

# The Investigation of Phase Morphology in Thermoplastic Olefins by Laser Scanning Confocal Fluorescence Microscopy

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## Introduction

Thermoplastic olefins (TPOs) are a class of polyolefin blends consisting of a polypropylene (PP) major phase and a minor phase of ethylene-butene or ethylene-propylene rubber (EBR or EPR, respectively).<sup>1-3</sup> The latter component serves as an impact modifier (IM), improving the ductility, crack resistance, and impact strength of the brittle PP homopolymer. Since TPOs are lightweight, inexpensive, and processable materials, they have become an increasingly popular alternative to steel in the automotive industry, being used for a wide range of automobile parts such as bumpers and fascia.

For most automotive applications, parts fabricated from TPO are painted in order to enhance their longevity and cosmetic appearance.<sup>4-7</sup> Since the surface free energy of TPO is low, a primer coat is required to achieve effective paint adhesion. A common primer for TPO systems is chlorinated polyolefin (CPO), a solution of which is applied to the surface of the part prior to the addition of a topcoat and clearcoat. Despite the use of CPO primers, however, a number of environmental and mechanical stresses often result in failure at the CPO-TPO and topcoat-CPO interfaces, leading to chipping, peeling, and bubbling of the painted surface. Such failure of painted TPO parts, along with the mechanical failure of TPO itself, has become extremely costly to automobile manufacturers. Through a deeper understanding of the nature

of these materials, scientists and engineers hope to meet the industry requirement for 10-year durable painted plastic parts.

One of the most important factors in the mechanical properties and paintability of TPO is the morphology, or microstructure, of the blend, described by the size, shape and location of rubber particles within the semi-crystalline PP matrix. These rubber particles act to dissipate energy within the PP phase, thus improving the mechanical properties of the material; high interfacial area between the two phases is therefore optimal, favouring a bulk morphology of small (1-20  $\mu\text{m}$ ) rubber particles evenly dispersed throughout the blend. The near-surface morphology of TPO is thought to have a direct influence on the activity of the primer and therefore paint adhesion. In the case of injection-molded TPO, the near-surface morphology is found to be quite different from that of the bulk; fast cooling and nonideal crystallization at the mold wall results in a rubber-rich layer several microns below the TPO surface. It is believed that primer activity is dependent upon the interaction of CPO molecules with this rubber layer. This feature of near-surface morphology is therefore crucial with respect to TPO paintability.

It is reasonable to infer that the method and conditions of processing will play a critical role in the morphology of TPO, and should therefore influence the final properties of the material. Most commercial TPO is fabricated by injection molding; in this process, there exist a number of varia-

bles(e.g. shear rate and injection temperature) that could influence the near-surface and bulk morphologies. As well, due to the size of the mold, shear forces are known to be dependent on distance from the gate, i.e. the entry-point of the melt into the mold; a consequent dependence of morphology on distance from the gate is therefore predicted. Clearly, in order to optimize processing conditions and to ensure the quality of molded parts, analytical tools are required to quickly and easily assess TPO morphology in three dimensions under a variety of processing conditions.

**Laser Scanning Confocal Fluorescence Microscopy in the Study of TPO.** A number of different imaging techniques have been used to investigate TPO morphology. Transmission electron microscopy(TEM) has the advantage of high resolution, allowing sub-micron features of blends to be imaged. However, differences in electron density between components of TPO are low, resulting in poor contrast between phases. Selective solvent etching can be used to remove the rubber phase and provide sufficient contrast, although the etching process tends to swell the blend and alter its morphology.<sup>8</sup> Raman imaging is a more non-invasive technique in which contrast is based on spectral differences between the components.<sup>4,5</sup> The main disadvantage of this technique is the need for complicated mathematical algorithms to convert data into meaningful images.

The imaging tool that we employ in our laboratory to address problems of TPO morphology is laser scanning confocal fluorescence microscopy (LSCFM). This technique is well established in the biological sciences, though it is only beginning to find a niche in the field of polymer blends.<sup>9-12</sup> In LSCFM imaging, contrast is provided by a small amount of fluorescent dye added to the system. Because of the confocal optics of the instrument, only light from a thin focal plane reaches the detector. By adjusting the focus, optical sections at different depths can be imaged, allowing a series of images to be collected at increasing(or decreasing) distances from the surface(called a "z-stack"). Thus, LSCFM gives the scientist fast and noninvasive "3-D vision" for peering through sev-

eral layers of the blend, in some cases without microtoming the sample.

Two previous studies of TPO morphology by LSCFM employed a mixture of dye and CPO dissolved in a common solvent.<sup>4,5</sup> The solution was applied to the surface of the TPO. As the dye diffused through the top layers, differences in the spectral properties of the dye in the PP and IM phases allowed these two components to be distinguished. The main objective of these experiments was not to study TPO morphology, but to identify the location the CPO after coating. However, since the dye was not covalently bound to the CPO, only the location of the dye could be identified. In another experiment, dye molecules were covalently attached to the primer via maleic anhydride groups on CPO, resulting in a fluorescent "tracer" that gave less ambiguous information on the location of CPO.<sup>6</sup> We bring a similar strategy to the fluorescent labeling of TPO for morphology studies by LSCFM.

**Strategy for the Fluorescent Labeling of TPO.** Our strategy for the fluorescent labeling of TPO involves the dissolution of a fluorescent tracer in the IM rubber phase, allowing "bright" IM droplets to be distinguished from the "dark" PP matrix.<sup>13</sup> As in ref. 6, this tracer is a polymer that has been covalently labeled with a fluorescent dye molecule, in this case Hostasol Yellow(Clariant). Important requirements for our tracer are: **1.** thermal stability under the conditions of blend formation, **2.** miscibility in the IM phase, **3.** immiscibility in the PP phase, **4.** good fluorescent properties of the dye in the IM phase.

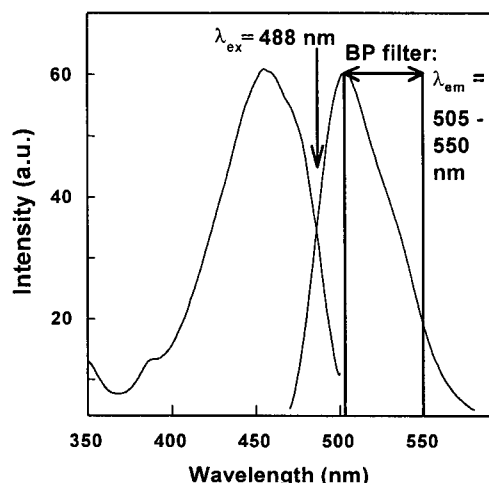
The TPO that we wish to study consists of PP as the major component and ca. 20 wt.% of the impact modifier EBR-9(containing 9 mol% butene). Although an ideal tracer for the IM phase would be EBR-9 labeled with Hostasol Yellow, EBR-9 is not commercially available with functional groups on the polymer for covalent labeling with the dye. However, the maleated form of the rubber EBR-28, containing 28 mol% butene and 0.071 mmol maleic anhydride per gram of polymer, is commercially available from Dupont Canada. We have therefore chosen to covalently attach a small

amount of an amino-functional Hostasol Yellow dye via imide linkages to anhydride groups on maleated EBR-28. The aim of the present work is to show that the fluorescent tracer synthesized in this manner meets the requirements outlined above, using model TPO blends made by solution blending in our laboratory.

## Results and Discussion

**Synthesis and Thermal Stability of the Fluorescent Tracer.** The result of reacting amino-functional Hostasol Yellow dye with maleated EBR-28 is the tracer molecule PLEBR-28, containing 0.036 mmol dye per gram of polymer. Residual anhydride groups along the chain were occupied by the addition of excess hexylamine following dye labeling.

The excitation and emission spectra of the fluorescent tracer PLEBR-28 are shown in Figure 1. The excitation and detection wavelengths for the LSCFM experiments are also indicated. The thermal stability of the labeled product was tested by annealing PLEBR-28 under vacuum at 240 °C for 20 min. After annealing, the tracer showed only 5 wt% detachment of dye, with less than 2 wt% gel formation due to crosslinking. This degree of



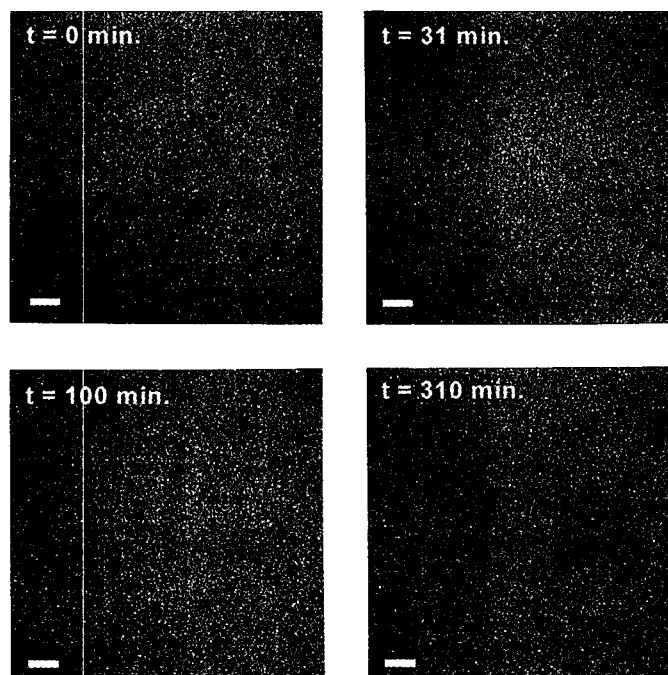
**Figure 1.** Excitation and emission spectra of PLEBR-28 in toluene. The 488 nm excitation line of the Ar ion laser and range of emitted light detected (505-550 nm) for LSCFM experiments are indicated.

thermal stability is more than sufficient for the incorporation of PLEBR-28 into TPO blends by injection molding.

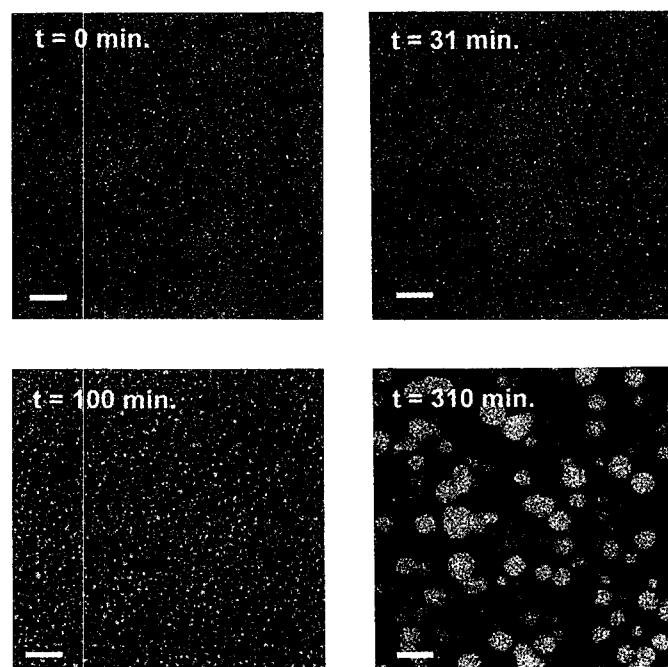
**Model Blends of TPO.** To test the behaviour of PLEBR-28 in various blends, model blends containing the labeled polymer were made by the process of solution blending. The components of the blend were first codissolved in hot xylenes at a total concentration of ca. 1 wt%, then precipitated into acetone. The resulting blend powders were pressed into films 30-50  $\mu\text{m}$ -thick at 150 °C for 90 s, under which conditions no phase separation was observed. The films were subsequently annealed at 175 °C in a vacuum oven for various times (up to 310 min) to promote phase separation of the major and minor components.

**Miscibility of PLEBR-28 in EBR-9.** The first "test blend" prepared in the above manner contained only 3 wt% PLEBR-28 blended with the impact modifier EBR-9. This simple system was used to determine whether the tracer was miscible in the IM phase. Confocal images of the blend at various annealing times are shown in Figure 2. Uniform fluorescence throughout the blend, even after 310 min annealing above the melting point of both components, indicates that PLEBR-28 is miscible in the impact modifier EBR-9 at a concentration of 3 wt%. As a tracer, the labeled polymer should therefore provide uniform fluorescence throughout the IM phase in TPO blends.

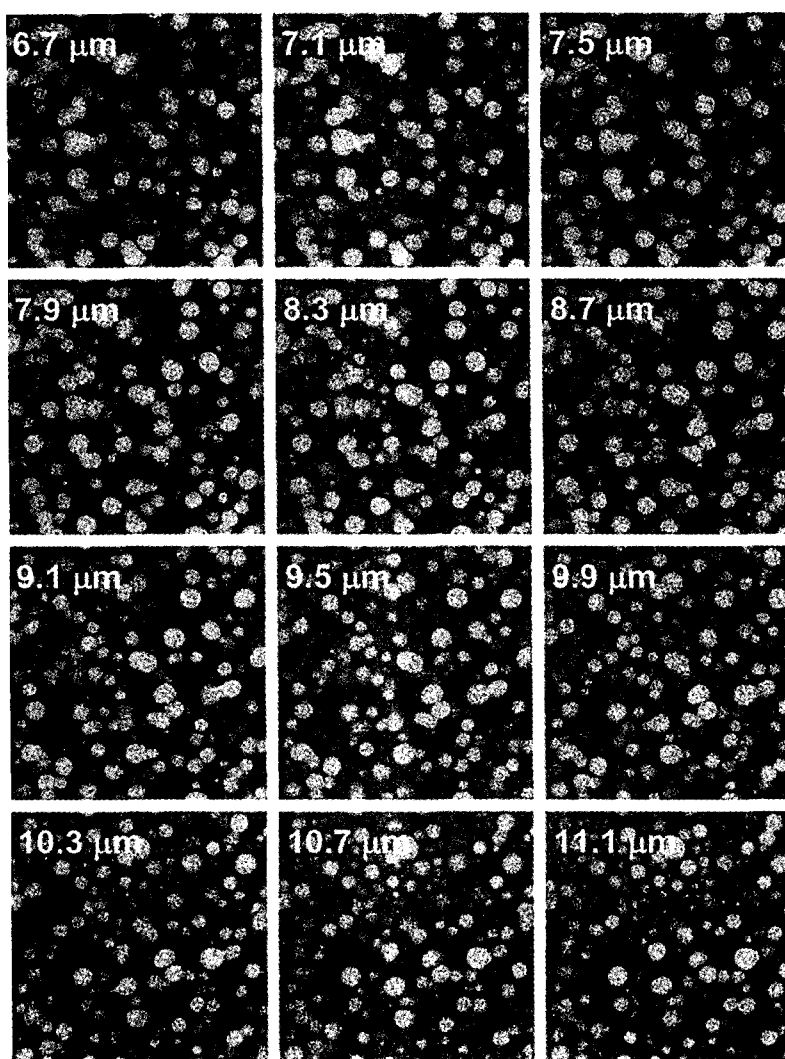
**PLEBR-28 as a Tracer in TPO Blends.** Once the miscibility of PLEBR-28 in the IM component was established, it remained to be seen whether this tracer would provide good fluorescence contrast between the IM and PP phases in TPO blends. To this end, a model blend was prepared with the composition 80/20(w/w) PP/IM, where the IM phase was identical to the blend shown in Figure 2 (i.e. 3 wt% PLEBR-28 in EBR-9). Confocal images after various annealing times are shown in Figure 3. From the figure, we see the beginnings of phase separation after 100 min annealing. After 310 min, continued phase separation between PP and EBR, along with coarsening of the minor phase, results in a population of bright IM droplets with diameters of 4-8  $\mu\text{m}$ . Since PLEBR-



**Figure 2.** LSCFM images of EBR-9+3 wt% PLEBR-28, after annealing at 175 °C for 0, 31, 100, and 310 min. The scale bars represent a distance of 20  $\mu\text{m}$ .



**Figure 3.** LSCFM images of PP/EBR 80/20(w/w) + 3 wt% PLEBR-28 with respect to EBR, after annealing at 175 °C for 0, 31, 100, and 310 min. The scale bars represent a distance of 10  $\mu\text{m}$ .



**Figure 4.** z-Stack of LSCFM images of PP/EBR 80/20(w/w)+3 wt% PLEBR-28 with respect to EBR, after 175 °C for 310 min. Distance from the air-film interface is shown in the upper left-hand corner of each image, with 0.4 μm “steps” between each image. The scale bar represents a distance of 10 μm.

28 is miscible in the IM phase(Figure 2), it is assumed that the tracer is dissolved in EBR-9 throughout the droplets. Clearly, the result is good fluorescent contrast between the two phases, suggesting both good fluorescence properties of the dye in the IM phase and immiscibility of the tracer in the PP matrix. Since only 3 wt% of PLEBR-28 was added with respect to the total IM polymer (dye concentration=0.00153 mmol dye/g EBR), the term “tracer” is certainly justified; with such a small amount of labeled polymer required to pro-

vide contrast, the morphology of the blend will not be affected by the tracer.

Finally, a z-stack of IM particles after 310 min annealing is shown in Figure 4, obtained by taking small steps of 0.4 μm between each image from 6.7 to 11.1 μm below the surface of the film. By following individual droplets through the z-stack, the height of particles can be obtained, confirming their spherical morphology, along with their location with respect to other particles in the matrix. As well, it can be seen from the z-stack that the

tracer is dissolved throughout the IM phase in three dimensions.

### Conclusions

From these results, we find that the dye-labeled polymer PLEBR-28 is an effective fluorescence tracer for LSCFM studies of TPO blends containing PP in the major phase and EBR-9 impact modifier. In collaboration with the Ford Motor Company, we are currently using this tracer in detailed investigations of the morphology of injection-molded TPO under various processing conditions and at different locations in the mold. Our results will hopefully open the door to a deeper understanding of TPO materials, including the relationships between processing, morphology, mechanical properties and paint adhesion.

**Acknowledgments:** The authors would like to thank Materials and Manufacturing Ontario(MMO) for support of this research. MM thanks NSERC Canada for a postdoctoral fellowship.

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### 알립니다

#### 학술진흥재단 학술지 평가 결과 A등급 판정

학술진흥재단에서 교육부의 의뢰로 실시한 각종 학술지에 대한 종합평가 결과 화학공학분야에서 <폴리머> 및 <Korea Polymer Journal>이 A등급 판정을 받았다.

이 평가는 논문이 실린 학술지의 등급을 교수 업적평가에 활용하거나 유사 학술지의 통폐합 등 학계에 적지 않은 영향을 미칠 것으로 보이며, 교육부는 앞으로 정부발주 사업의 연구실적 심사 자료나 한국과학인용색인(KSCI), 한국사회과학인용색인(KSSCI) 등 학문평가 척도로 활용할 계획이다.

학술진흥재단에 등록된 학회 수가 모두 1,520개에 발행 학술지가 2,600여개일 정도로 난립하고 있으며, 일부는 논문게재에 학연과 친분관계가 영향을 주고 초청논문 등 검증을 거치지 않고 실는 경우도 있어, 앞으로 대학들은 논문을 몇 편 발표했느냐 보다 어떤 수준의 학술지에 실었느냐를 따져 연구업적을 평가하게 될 전망이다.