# Light diffusing polycarbonate—polycycloolefin blends

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Light diffusing polymers have found application fields such as lighting bodies and materials for sunroofs, especially those of industrial buildings. Translucent roofs made of polycarbonate (PC) protect against sun irradiation and eliminate shortcomings of steel wire reinforced glass which is difficult to cut [1, 2]. Light diffusing materials are also an excellent choice for applications in projection systems as a method for hiding scratches or imperfections in rear projection screens or thin layer decoration sheets [3]. Other application fields of light diffusing polymers are following: luminaries, illuminated signs, especially backlit translucent signs, skylights, automotive sunroofs, covers for automotive lights, etc. [4].

Inorganic additives and pigments are commonly incorporated into the polymer matrix in order to introduce scattering of light. Particles of $BaSO_4$ are commonly used and $TiO_2$ ZnO, ZnS, CdS, $CaCO_3$ have also been applied for this purpose. White pigments such as $TiO_2$, ZnO, ZnS decrease the light transmission so much that it limits their application range. When the pigment concentration is decreased, no significant scattering can be observed and the material remains transparent [4, 5].

Another serious problem consists in a decrease of molecular weight of polycarbonate samples filled by inorganic fillers, such as $TiO_2$. The degradation depends on the type of the inorganic pigment and its concentration. It is believed that inorganic pigments are involved in degradation reactions taken place during injection molding, especially when traces of water (e.g., from air humidity) are present in the polymer. Decrease of a molecular weight might have a negative impact on mechanical and other properties of the polymers. When 1.5 wt.% of $TiO_2$ is added into polycarbonate matrix, then 0.15–0.2 wt.% of water in polycarbonate is enough to cause marked degradation of the matrix [5].

Inorganic particles are difficult to disperse evenly and, since they are hard and irregularly shaped, they tend to abrade the processing equipment. Moreover, molded articles produced from such composition have an uneven surface. Pits and holes, caused by large particle size of $BaSO_4$, can be observed on the surface [6, 7].

Some of the above-mentioned drawbacks of rough, unevenly dispersed and irregularly shaped inorganic pigments (especially matrix degradation, rough surface, etc.) can be overcome by using organic particles based on various polymers, such as polyalkylmethacrylate and polyalkylacrylates [8, 9]. On the other hand, there is a considerable drawback of polyacrylates and polymethacrylates based light diffusers, namely their poor thermal stability, which prevents their application as lighting bodies [9]. Block copolymers polycarbonate-co-poly(ethylene-butylene) have also been approved as a powerful light-diffuser for polycarbonates [10]. Unfortunately, such block copolymers have to be synthesized under special conditions which might complicate their possible production. Therefore, application of blends instead of block copolymers seems to be more convenient from practical reasons assuming that domains of the dispersed phase, which differ considerably in refractive index from the polymer matrix, work as light diffusers [11, 12]. The scattering effect of polyolefin micro-phase dispersed in polycarbonate is powerful enough even in very low concentration. Low content of such light diffuser is essential for preserving good mechanical, thermal and other properties of polycarbonate [10].

In this work, we describe polycycloolefin–polycarbonate blends, which possess excellent light-diffusing properties of the above-described polycarbonates–polycarbonate-co-poly(ethylene butylene) blends on the one hand and, on the other, they can be easily prepared and processed. Polycarbonate blends with hydrogenated polystyrene (HPS) seem to be particularly attractive since HPS is easily available by hydrogenation of the common polymer [13]. Therefore, we have focused our study on testing of HPS as a possible light diffuser for polycarbonate matrix and compare it with other commercially available polycycloolefins Apel and Arton (Fig. 1).

*Polycycloolefins Apel and Arton* were obtained from Japan Synthetic Rubber and Mitsui Corp., respectively. Polycarbonate Makrolon 1243 used in this work is commercially available from Bayer AG.

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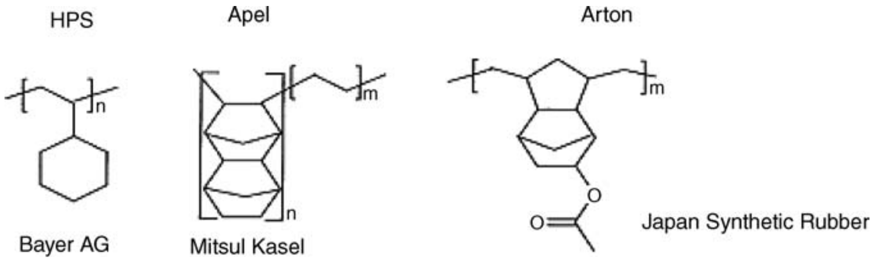

*Figure 1* Chemical structures of used polymers.

*Hydrogenated polystyrene* was synthesized as follows: 117.82 kg of distilled cyclohexane was heated to 50 °C in the reactor (volume 500 l) equipped with a stirrer under nitrogen. Then within 4 hr 48.29 kg of polystyrene was added into the reactor and after its complete dissolution the solution was stirred for 24 hr at 70 °C. After subsequent cooling of the solution 53.32 kg of methyl-*tert*-butylether was added at 50 °C in nitrogen atmosphere. Then the mixture was cooled to room temperature. An autoclave (volume 40 l) equipped with stirrer was filled by 21.943 kg of this polystyrene solution and then 625 g of Ni-catalyst dissolved on 2.95 l of methyl-*tert*-butylether was added to the reaction mixture. After that hydrogen pressure in the autoclave was maintained at 100 bar and the stirred reaction mixture was heated at 160 °C. The reaction pressure was automatically kept at 100 bar during hydrogenation. After consumption of hydrogen had ceased the reaction mixture was further stirred for 2–4 hr. After removal of the catalyst by filtration the hydrogenated polymer was isolated by evaporation of the solvent.

*Blending of polycycloolefins with polycarbonate* (typical example): a twin screw extruder (Haake Rheomex TW 100) in connection with the processing unit Haake Rheocord 90 was heated at 300 °C and dosed by 95 g polycarbonate and 5 g polycycloolefin using Katron-Soder T 20 dosing unit. Blending took place in molten state at speed 40 screw revolutions per minute. Molten polymer blends were passed through round-shaped nozzle and transported for granulation from the extruder to a cooling trough by conveyor belt.

*Double-layered sheets were extruded as follows:* Pellets of polycarbonate–polycycloolefin blend were co-extruded under screw speed 38 revolutions per min using special extruder S-70 (Bayer AG) into double-layered sheets (either of the layers was 1 mm thick) with 60 $\mu$m thick UV protective layer (Bayer AG-DP1 1244/5–55/0.54). The temperature in the dosing space was maintained at 270 °C, in the first zone the temperature was kept at 280 °C, the second zone was heated at 270 °C and the temperature of the third zone was 260 °C. The fourth to sixth zone and the outlet were maintained at 250 °C.

*Haze experiments* were carried out using hazemeter HazeGard (BYK-Gardner) according to ASTM-1003/290. *Transmittance* was measured using Perkin-Elmer Lambda 900 Photometer using air as a reference (100% transmittance).

*Glass transition temperature* was determined by calorimetric experiments using Mettler DSC-30 at heating rate 20 °C/min in nitrogen.

*Tensile tests* were carried out at room temperature using Instron 5566 universal testing machine at a speed of 5 mm/min according to DIN ISO 527 on 170 mm × 10 mm × 4 mm specimens.

*Impact tests* were performed on 80 mm × 10 mm × 4 mm specimens using registered fall-apparatus (Bayer AG) at room temperature (fall height 40 mm, pin diameter 4 mm) according to DIN ISO 179.

To determine light scattering properties of polycycloolefin domains in polycarbonate, haze was measured in the respective samples of the blends. Haze is defined as a part of transmitted light which was scattered by more than 2.5° during passing through the sample [9] as is shown in Fig. 2. UV-Vis spectra of the blends were also measured which make possible to determine the scattering effect in any individual wavelength. Haze, which is very commonly used for characterization of opalescent polymers, includes all polychromatic light and therefore it does not give any information about the power of light scattering in different wavelength.

The spectra of the polycarbonate containing 3 wt.% HPS are presented in Fig. 3. Total transmittance is divided into direct (linear) transmittance and scattered (dif-

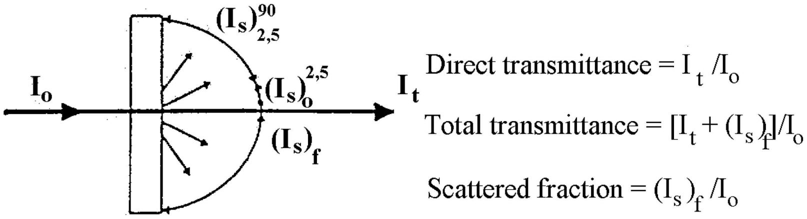

*Figure 2* Light scattering in polymer blends.

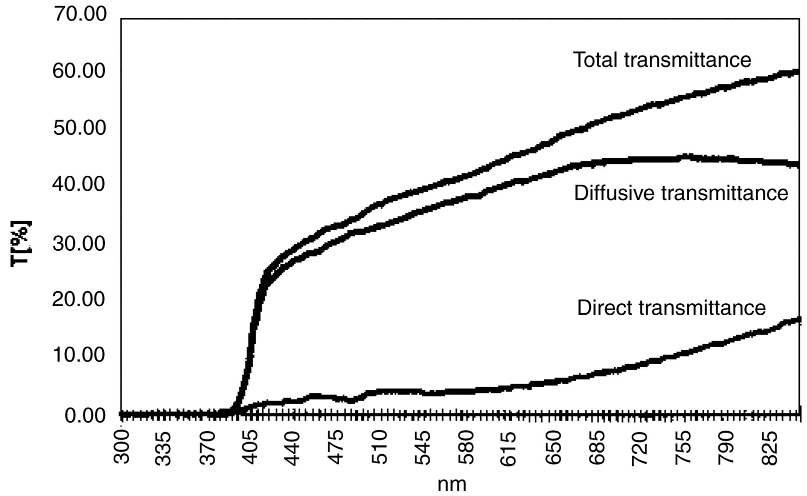

*Figure 3* UV-Vis spectrum of polycarbonate containing 3 wt.% HPS.

fuse) transmittance because of the light scattering effect. The spectra of translucent samples show typical pattern of transmittance. The pattern is characterized by high scattering component and very tiny direct component especially in lower wavelengths range. Chemical composition and haze of 0.5 and 2 mm thick tested samples are shown in Table 1. The content of the light diffuser in the matrix varies in the range of 1–5 wt.%.

It is obvious from Table 1 that the concentration 1 wt.% HPS in polycarbonate is too low to scatter light sufficiently even in 2 mm thick sample. On the other hand, 3 wt.% HPS scattered light in the polycarbonate matrix considerably (87%) in 0.5 mm thick sample and the thicker sample (2 mm) scatters the transmitted light completely. A total of 5 wt.% HPS in polycarbonate was enough to scatter all transmitted light in both 0.5 and 2 mm thick samples. The

TABLE 1 Composition, haze and transmittance of polycycloolefin–polycarbonate blends

| Sample no | Thickness (mm) | Light diffuser | Polycycloolefin concentration (wt.%) | Haze (%) | Total transmittance at 450 nm | Total transmittance at 700 nm |
|---|---|---|---|---|---|---|
| 1 | 0.5 | HPS | 1 | 17 | 82 | 87 |
| 2 | 0.5 | HPS | 3 | 87 | 63 | 77 |
| 3 | 0.5 | HPS | 5 | >99 | 52 | 68 |
| 4 | 2 | HPS | 1 | 32 | 69 | 82 |
| 5 | 2 | HPS | 3 | >99 | 32 | 54 |
| 6 | 2 | HPS | 5 | >99 | 23 | 40 |
| 7 | 2 | Apel | 1 | 45 | 44 | 65 |
| 8 | 2 | Apel | 5 | 97 | 14 | 39 |
| 9 | 2 | Arton | 1 | 24 | 56 | 75 |
| 10 | 2 | Arton | 5 | 91 | 22 | 50 |

TABLE 2 Glass transition temperatures and mechanical properties of HPS–polycarbonate (PC) blends

| Measured property (unit) | Sample A | Sample B |
|---|---|---|
| Composition (wt.%) | (99% PC + 1% HPS) | (95%PS + 5% HPS) |
| Glass transition temperature, $T_g$(°C) | 141 | 141 |
| Notched impact resistance | | |
| Impact strength at RT (kJ/m$^2$) | 7.6 | 3.5 |
| Fracture pattern | Brittle | Brittle |
| Impact resistance | | |
| Impact strength at RT (kJ/m$^2$) | 213 | 213 |
| Fracture pattern | Tough | Tough |
| Deformation behavior | | |
| Young's modulus | 1990 ± 100 | 1960 ± 100 |
| Tensile strength at yield (MPa) | 61.0 ± 0.1 | 61.6 ± 0.3 |
| Elongation at yield (%) | 5.8 ± 0.1 | 6.2 ± 0.3 |
| Tensile strength at break (MPa) | 62.9 ± 1.4 | 61.9 ± 0.8 |
| Elongation at break (%) | 90.9 ± 1.2 | 95.1 ± 2.2 |

data in Table 1 indicate that 3 wt.% of polycycloolefin is enough to scatter light considerably in both 0.5 and 2 mm samples. The thickness 2 mm is common for samples used for light scattering experiments (which makes it possible to compare data) and the thickness 0.5 mm corresponds to that of the individual layer of double layered sheets commonly used as an opalescent sunroofing material.

Light scattering effect of the individual light diffusers differs in their concentration within the polycarbonate matrix (thickness of samples was 2 mm). In the lower concentration (1 wt.%), the haze increases in the order Apel>HPS>Arton while in the higher concentration (5 wt.%) the order was different (HPS>Apel>Arton). No experiments have been done in order to explain this phenomenon but it can be assumed that the morphology of the individual blend plays an important role in light scattering properties of these polycycloolefin containing polycarbonate samples. In contrast, the chemical structure of the polyolefin does not seem to play as pivotal role in light-scattering properties of the investigated samples as physical structure does, provided that refractive indices, which depend on the individual chemical composition, differ considerably.

For many applications, especially for sunroofs, the light diffusing plastics have to be both hazy but light transmittable. From this point of view, the samples 2 and 5 show the best results since the transparency is high enough and the light is scattered substantially (sample 2) or completely (sample 5).

Mechanical properties of HPS–polycarbonate blends are shown in Table 2. E-module of the blends is approximately by 15% lower than that of the pure polycarbonate. Yield stress as well as tenacity decreased very slightly after blending. Notched impact resistance of the blends is comparable with some other common polymers (e.g., various polyamides prepared by polycondensation), but it is lower than that of the polycarbonate blends with polyesters and acrylonitrile-butadiene-styrene copolymer [14]. No substantial effect of HPS concentration on impact resistance (both with and without notch) was observed in the concentration range 1–5 wt.%. Both elongation at break and elongation at yield are roughly comparable with those of polycarbonate for injection molding of thin-walled articles, but lower than those of injection molding type of polycarbonate for compact discs production (the decrease of the mentioned phys-

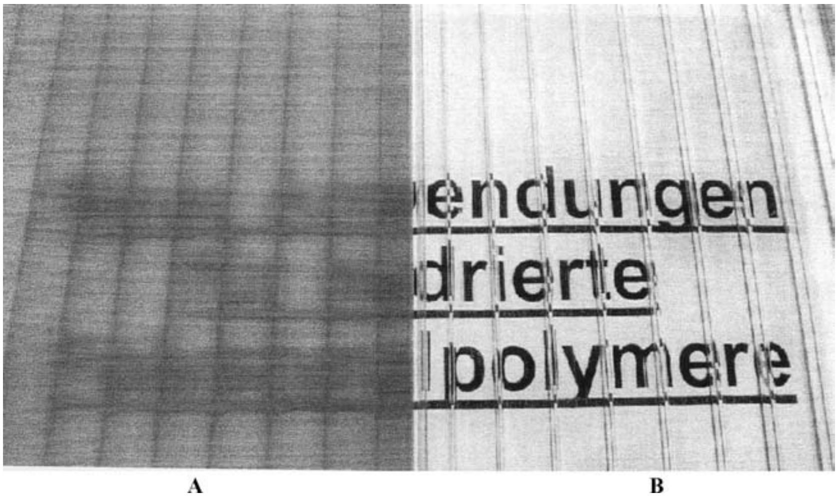

*Figure 4* Photograph of a text behind light diffusing (A) and transparent (B) double layered sheet.

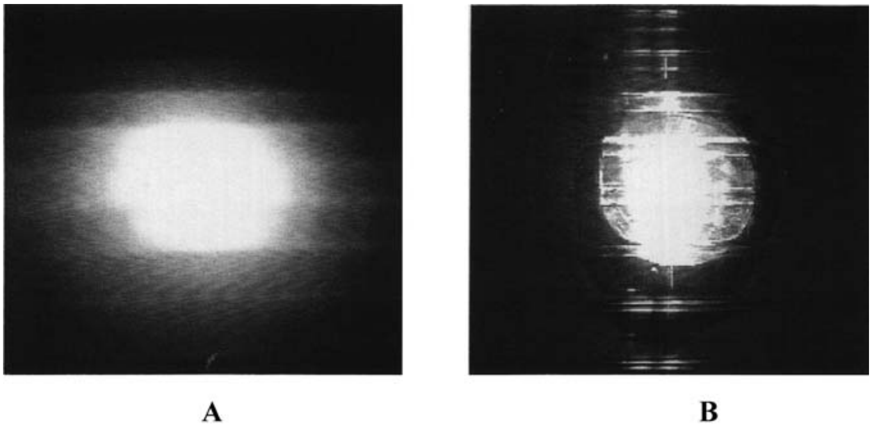

*Figure 5* Photograph of the source of light behind double layered sheet. (A) Light diffusing polycarbonate (3 wt.% HPS), (B) transparent polycarbonate.

ical properties by 5–10% and 3–5% respectively was observed) [14]. Glass transition temperature decreased from 150 °C (pure polycarbonate) to 141 °C in both samples of blends. This might indicate that isotactic fraction of HPS ($T_g = 95$ °C) [15] is partly dispersed on the molecular level and its plasticizing affect takes place.

In contrast to double-layered sheet of pure polycarbonate that of the blend (3 wt.% HPS in polycarbonate) shows considerable light scattering as is shown in Fig. 4. The sheet based on the blend (3 wt.% HPS in polycarbonate) is semitransparent but it transmitted light substantially. The same sheet of pure polycarbonate is transparent. Source of light behind the sheet of the blend is visible only very unclearly, while the bulb can be easily recognized behind the same sheet of pure polycarbonate as is obvious from Fig. 5. Light is distributed almost uniformly when it passes through the sheet made of the composite.

It can be concluded that polycycloolefin containing polycarbonate blends show considerable light diffusing effect, especially polycarbonate containing 3 wt.% of hydrogenated polystyrene show good balance of high values of transmittance and substantial haze. HPS containing polycarbonate show relatively small deterioration of mechanical properties (except of notched impact resistance) in comparison with pure polycarbonate. Polycarbonate light-diffusing blend can be extruded to double layered sheets which are commonly used for sunroofs.

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