

HIGH IMPACT POLYSTYRENE WITH ENHANCED ENVIRONMENTAL STRESS CRACKING RESISTANCE

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Great improvements in the environmental stress cracking resistance (ESCR) of high-impact polystyrene grades (HIPS) have been recently achieved, granting their use in new applications in fatty food packaging. This work focuses on the correlation among composition, morphology and ESCR of three commercial ESCR HIPS grades and four HIPS batches prepared in lab scale. The morphology of samples was analyzed by low angle light laser light scattering (LALLS) and transmission electron microscopy (TEM), and they were submitted to flexural ESCR tests with two fatty agents. Large-size rubber particles (dispersed phase) and high molecular weight PS (matrix phase) were confirmed as the key parameters to obtain HIPS with good ESC resistance. Besides, very high viscosity polybutadiene and high *cis* content (> 96% *cis* isomer) were decisive to obtain improved ESCR to fatty agents. Optimal ESCR regarding the fatty agents was obtained for HIPS containing around 7.5% of such high *cis*-polybutadiene, with low rubber crosslinking. The HIPS samples prepared in lab scale were very suitable for application in fatty food packaging.

Keywords: *environmental stress cracking, high impact polystyrene, HIPS, chemical resistance, morphology.*

Introduction

Polystyrene (PS) toughness may be greatly improved 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 [1,2], 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) [3-5]. The ESCR improvement of HIPS has allowed its use in refrigeration cabinets replacing ABS and HIPS/Polyethylene (PE) blends [6]. 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 that are commonly used as foaming agents for polyurethane in thermal insulation [7]. However, standard HIPS and even some ESCR grades of HIPS are prone to undergo environmental stress cracking (ESC) when used in fatty food packaging, since chemical attack on the stressed material may result in polymer embrittlement [8]. The ESCR is basically related to the retention of the original mechanical properties when the stressed material or package is in contact with a particular aggressive chemical agent, bearing in mind that, in general, these agents would show no effect on non-stressed material.

Stress is typically originated during the manufacturing process and/or handling, and the level of stress plays a key role in the ESC process. Accordingly, three stress ranges were identified [9]: (i) higher than 15 MPa, where dry crazes are formed regardless of the presence of a chemical agent; (ii) in the 5 to 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.

Also, 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 will dictate, to some extent the growth rate at the crack tip [8].

Commercial HIPS classified as ESCR grades usually contain large rubber particles, although this characteristic tends to decrease polymer stiffness and may even decrease its impact resistance [10]. A common strategy to achieve ESCR HIPS is producing polystyrene of low molecular weight until phase inversion takes place, aiming to decrease viscosity of polystyrene in styrene phase, resulting in large rubber particles dispersed in low molecular weight PS in the product. However, high molecular weight PS is required to improve ESCR [11]. Also, in the final stages of HIPS production, aiming to remove non-reacted styrene and oligomers in the so-called devolatilization, PB is partially crosslinked as a consequence of the high temperature [3].

On this context, the aim of this work is to evaluate the ESCR of different HIPS to fatty agents, determining the optimal balance among rubber particle size, molecular weight of the PS matrix, rubber crosslinking and content to achieve improved ESCR HIPS, and thus, new applications for the material in fatty food packaging.

Experimental

The study was performed in seven HIPS samples, being three commercially available HIPS classified as ESCR grades (samples A, B and C) and four different HIPS obtained in lab scale with varying PB content, viscosity and microstructure (samples D, E, F and G). The main characteristics of these samples are summarized in Table 1. The selected commercial HIPS were produced using different technologies and represent the state-of-art for ESCR grades, being largely utilized for thermoformed refrigeration cabinets.

Samples D to G were prepared via in-situ polymerization of styrene in the presence of different PB in a 1.8 L stirred batch reactor at 112°C, peroxide initiated (450 ppm of 1,1-di-(t-butylperoxy) cyclohexane) with a chain transfer agent (t- dodecyl mercaptan - TDM), to control PS molecular weight, and 2% of mineral oil, used as internal lubricant. When styrene conversion was completed, the polymer was devolatilized at 230°C to remove non-reacted monomer and also to promote

controlled rubber crosslinking. The polymerization conditions to obtain the HIPS samples were previously described [12]. A commercial high-viscosity PB grade (260 mPa.s in a 5.43 wt% toluene solution at 25°C, ISO standard 3105) with medium cis isomer content (38%), obtained by anionic polymerization with Butyl-Lithium, industrially employed in the ESCR HIPS production, was used to prepare sample D. A very high-viscosity PB grade (300 mPa.s in a 5.43 wt% toluene solution at 25°C) was used for the E, F and G samples production. This PB has high 1,4-cis isomer content (96% min.) and is produced with Neodymium (Nd) based catalyst [13]. A detailed description of the production processes of such rubbers may be found in the literature [14,15]. Considering the main characteristics of the evaluated HIPS samples (Table 1), the samples E, F and G, prepared with the high cis-PB, differ in the rubber content and particle size, whereas in all of them the particles are dispersed in a high molecular weight PS matrix and show high swelling index due to the low rubber crosslinking.

Table 1 – Main characteristics of the HIPS samples.

Sample	Mw × 10 ⁻³ (g/mol)	PB content (wt%)	RPS, D50 (µm)	Gel phase content (wt%)	Swelling index
A	165	8.7	4.3	26.6	15.8
B	176	8.2	4.3	27.2	15.1
C	160	8.4	5.2	23.2	19.0
D	213	7.4	3.3	24.9	16.4
E	205	5.2	5.5	14.2	22.7
F	195	7.0	8.7	12.7	26.5
G	199	7.6	10.0	17.0	23.8

The PS weight-average molecular weight (Mw) of the HIPS samples was measured by gel permeation chromatography (GPC), after removing the rubber fraction, on a Waters chromatograph pump 515 with a Waters refractive index detector 2410 using THF as eluent (1 mL/min). Four Styrogel HR 5E columns and polystyrene standards were used.

PB content (wt%) was measured by using a titration method based on the reaction of PB double bounds with iodine (Wijs reagent). The non-reacted 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 [16]. The PB content in the HIPS samples was also determined by gel content, i.e. the insoluble fraction of HIPS in toluene/methyl ethyl ketone (MEK), according to the Ruffing phase separation technique [17]. 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 remain as insoluble fraction after the PS matrix solubilization. Thus, 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.

Rubber particle size (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 [17] was dispersed in 25 mL of methyl ethyl ketone (MEK) and maintained in ultrasound for approximately 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 D50, which means that 50% of the rubber particles are smaller than the indicated value, not considering very large rubber particles that could have been formed by gel agglomeration. RPS distribution and morphology was qualitatively assessed by transmission electron microscopy (TEM) using a Philips electron microscope, model EM208S operating at 80 kV [18, 19]. 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 [20].

HIPS specimens (type I in ASTM standard D 638) for the ESCR tests were injection molded under injection pressure of 120 bar and melt temperature profile of 210/215/215/220°C and mold temperature = 50°C. The fixture to submit the specimens to a constant flexural strain during the test was assembled based on ISO standard 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, named oleic mixture), and maintained over the central region of the bent specimen for 24 hours 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 ESCR HIPS grades are generally resistant to the polyurethane expansion agents (Freon and cyclopentane), but are prone to failure on thermal cycling tests when in contact with fat.

The initial stress level (σ) 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 calculated by $\sigma = E \cdot B / (2 \cdot R + B)$ [21]. Thus, the specimens in this study are under 13 to 14 MPa, and, according to the Bubeck's classification [9], in this range the time to fracture is dependent on the penetration rate of the chemical agent through the pre-established dry crazes.

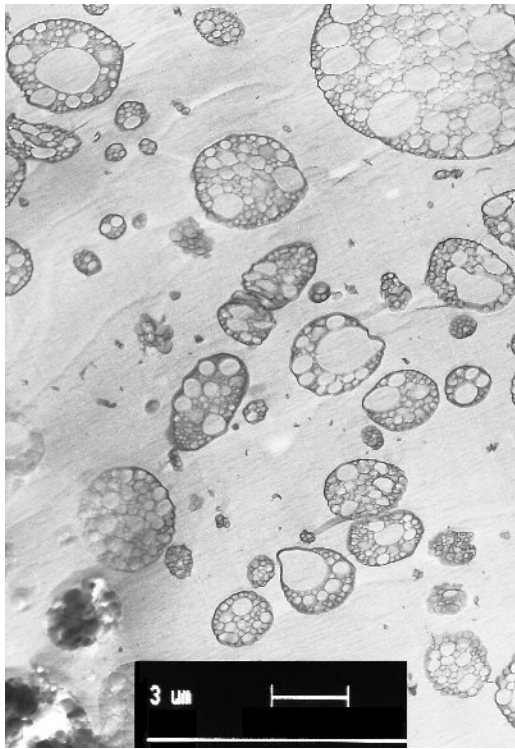
After 24 h, the specimens were removed from the fixture and the chemical agent was completely wiped up from the specimen surface. Then, after a relaxation period of 30 min, tensile tests were carried out and the results were compared to those of the samples that had been subjected to the same flexural load, for the same period of time and temperature, but without chemical attack. Tensile testing was carried out in a Zwick Z010 equipment with 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 as residual property in relation to the specimen with no chemical attack.

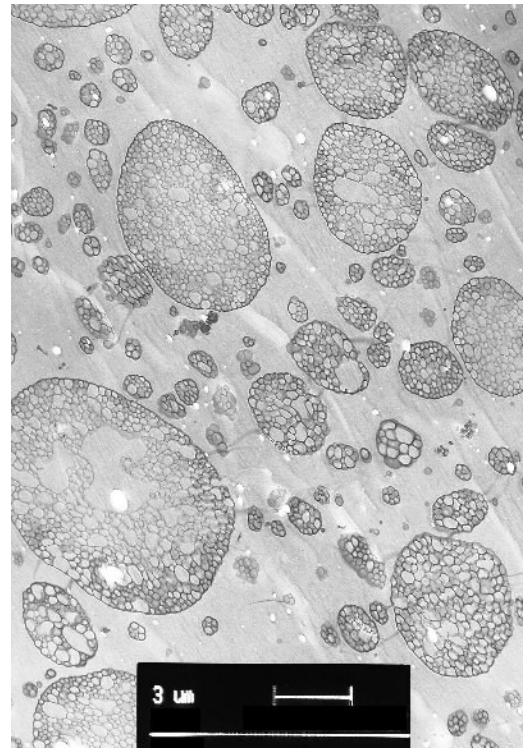
Results and Discussion

The main characteristics expected to determine ESCR of HIPS samples, especially Mw of the PS matrix, RPS (D50) and rubber content and crosslinking are presented in Table 1. Samples A, B and C, typical commercial ESCR HIPS grades, present a balance of relatively low Mw (from 160,000 to 176,000 g/mol), D50 greater than 4.0 μm and medium cis PB content (higher than 8 wt%), as can be seen in Table 1. 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, E, F and G were produced in the lab aiming at a PS with Mw around 200,000 g/mol. Sample D contains 7.4 wt% of medium cis and high viscosity PB used for ESCR HIPS, probably the same PB used in the samples A, B and C. But due to the high Mw of the PS in the sample prepared in the lab scale, particle growth was hindered during phase inversion (D50 = 3.3 μm). The samples E, F and G with PS matrix of Mw around 200,000 g/mol and with 5.2, 7.0 and 7.6%, respectively, of PB with high cis content and very high viscosity, showed a RPS D50 range between 5.5 μm (sample E) and 10 μm (sample G), as measured by LALLS.

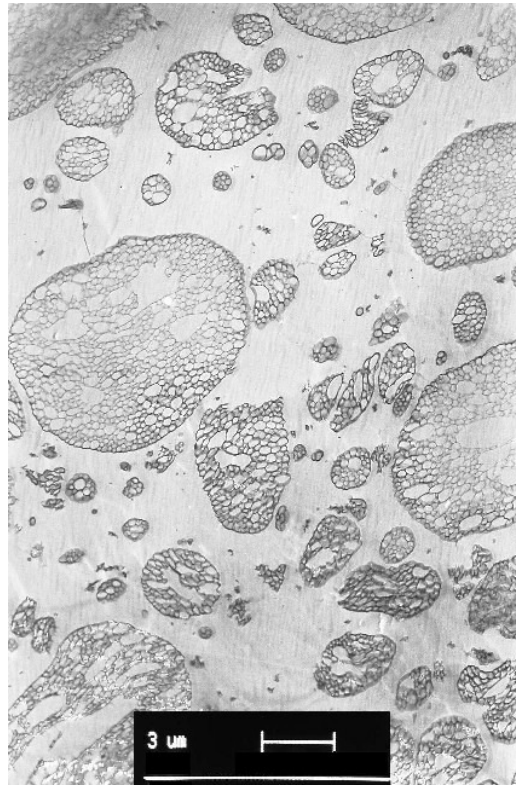
An important characteristic of HIPS with high cis PB is the low rubber crosslinking during devolatilization, as shown by the high swelling index values. This in turn leads to a low gel phase content measured by the Ruffing method [22]. However, it is important to bear in mind that this method may misjudge the overall gel content. In fact, the low PB crosslinking permits the partial extraction of occluded PS during the separation of the PS matrix by solubilization, which leads to an underestimation of the gel content. Also, LALLS could overestimate the RPS due to gel swelling during dispersion in ethanol. This fact is important for samples E, F and G that present low rubber crosslinking. Nevertheless, LALLS was the analytical technique used here because it is widely applied to determine RPS in HIPS. Only by applying complex stereological methods for TEM micrographs, actual RPS could be precisely determined [18, 19]. Complementing LALLS measurements, qualitative RPS and particle size distribution in the HIPS samples could be observed in the TEM micrographs showed in Figure 1 (commercial samples) and 2 (lab samples), revealing the salami cell structure of the rubber particles [19].



(a)



(b)



(c)

Figure 1 - TEM micrograph of HIPS samples A (a), B (b) and C (c) - magnification of 3.2 Kx.

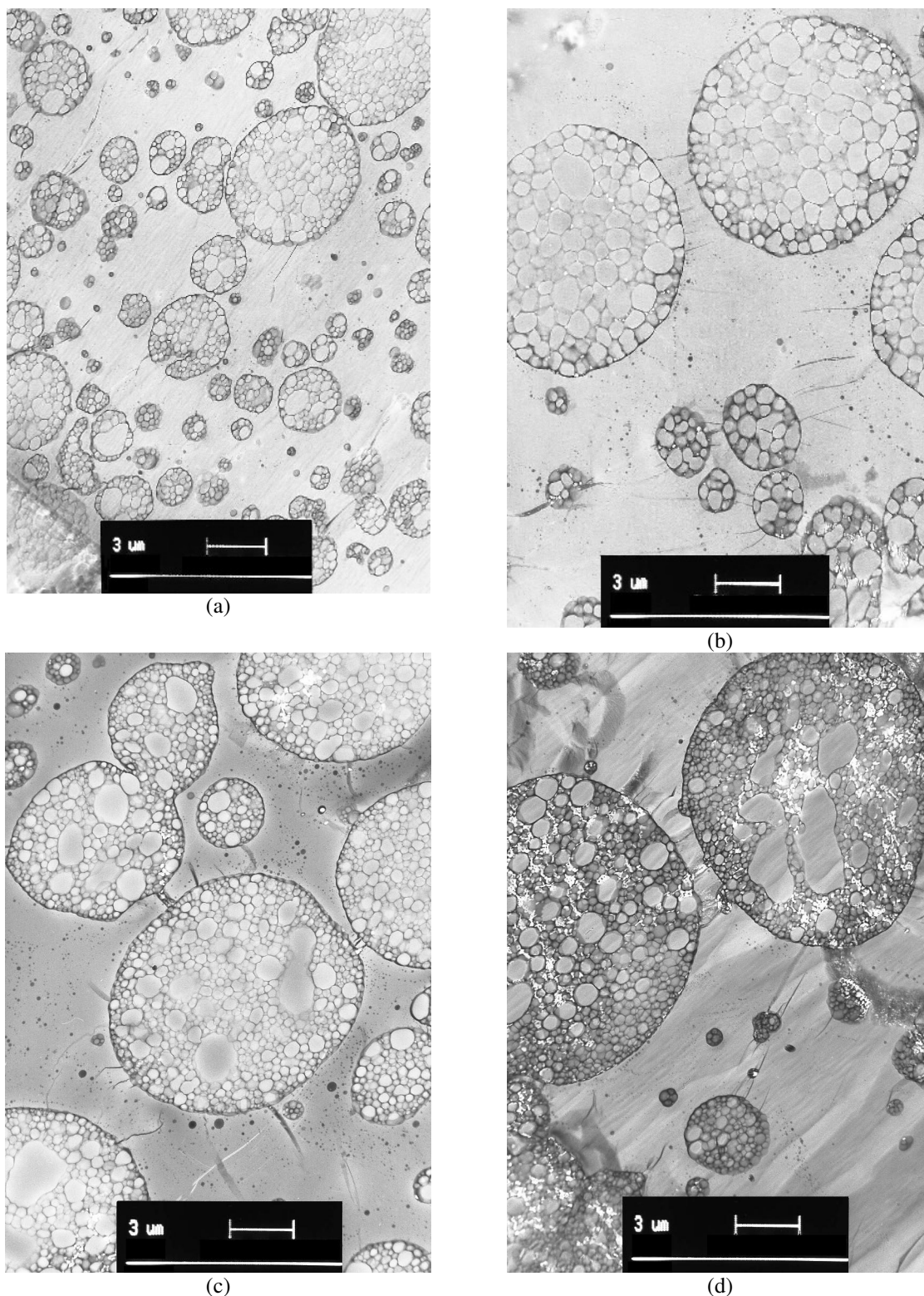


Figure 2 - TEM micrograph of HIPS samples D (a), E (b), F (c) and G (d) - magnification of 3.2 Kx.

Table 2 shows the ESCR of the different HIPS samples evaluated when exposed to a oleic mixture and sunflower oil. It can be seen by residual mechanical properties that all samples are very resistant to the oleic mixture, maintaining their tensile properties nearly unaffected after testing. 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.

Table 2 – ESCR evaluation of the various HIPS samples.

Sample	ESCR – Oleic mixture		ESCR – sunflower oil	
	Tensile strength ¹ (%)	Strain at failure ² (%)	Tensile strength ¹ (%)	Strain at failure ² (%)
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

¹ Residual average tensile strength after ESCR evaluation

² Residual average strain at failure after ESCR evaluation

Although samples A and B share the same D50, sample A presents the lowest ESCR to sunflower oil due to its PS low Mw. Sample C, which also has a low PS Mw, manages to keep a high ESCR due to a balance of higher D50 (5.2 μm) and lower PB crosslinking (evaluated by the higher swelling index) in comparison with commercial samples A and B. Comparing the samples produced in-house (D to G), the sample with the highest PS Mw, i.e. sample D, shows the lowest D50 and consequently the lowest ESCR, confirming that high RPS is decisive to acquire ESCR to fat.

Comparing samples E, F and G, produced with high cis PB and equivalent PS Mw, a higher ESCR was found for the sample with higher PB content, which in turn led to higher D50. The presence of a very high viscosity PB with high cis content yielded a HIPS with higher RPS than for those with medium cis PB.

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

According to Bubeck [9], the ESC phenomenon in HIPS may take place through four stages comprising (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. The HIPS characteristics found in sample G are decisive for the first stage stated for the ESC process. Nucleation 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 [18] 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 low density of larger crazes. This reveals to be a key factor to obtain samples of

HIPS with high ESCR [9]. In the second stage, the chemical agent migrates from the surface to the tip of a craze in a diffusion process, which is promoted under circumstances of high temperature, long period, and low viscosity of the chemical agent. The presence of the chemical agent at the tip of the craze increases the craze propagation rate, i.e. the third stage, which precedes failure. A high molecular weight of the PS is determinant in order to slow down the failure process, stabilizing craze growth and decreasing the craze propagation rate.

Conclusions

The ESC resistance of various HIPS samples in presence of fatty agents was studied taking account differences in their morphology and composition. Large rubber particle sizes dispersed in a high Mw PS matrix were confirmed as key factors to achieve good ESCR in HIPS. Very high viscosity PB with high cis microstructure (> 96% cis isomer) was found to lead to improved ESCR. Optimal resistance performance to fatty agents was obtained for a HIPS sample (sample G) containing around 7.5% of high cis PB with low rubber crosslinking.

The HIPS characteristics found in sample G are decisive for the first stage of the ESC process, where nucleation and formation of crazes are observed. In fact, the rubber particles are under hydrostatic pressure 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 the following steps of ESC phenomenon, when the chemical agent diffuses from the surface to the tip of a craze, the high molecular weight of the PS is determinant to stabilize craze growth and to decrease the craze propagation rate. Regarding ESCR, the characteristics found in the sample G were very suitable for a HIPS to be applied in fatty food packaging.

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