

High Gloss of Extruded High Impact Polystyrene Sheet. A Microscopical Study of Sheet Morphology

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INTRODUCTION

A highly desirable property of refrigerator inner doors in the market place is a bright, glossy appearance. Most commercial high impact polystyrenes, when extruded into sheet and subsequently vacuum-formed, produce doors of inherently low gloss. In order to produce a high impact polystyrene inner door of satisfactory appearance as well as desirable physical properties, it was necessary to learn something about the nature of gloss formation in such a material.

A previous paper presented by Carhart at the SPE 18th ANTEC in January 1962¹ described in detail some of the processing techniques for securing glossy sheet, evaluated these methods on the basis of resultant physical properties, and discussed to some extent their mechanism. This paper will discuss the gloss phenomenon from the point of view of sheet morphology and will describe investigations which led to a better understanding of one of the methods of obtaining gloss—"glazing."

NORMALLY EXTRUDED SHEET

Most high impact polystyrenes may be classified as heterogeneous or two phase polymeric systems. Dispersed in the polystyrene matrix are styrene-butadiene copolymer particles. The composition, structure, and dispersion of these copolymer particles has an influence on the material properties.² It is these particles which give the material its impact resistance.

Examination of the sheet surface with vertical illumination, and of microtome cross sections in phase contrast showed that these copolymer particles have a profound effect on the sheet gloss. Microtome cross sections were prepared by the technique developed by Traylor,⁵ which provides thin sections for study with the phase contrast microscope with no alteration of the relationship of the two phases in high impact polystyrene.

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Figure 1 shows photomicrographs of the surface and cross section of a normally extruded natural high impact polystyrene sheet. The spongelike particles distributed throughout the sheet are the copolymer particles. Their presence in, and protrusion from, the surface causes the sheet to have a low gloss.

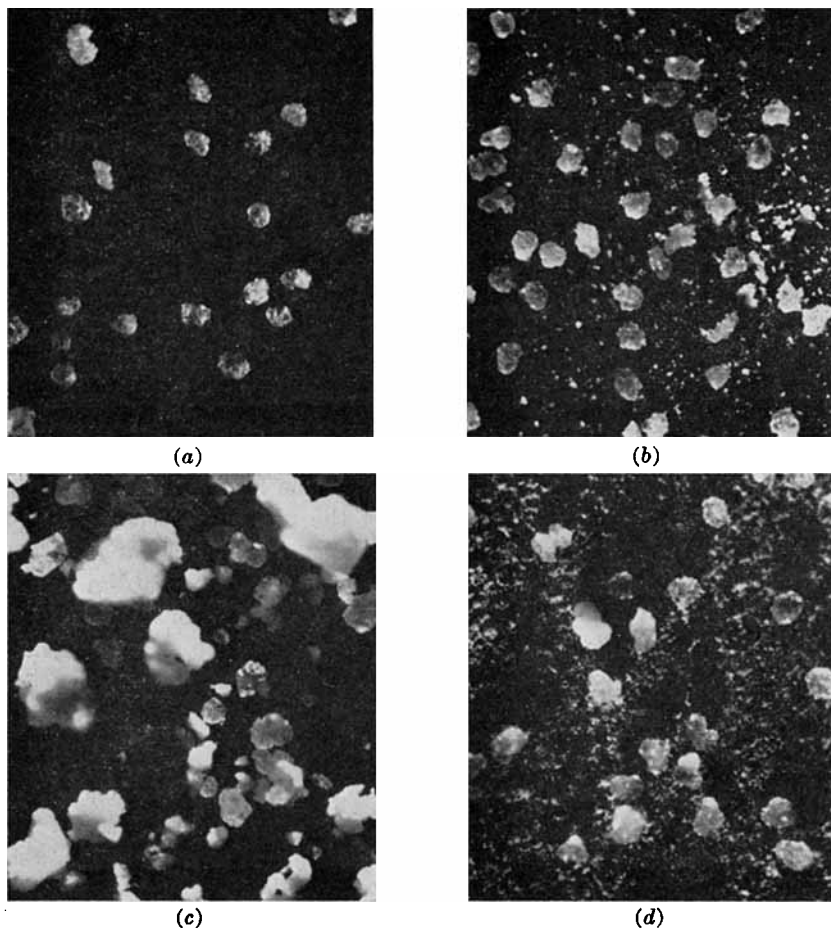


Fig. 1. Decomposition with coarse Seed at 50°C. run *F*: (a) original seed (66–76 μ); (b) 3 hr seed and some fines; (c) 10 hr. seed, flocculates and loose fines; and (d) 16 hr. seed and many fines, no flocculates. 50 \times .

The gloss of this particular sheet was 40 as measured with a 60° Photovolt Model 610 glossmeter. This instrument has an arbitrary gloss scale, calibrated from 0 to 100. High meter readings indicate high gloss.

It is interesting to note that size of the copolymer particles has a definite influence on gloss level of the sheet. Figure 2 shows phase contrast photomicrographs of cross sections of two sheets extruded under identical conditions, but from different lots of the same polymer. A had a gloss of

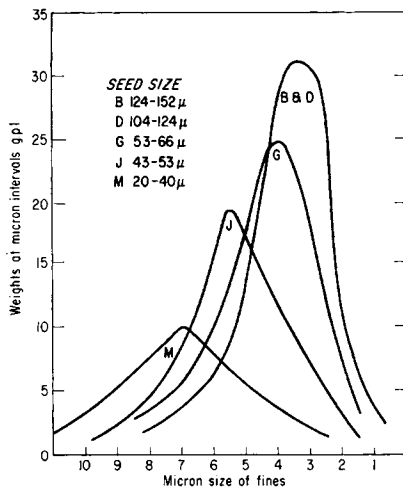


Fig. 2. Decomposition with coarse seed at 50°C. Effect of seed size on the weight distribution of fines formed.

15 while *B* had a gloss of 60. There is a distinct difference in copolymer particle size.

GLOSS IMPROVEMENT TECHNIQUES

A given polymer, with good extrusion practice, will produce sheet which will have reproducible strength, creep, and impact properties. Such physical properties are criteria for selection of polymers for specific applications. In the study of gloss improvement methods it was necessary to determine whether any significant differences in the physical properties of the sheet were produced by the various methods. The physical tests so employed were completely described previously.¹ Observed changes in the surface properties of sheet have been explained by changes in the morphology of the sheet as observed with the microscope.

Film Lamination

For a number of years film lamination techniques have been used in the refrigeration industry. Normally a 1 or 2 mil biaxially oriented polystyrene film is laminated to high impact polystyrene sheet by means of heat and pressure.¹ Application of this film results in a very smooth, optically homogeneous surface of extremely high gloss (Fig. 3), Glossmeter reading 100+.

However, this increase in gloss is obtained at a sacrifice of a key physical property—falling dart impact strength.¹ It is easy to see why this is so (Fig. 3).

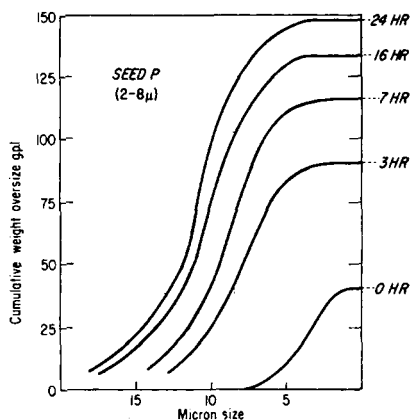


Fig. 3. Decomposition with fine seed at 50°C. Cumulative weight oversize curves. Run P.

Gloss Transfer

It is also possible to impart a high gloss to high impact polystyrene sheet by pressing it, while hot, against a nonadhering smooth surface.¹ This mechanical technique compresses the sheet, forcing protruding copolymer particles into the sheet, as in Figure 4A. Upon cooling, this frozen-in

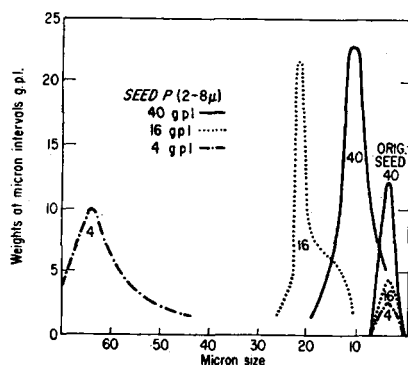


Fig. 4. Decomposition with fine seed at 50°C. Effect of seed quantity on the particle size of the product.

deformation produces a very smooth sheet surface. The drawback of this technique is that, upon subsequent heating in the vacuum forming operation, the elastic copolymer particles return to their preferred spherical shape, popping up all over the surface (Fig. 4B). Since the desired objective was a glossy, vacuum-formed part, this technique was quickly abandoned.

High Shear Extrusion

Based upon their rheology work, Monsanto Chemical Company suggested a gloss improvement method, the development of which was undertaken jointly by Monsanto and General Electric Co. It was possible to produce extruded high impact polystyrene sheet of high gloss levels by modifying the die lip profile and increasing the pressure in the extruder

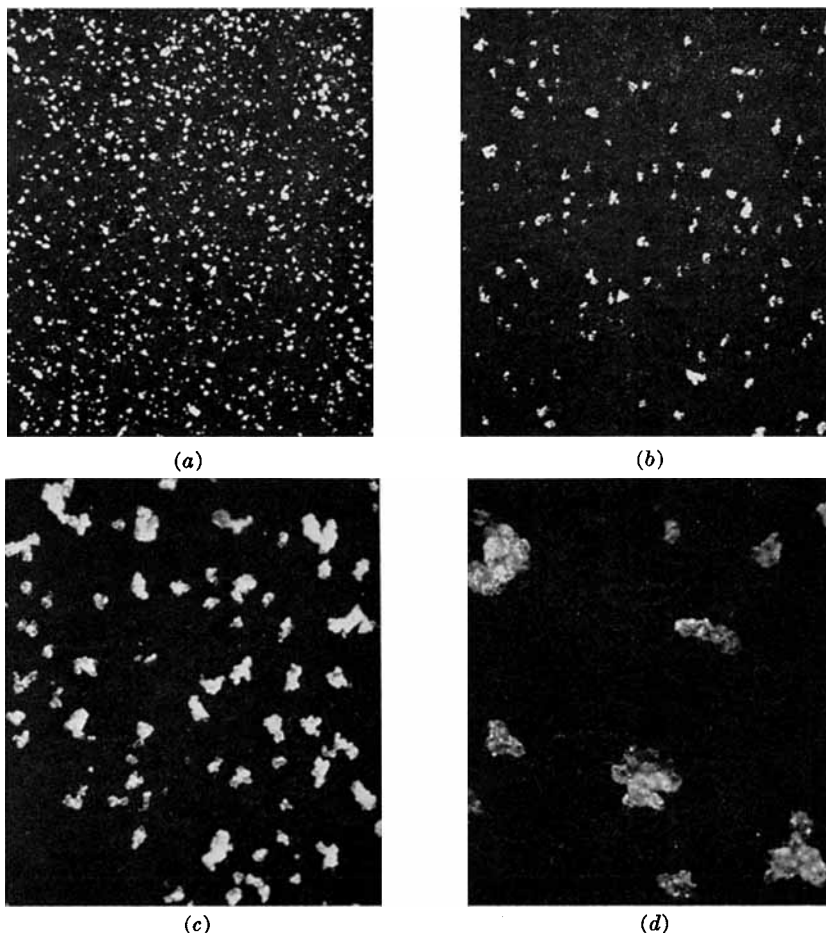


Fig. 5. Decomposition with fine Seed at 50°C. Run *P*: (a) original seed (2-8 μ), (b) product from 40 g./liter seed, (c) product from 16 g./liter seed, and (d) product from 4 g./liter seed. 100 \times .

manifold.^{1,3} This increased manifold pressure resulted in extremely high shear rates in the molten polymer.

In Figure 5 are photomicrographs of cross sections of natural high impact polystyrene of different gloss levels. The normally extruded sheet had a gloss of 45. Those with gloss levels of 84 and 98 were extruded under high shear conditions. In the normally extruded sheet the distribution of large

copolymer particles was uniform throughout the thickness of the sheet. In high gloss sheet there were distinctly fewer large copolymer particles in the area just below the sheet surface. Gloss level increased with increased shear and increased width of this "rubber-shy" stratum. In sheets of 98 or 100 gloss it was as wide as 0.5 mil.

Gloss increases secured in this way resulted in drastic losses of impact properties.¹ The "rubber-shy" stratum, occasioned by migration of the larger rubber particles from the surface toward the center of the sheet, behaved in impact much the same as a general-purpose styrene laminate.

Glazing

Another gloss improvement technique known as "glazing" had been in commercial use for some time. However, in spite of its long use, little information was available regarding the process variables, and no information about its mechanism.

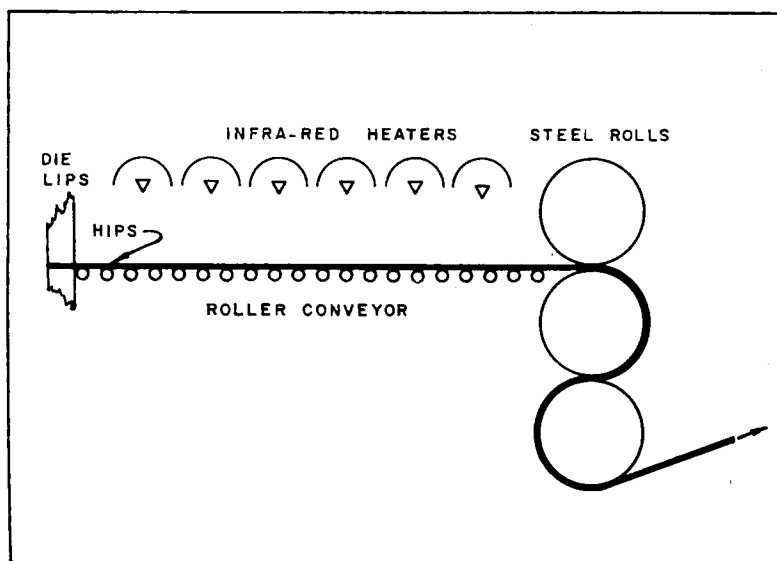


Fig. 6. Schematic diagram of glazer.¹

Figure 6 is a schematic diagram showing the glazing process. Heat is supplied to the sheet surface by means of infrared heaters located above the sheets between a conventional sheet extrusion die and the take-off steel roll stack. During the travel of the sheet over the water cooled conveyor, from the die to the rolls, its overall mass is being cooled. Its surface, however, is maintained at a high temperature for a controlled distance from the die. Height of heaters, rate of sheet take-off, and number of heaters "on" are the necessary variables to be optimized for good glazed sheet production. It is possible by this method to achieve a high gloss

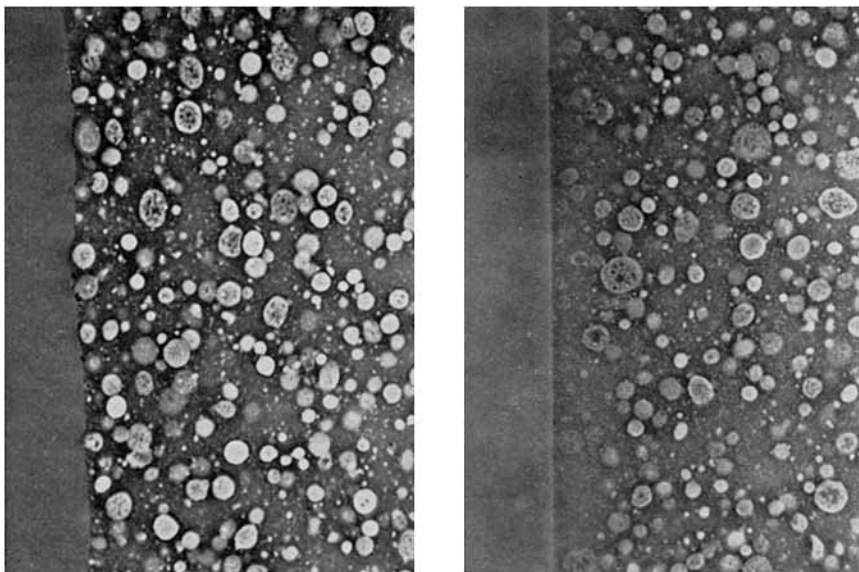


Fig. 7. Cross sections of high impact polystyrene sheet: (A) unglazed; (B) glazed 490 \times .

sheet which retains most of its gloss on vacuum forming yet suffers only slight loss of physical properties.^{1,3}

In cross sections of titanium dioxide-filled, high impact polystyrene sheet it was not possible to distinguish any difference between normally extruded and glazed sheet. The sheet surface of the latter was smoother, but there was no evidence of stratification of copolymer particles as had been observed in the high shear sheet. It was only by careful examination of unpigmented glazed sheet that insight into the morphological change was detected.

In Figure 7, comparison photomicrographs of cross sections of unglazed, and glazed sheet, it can be seen that, in addition to smoothing the sheet surface, glazing effected a change in the refractive index of the copolymer particles near the sheet surface. This refractive index change is evidenced by a decrease in contrast between the bright copolymer particles and the dark polystyrene matrix. The more intense the glazing (higher gloss), the deeper the refractive index change penetrated into the sheet.

Measurements with an A. O. Baker interference microscope⁴ showed that both the styrene matrix and the copolymer particles had increased in refractive index with glazing. The copolymer particles, beginning with a lower refractive index than polystyrene, increased more than did the matrix bringing the two closer together. Refractive index measurements made on the same cross section of unglazed and glazed sides of the sheet showed changes of 0.00316 in the polystyrene and 0.00428 in the copolymer particles. On the unglazed side, the refractive index difference between copolymer particles and matrix was 0.00184; on the glazed side 0.00072.

Glazing, produced a sheet surface not only smoother, but also more optically homogeneous. This homogeneity was achieved without removal of the copolymer particles.

SURFACE OXIDATION

It was shown¹ that excessive glazing resulted in not only reduction of physical properties but also a color change in the sheet surface. This shift in color was toward the yellow and particularly obvious in natural or white

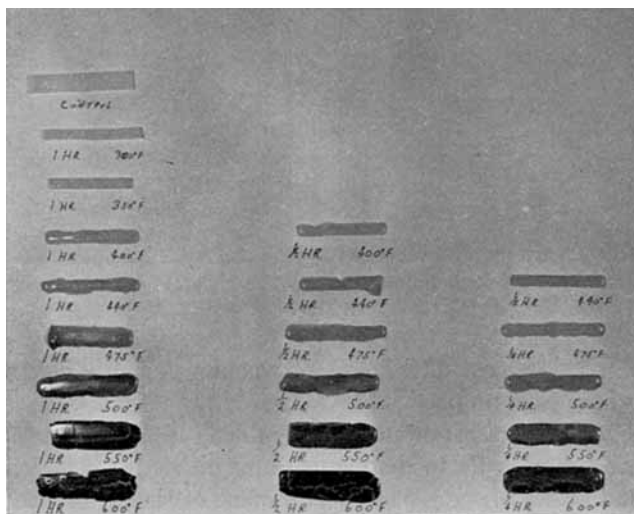


Fig. 8 Natural high impact polystyrene, air oxidized.

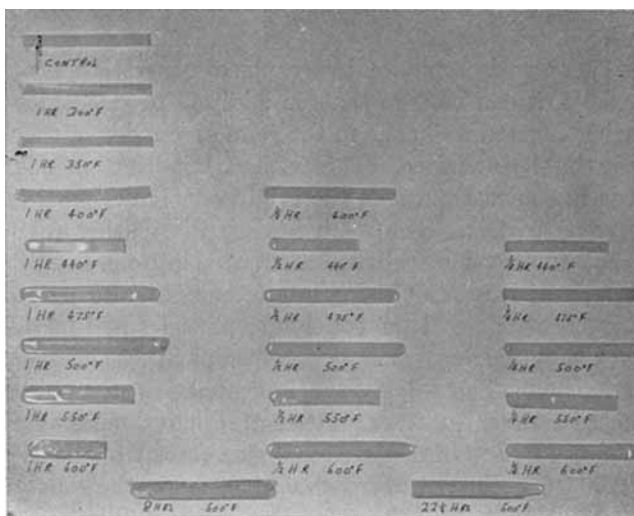


Fig. 9 Natural high impact polystyrene, sealed in nitrogen.

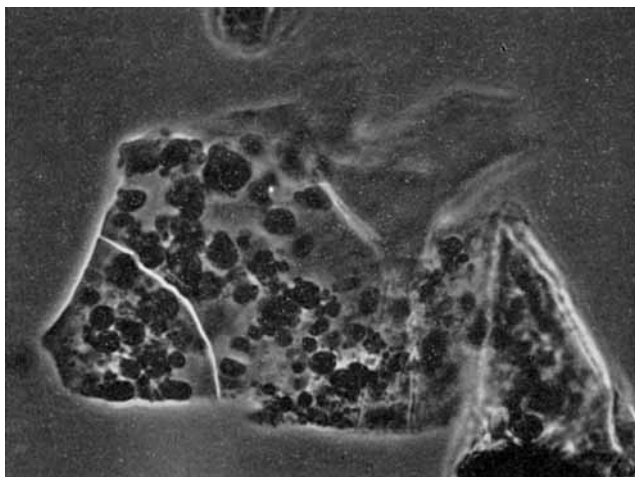


Fig. 10. Surface fragment, air-oxidized for 1 hr. at 500°F. 610 \times .

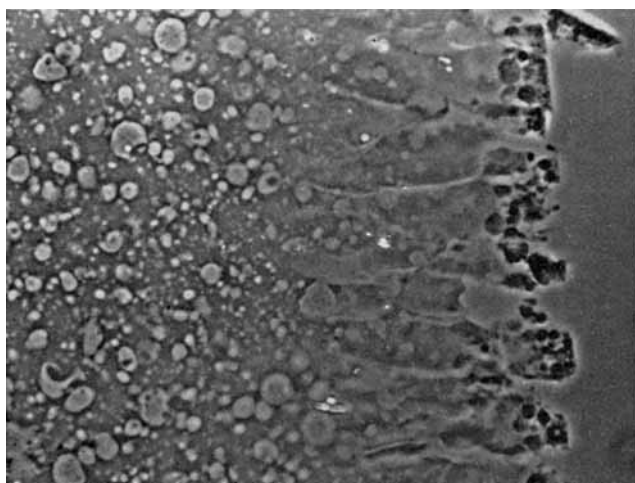


Fig. 11. Cross section, air-oxidized for 1 hr. at 500°F. 350 \times .

sheet. Results of molecular weight determinations¹ indicated polymer degradation.

In order to determine if this degradation were the result of heat alone or heat and oxidation, one group of natural high impact polystyrene strips was placed on glass slides and another group sealed in glass tubes in a nitrogen atmosphere. Both groups were placed in an oven at various temperatures for 15 min., $\frac{1}{2}$ hr., and 1 hr.

Figure 8 shows the resultant changes effected in those samples subjected to air oxidation. Those samples which experienced 400°F. or higher softened and flowed and became increasingly more discolored with increased exposure. A decided color change was apparent in 1 hr. at 350°F.;

actual charring occurred in 1 hr. at 600°F. Exposure for 5 min. at 400°F. produced some discoloration.

This discoloration and embrittlement was a surface phenomenon. The underside (the side against the glass slide), in all but the extremely degraded samples, was apparently unaffected. The penetration into the material increased with increased exposure.

The strips sealed in nitrogen exhibited no such yellowing (Fig. 9). With increased exposure the strips became more and more translucent—more optically homogeneous. Even after 22 hr. at 500°F. there was no yellowing and no embrittlement.

Examination at high magnification of the air oxidized material showed the source of the yellow-brown color. In brittle fragments from the surface of a sample which had been exposed for 1 hr. at 500°F. (Fig. 10), it was apparent that the copolymer particles had suffered the major color change. In microtome cross sections (Fig. 11) it was possible to see the transition from unaffected area, evidenced by normal contrast between copolymer particles and matrix, through the area in which the two refractive indices were almost equal, out to the extremely brittle surface containing the brown copolymer particles.

In microtome cross sections of the samples sealed in nitrogen the effect was uniform throughout. The change of refractive index of the copolymer particles, as evidenced by decrease in their degree of contrast with the matrix, was greater with greater exposure.

The change of refractive index of the copolymer particles was produced by heat alone. Degradation, yellowing of the copolymer particles and embrittlement of the matrix, was produced by oxidation. Apparently, the ideal glazing system should consist of heating the sheet surface in an inert atmosphere. Such a system would produce high gloss with no degradation.

CONCLUSION

The application of the microscope in this investigation provided much information which could have been obtained in no other way. Visual evidence of the morphological changes produced by the gloss improvement techniques contributed to understanding the losses in physical properties and shortened the route to finding a satisfactory method of gloss improvement of high impact polystyrene sheet.

The absence of copolymer particles in the surface of the high gloss sheet produced by high shear extrusion and its similarity to film laminate (a system previously proven unsatisfactory) caused its quick abandonment as a considered method.

The impracticality of smoothing the sheet surface by compression and having the copolymer particles protrude with subsequent vacuum forming quickly ruled out gloss transfer as a desirable technique.

The exact nature of the chemical change which occurs in the copolymer particles with glazing has not been completely investigated. However, in

properly glazed sheet, the morphological relationship of copolymer particles and matrix has not been altered. There are still copolymer particles in the surface of the sheet. The oxidation experiments have pointed out the necessity for careful control of the glazing process for maintenance of maximum physical properties in extruded sheet. Although presently impractical, glazing in an inert atmosphere seems desirable.

In this instance, the microscope provided information which allowed purchase of equipment and conversion of a large-scale manufacturing method to be done with a reasonable degree of confidence.

References

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Synopsis

Morphological changes effected in the two-phase high impact polystyrene system by several methods of securing high surface gloss of extruded sheet were studied microscopically. In the glazing process changes occur in refractive index of the copolymer particles and in the matrix. Excessive glazing may result in oxidative damage. The effects of temperature and oxidation and temperature alone on the copolymer particles have been investigated.

Résumé

Nous avons étudié par microscopie les changements morphologiques affectant un système à deux phases de polystyrène de haut impact par diverses méthodes d'obtention de surfaces fortement vernies de la feuille extrudée. Dans le processus de vitrification, des changements se présentent dans l'indice de refraction des particules de copolymère et dans la matrice. La vitrification trop poussée peut résulter d'une dégradation oxydative. Les effets de température et d'oxydation et de température seule sur les particules de copolymère ont été envisagées.

Zusammenfassung

Morphologische Veränderungen, die am zweiphasigen, schlagfesten Polystyrolsystem bei verschiedenen Methoden zur Erzeugung eines hohen Oberflächenglanzes von extrudierten Folien auftraten, wurden mikroskopisch untersucht. Beim Glänzungsprozess treten Änderungen des Brechungsindex der Copolymerpartikel und der Matrix auf. Zu starke Glanzung kann zur oxydativen Schädigung führen. Der Einfluss von Temperatur und Oxydation sowie von Temperatur allein auf die Copolymerpartikel wurde untersucht.

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