swelling index also present large rubber particles, we tried to show that this correlation (swelling index  $\times$  ESCR) is not entirely straight-forward. The swelling index of the HIPS may be easily varied, but, without adjusting RPS, this will not guarantee a better ESCR to fat.

This can be appreciated when one compares ESCR with sunflower oil of samples A and B. Although samples A and B share the same  $D_{50}$ , sample A presents the lowest ESCR to sunflower oil because of its low  $\overline{M}_w$ , apart from having the largest RPS  $< 1 \mu\text{m}$  and lowest  $D_{10}$ . Sample C, which also has low  $\overline{M}_w$ , manages to keep a high ESCR because of the balance of high  $D_{50}$  ( $5.2 \mu\text{m}$ ), low PB crosslinking (high swelling index), and the lowest content of small particles (see RPS  $< 1$  and RPS  $< 2 \mu\text{m}$ ) in comparison with commercial samples A and B. Comparing the samples produced in-house (D–G), the sample with the highest  $\overline{M}_w$ , i.e., sample D,

TABLE III  
Residual Properties of the Various HIPS Samples After ESCR Tests

Sample	ESCR—Oleic mixture		ESCR—sunflower oil	
	Tensile strength <sup>a</sup> (%)	Strain at failure <sup>b</sup> (%)	Tensile strength <sup>a</sup> (%)	Strain at failure <sup>b</sup> (%)
A	97	91	72	24
B	100	100	90	68
C	100	100	89	61
D	93	93	88	61
E	100	100	95	88
F	100	100	98	100
G	100	100	100	100

<sup>a</sup> Residual average tensile strength after ESCR evaluation.

<sup>b</sup> Residual average strain at failure after ESCR evaluation.

shows the lowest  $D_{50}$  and smallest RPS  $< 2 \mu\text{m}$  and consequently the lowest ESCR, confirming that large RPS is decisive regarding ESCR to fat.

Comparing samples E–G, produced with high *cis* PB and equivalent  $\overline{M}_w$ , a higher ESCR was found for higher PB content, which in turn led to higher  $D_{50}$ . The presence of a very high viscosity PB with high *cis* content yielded HIPS with RPS larger than for those with medium *cis* PB, with lowest content of small particles. The low content of small particles in samples E–G is confirmed by TEM images and can be explained by the low grafting efficiency of high *cis* PB. Regarding PB microstructure,<sup>16</sup> 1,2 vinyl isomer is the preferred grafting site for growing radical chains of PS. As there is a lower content of 1,2 vinyl isomer in high *cis* PB ( $< 0.5\%$ ) than in medium *cis* PB ( $\sim 10\%$ ), lower grafting means less compatibility between the PB and PS phases. This suggests that the smaller particles are more grafted than the larger ones.

Samples G and F cover the main factors that are understood to promote high ESCR to fat, namely, a high content of large rubber particles and a low content of small particles dispersed in a high molecular weight PS matrix, with low PB crosslinking. The combination of these factors results in a HIPS grade with

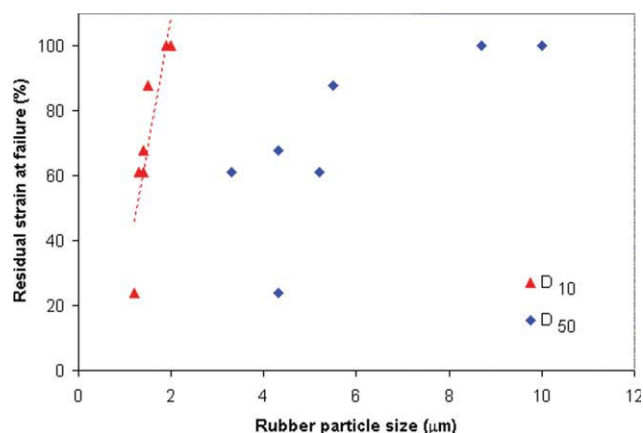
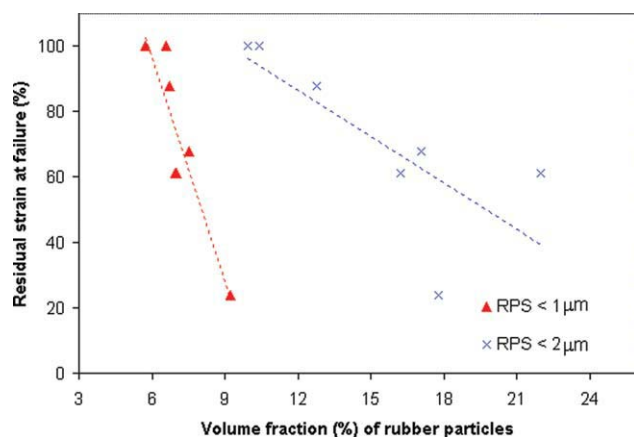


Figure 5 Correlation between RPS and residual strain at failure (%) after ESCR test with sunflower oil for  $D_{10}$  and  $D_{50}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





**Figure 6** Correlation between volume fraction of rubber particle (%) and residual strain at failure (%) after ESCR test with sunflower oil for RPS < 1  $\mu\text{m}$  and RPS < 2  $\mu\text{m}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

excellent ESCR and superior mechanical properties (stiffness and impact strength) than usual ESC resistant HIPS, which is a consequence of an optimized content of high *cis* and very high viscosity PB. These characteristics justify the high ESCR when considering the four stages of the ESC phenomenon:<sup>12</sup>

- i. nucleation and formation of crazes;
- ii. transport of the chemical agent from the surface to the craze tip;
- iii. increase of craze growth rate by chemical attack; and
- iv. failure.

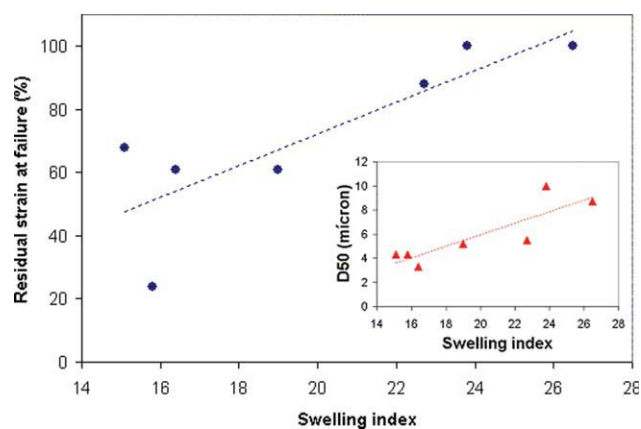
Nucleation and formation of crazes is dependent on temperature and applied stress, as described earlier, and also on the difference of thermal expansion coefficients between the PS matrix and the rubber particles. In fact, the rubber particles are under hydrostatic pressure<sup>21</sup> and this effect is more pronounced for larger rubber size and lower PB crosslinking, allowing the occurrence of a high density of small crazes instead of less crazes of larger size. In other words, we can refer the high density of small crazes as a high fibril volume fraction. These characteristics (larger RPS and lower PB crosslinking) together with reduction in the content of small particles are key factors to obtain high ESCR. Small rubber particles have very low efficiency in the first stage of ESC phenomenon, nucleating a small density of large crazes which are more prone to liquid flow and failure. For the same rubber content, the effect of reducing the fraction of small rubber particles (<1 and 2  $\mu\text{m}$ ) is to increase the content of larger rubber particles (>2  $\mu\text{m}$ ). With this approach, it is possible to increase  $D_{50}$  and the content of large rubber particles and to maintain constantly the

rubber content in HIPS. As referred previously, PB rubber is generally more expensive than styrene, and higher rubber content increases the final cost of HIPS.

Although it is well known that an increase in RPS affects ESCR, the findings of this work indicate that if the  $D_{50}$  is larger than 6  $\mu\text{m}$ , this effect is much less distinct, as shown in Figure 5. So, the efforts to improve performance of ESC resistant HIPS should be addressed to decrease the fraction of rubber particles <1 and 2  $\mu\text{m}$  and not just to increase fraction of large particles.

In second stage of ESC phenomenon, the chemical agent migrates from the surface to the tip of a craze by diffusion, which is promoted under the following circumstances: high temperature, long period of time, and low viscosity of the chemical agent. As small rubber particles nucleate larger crazes, the transport of the chemical agent from the surface to the craze tip speeds up. The presence of the chemical agent at the tip of the craze increases the craze propagation rate, i.e., the stage that precedes failure. A secondary effect on improving ESCR of HIPS is attributed to PS with high molecular weight for slowing down the failure process, stabilizing craze growth and decreasing craze propagation rate.

In this study, the reduction of small rubber particles fraction in HIPS was achieved by using a high *cis* PB of very high viscosity. As explained previously, high *cis* PB has a low grafting efficiency and, regarding PB microstructure, 1,2 vinyl isomer is the preferred grafting site for growing radical chains of PS. As there is a lower content of 1,2 vinyl isomer in high *cis* PB (<0.5%) than in medium *cis* PB (~ 10%), lower grafting means less compatibility between the PB and PS phases. During HIPS production, the effect of low PS grafting onto PB high *cis* backbone is to suppress formation of the small rubber particles, which is determinant to increase  $D_{50}$ .



**Figure 7** Correlation between swelling index and residual strain at failure (%) after ESCR test with sunflower oil for  $D_{50}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Besides the ESCR improvements, HIPS produced in-house with high *cis* and very high viscosity PB (samples E–G) presented higher elastic modulus and impact resistance than HIPS containing medium *cis* PB, which is desired for thickness reduction in food packaging and refrigeration cabinets.

### CONCLUSIONS

HIPS samples with distinct morphologies and composition were evaluated in relation to their ESCR to oleic mixture and sunflower oil, which showed to be a more aggressive chemical agent. Commercial ESC resistant grades of HIPS were studied along with in-house produced HIPS samples based on high *cis* and very high viscosity PB.

It was found that HIPS samples with a lower fraction of small particles (<1 and 2  $\mu\text{m}$ ) showed better ESCR to sunflower oil. Although it is well known that an increase in RPS affects ESCR, the findings of this work indicate that this effect is less pronounced if the  $D_{50}$  is larger than 6  $\mu\text{m}$ . In the studied samples, swelling index also has shown a good correlation with ESCR to sunflower oil, although samples with higher swelling index also present higher  $D_{50}$ , and therefore, some superposition between these factors is expected.

Larger rubber size and lower PB crosslinking can nucleate a high density of small crazes, which are decisive to resist to ESC. On the other hand, small rubber particles have very low efficiency in the first stage of ESC phenomenon, nucleating a small density of large crazes that are more prone to liquid flow and failure. For the same rubber content, the effect of reducing the fraction of small rubber particles (<1 and 2  $\mu\text{m}$ ) is to increase the content of larger rubber particles (>2  $\mu\text{m}$ ). With this approach, it is possible to increase  $D_{50}$  and the content of large rubber particles and to maintain constantly the rubber content in HIPS.

In this study, the reduction of small rubber particles fraction in HIPS was achieved by using a high *cis* PB of very high viscosity, that has a low grafting efficiency because of the low content of 1,2 vinyl. During HIPS production, the effect of low PS grafting onto PB high *cis* backbone is to suppress formation of the small rubber particles, which is determinant to increase  $D_{50}$ .

Besides the ESCR improvements, HIPS produced in-house with high *cis* and very high viscosity PB (samples E–G) presented higher elastic modulus and impact resistance than HIPS containing medium *cis* PB, which is desired for thickness reduction in food packaging and refrigeration cabinets.

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