# Hierarchically Porous Polymeric Materials from Ternary Polymer Blends

Jun Wang<sup>a</sup>, Benoît H. Lessard<sup>b</sup>, Milan Maric<sup>b</sup>, Basil D. Favis<sup>a,\*</sup>

 <sup>a</sup> CREPEC, Department of Chemical Engineering, École Polytechnique de Montréal, Montréal, Québec, H3T 1J4, Canada
 <sup>b</sup> CREPEC, Department of Chemical Engineering, McGill University, Montréal, Québec, H3A 2B2, Canada

\*Corresponding author. Email: <u>basil.favis@polymtl.ca</u>. Telephone: +1 514 340-4711 ext. 4527. Fax: +1 514 340-4159.

# Abstract

Hierarchically porous polymers with controllable pore size were successfully generated through a novel polymer blending strategy in an A/B/C-B-C ternary blend system. Polylactide, highdensity polyethylene/styrene-ethylene and butylene-styrene copolymer (PLA/HDPE/SEBS) was used as a model system to demonstrate this technique. During melt blending, the SEBS was driven into the HDPE phase owing to the presence of the PE block in the copolymer. With proper volume fractions of PLA/HDPE/SEBS (e.g., 50/25/25), a bi-modal, dual co-continuous morphology was obtained and hierarchically porous polymeric materials were further generated by selectively removing the PLA and SEBS phases. Annealing and compositional variation were further employed to control the pore size and it is shown that the length scales of the two cocontinuous morphologies can be controlled independently. Keywords: hierarchically porous polymer, polymer blend, annealing, morphology control

# **1. Introduction**

Hierarchical structures, defined as a structure containing elements on difference length scales, are commonly found in nature (e.g., bone and wood) [1]. In human society, these structures have also been constructed, ranging from macroscopic architectures (e.g., Eiffel Tower) to microscopic drug delivery devices (e.g., Multistage nanovectors) [2, 3]. Hierarchically porous materials have been of great interest recently owing to their potential applications in separation [4, 5], catalysis [6], energy storage and conversion [7], drug delivery and tissue engineering [8-11]. When used as scaffolds in tissue engineering, the primary pore size of the hierarchical system ranges from several to hundreds of microns to host different cells for growth [12]. The secondary or higher level of the hierarchical structures (length scale down to nanometer size) are constructed to mimic the extracellular matrix (ECM) features as well as to create the opportunity to introduce drugs, nutrients or nanoparticles, which can facilitate cell adhesion, proliferation and differentiation [9, 13, 14]. Although a few reports have been published for generating hierarchically porous materials for tissue engineering, the precise control over the pore size of the final structures, and in particular the independent control of the different length scales, is indeed challenging [8-10, 14-16].

Polymer blending is an interesting approach to produce porous materials by utilizing the cocontinuous morphology which is characterized by each component being interconnected throughout the blend [17]. The selective extraction of one phase in the system results in a three dimensional (3D) porous polymer with full continuity. Using this strategy, it has been demonstrated that by controlling composition, interfacial properties and subsequent annealing conditions, the pore size can be tailored ranging from about 100 nm to hundreds of microns while the porosity varied from 30% to 95% without losing the interconnectivity [17-22]. However, those results were obtained in a unimodal porous system. In this letter, we report a novel ternary polymer blending strategy to generate hierarchically porous, dual continuous polymeric materials with independent pore size control.

# 2. Experimental

#### 2.1 Materials and blend preparation

The two homopolymers HDPE 3000 and PLA 3001D were supplied by Petromont and NatureWorks respectively. The block copolymer SEBS G1652 with 30% PS was kindly provided by Kraton. The rheological tests were performed on a MCR 501 rheometer under nitrogen. A parallel-plate configuration was used with a gap of 1 mm. All the samples were blended in a Brabender internal mixer at 200°C for 7 min with the rotor speed of 50 RPM under N<sub>2</sub>. After mixing, the samples were cut from the blades and put into ice water immediately to freeze-in the morphology. Subsequently, quiescent annealing of the blends was performed on a hot press with a constant N<sub>2</sub> flow.

#### **2.2 Selective extraction and continuity**

Cyclohexane and 0.5 mol/L NaOH of MeOH/water (40/60, 60°C) solution were used to selectively remove SEBS and PLA phases respectively. Chloroform was used to extract both SEBS and PLA simultaneously as needed. The continuity is calculated after the extraction step using the following equation:

Continuity (%) = 
$$\frac{m_i - m_f}{m_i} \times 100\%$$

where  $m_i$  and  $m_f$  are the initial weight and final weight respectively of the porogen phase(s).

#### 2.3 Morphology and pore size

The blends were cryogenically microtomed using a Leica RM2165 microtome equipped with an LN21 cooling system and the morphology was then characterized by AFM and SEM. Before SEM analysis, selective solvent extraction of different phases was performed; the samples were dried overnight at 60°C under vacuum for 24h and then coated with a gold layer by plasma sputtering. SEM observations were conducted using a JEOL JSM 840 scanning electron microscope operated at 2 kV. For the AFM analysis, the tapping mode was used on a Dimension 3100 scanning probe microscope equipped with a Nanoscope IIIa control module. The pore size and distribution of the extracted samples were examined by mercury intrusion porosimetry (MIP) (AutoPore IV 9500) and the volume median diameter is used to characterize the pore size. The surface tension = 0.485 N/m and contact angle 140° were used for all samples. The detailed information for using MIP to characterize porous polymers has been reported previously [23].

### 3. Results and discussion

#### 3.1 Interfacial tension and rheology

The interfacial tensions of different polymer pairs were examined and are listed in Table 1. The interfacial tension of PLA/PE was measured directly by the breaking thread method as described previously [24]. The interfacial tensions of PE/PS, PLA/PS and PE/SEBS were obtained from the literature [17, 18, 22, 25, 26]. As SEBS is essentially composed of PS and PE blocks and the interfacial tensions of PLA/PE are comparable, the interfacial tension of PLA/SEBS

is estimated to be close to that of PLA/PE. With the above analysis, and according to Harkins theory [27], the SEBS is expected to be driven into the HDPE phase after the melt blending of PLA/HDPE/SEBS owing to the much lower HDPE/SEBS interfacial tension.

Polymer pairs	Interfacial tension $\gamma$ (mN/m)
PLA/PE	$5.0 \pm 0.49$
PE/PS	$4.9\pm0.6$
PLA/PS	5.2*
PE/SEBS	0.72
PLA/SEBS	$pprox\gamma_{ m PLA/PE}$

Table 1. Interfacial tensions between different polymers at 200°C (PE/SEBS at 195°C)

\* Averaged from Ref. [17], [25], [26].

The rheological properties of the polymers are shown in Fig. 1. It can be seen from the figure that the complex viscosities of PLA and HDPE used in this study are comparable and significantly lower than that of the SEBS; the viscosity of the HDPE/SEBS (50/50) blend lies in between the viscosities of HDPE and SEBS as expected. The elastic modulus follows a similar trend as the complex viscosity. It should also be noted that even at very low angular frequency, the SEBS and HDPE/SEBS blend still present a high elastic modulus, indicating the presence of a yield stress which has been reported previously [28]. The time sweep was also performed for a period of 60 min to examine the thermal degradation of the polymers and it was found that the complex viscosities of HDPE and SEBS showed negligible changes at 220°C (Fig. S1 in the

Supporting Information). For the PLA, the complex viscosity decreased  $\sim 10\%$  and  $\sim 20\%$  at 200 and 220°C, respectively.



Figure 1. Complex viscosity and elastic modulus as a function of angular frequency at 200°C.

#### 3.2 Blend morphology and pore size

Fig. 2 ( $a \sim c$ ) shows the morphology of the PLA/HDPE/SEBS ternary blends of different volume fractions after extracting SEBS with cyclohexane. As can be seen from the images, the SEBS phase was located in the HDPE phase as expected and gradually formed a finer, second, interpenetrated network within the interconnected HDPE phase as the SEBS concentration increased. The phase identification was further confirmed by removing the PLA phase in the blend with volume fraction 50/25/25 (Fig. 2 *d*). Meanwhile, the hierarchically porous materials were successfully generated and the pore sizes were determined by MIP. The selective extraction of SEBS results in pores with a diameter of 438 nm and the removal of the PLA leads to larger pores of 3.3 µm. The continuities of PLA and SEBS in the different ternary blends were also examined to demonstrate the interconnectivity of the PLA and SEBS phases (Table S1 in the Supporting Information). It is not surprising that the PLA phase maintains high continuity (> 97%) in all samples examined here since the volume fractions were all set at 50%. The continuity of SEBS is high even at low concentrations and reaches 88% continuity at 5% volume fraction. This is an exceptionally high level of continuity for such a low volume fraction of SEBS. However, it is not unreasonable if the following three factors are considered: 1) all the SEBS is confined to the HDPE phase which increases its effective concentration for continuity development; 2) in a low interfacial tension system such as PE/SEBS, the dispersed phase forms highly stable fibers during melt blending and a higher continuity is expected due to a thread-thread coalescence mechanism [18, 28]; 3) the extraction of SEBS was performed following the selective removal of the PLA phase which introduces an interconnected porosity into the samples and thus significantly increases the surface area of the samples contacting the solvent.





Pore Diameter (µm)

Figure 2. SEM and MIP results: a) ~ c): PLA/HDPE/SEBS (50/45/5, 50/35/15, 50/25/25, SEBS extracted by cyclohexane); d) PLA/HDPE/SEBS (50/25/25, PLA and SEBS extracted by chloroform); e) PLA/HDPE (50/50, PLA extracted by chloroform); f) HDPE/SEBS (50/50, SEBS extracted by cyclohexane); g) Mercury Intrusion Porosimetry (MIP) results.

The pore sizes of the porous materials resulting from the ternary blend of PLA/HDPE/SEBS (50/25/25) were compared to those of the binary systems HDPE/PLA (50/50) and HDPE/SEBS (50/50) (Fig. 2:  $d \sim g$ ). The size of the submicron scale pores resulting from the removal of the SEBS from the ternary system was found to be similar to that of the binary blend of HDPE/SEBS (438 vs. 392 nm), while the size of the larger pores by removing the PLA are much smaller in the ternary system as compared to the binary blend of HDPE/PLA (3.3 vs. 12.0 µm). This difference is significant and can be explained from two possible viewpoints. The addition of SEBS creates a very low interfacial tension system with HDPE and thus very fine microstructures. This results in a cascade-type effect where the finely dispersed HDPE imposes a finer structure on the PLA even though the HDPE/PLA interfacial tension remains high. A similar effect has already been reported for multiple phase systems where the compatibilization of one of the pairs results in significantly reduced phase sizes for the other components [29]. Another possible explanation for the phase size difference may be related to the high viscosity of the SEBS phase. It has been shown previously in binary co-continuous polymer blends that increasing the viscosity of either phase can reduce the coalescence, leading to a smaller phase size [30]. Compared to the HDPE in HDPE/PLA, the HDPE/SEBS "blend phase" in the ternary blend has a much higher viscosity (Fig. 1) which suppresses the coalescence of PLA during blending and thus results in a smaller PLA phase. In any case either, or both of the above explanations in combination, would tend to result in a reduced PLA phase size.

The microstructures of the blends were further examined by AFM under the tapping mode. In the ternary blend of PLA/HDPE/SEBS (50/25/25), as can be seen from Fig. 3 a, three phases can be observed; and according to the previous SEM results, the larger bright phase is the PLA phase while the two smaller phases are HDPE and SEBS. By further zooming in (Fig. 3 b and c), the HDPE and SEBS phase can be identified as the SEBS block copolymer that has a typical microphase-separated morphology. The characteristic morphology of SEBS was further confirmed by observing the pure SEBS (Fig. 3 d). A number of nano-inclusions with diameter 30~300 nm are also observed (Fig. 3 b and c), and they seem to be only located within the SEBS phase. The subinclusion phenomenon was also observed in other polymer blend systems, but the mechanism for their formation remains poorly understood [31-34]. In the present case, the nanoinclusions are considered to be PLA droplets since their smooth curvature and distinct interface between the inclusions and the surrounding SEBS indicates a high interfacial tension. They are probably entrapped in the SEBS phase owing to the high viscosity of SEBS during processing. Further evidence to confirm that the nano-inclusions are PLA is that such inclusions were not observed in the binary blend of HDPE/SEBS, but are observed in the PLA/SEBS blend (Fig. 3 e and f).



Figure. 3 AFM phase images: a, b, c) HDPE/PLA/SEBS (25/50/25) at different magnifications; d) pure SEBS; e) HDPE/SEBS (50/50); f) PLA/SEBS (50/50).

It is worthy to stress that SEBS preserves its microphase-separated morphology after melt blending (Fig. 3 *c vs. d*). Since copolymers with degradable blocks have been synthesized and used to generate meso-porous unimodal polymeric materials [35], the present systems also provide a novel promising avenue to fabricate hierarchically macro-meso porous materials providing the C block in the C-B-C copolymer can be designed to be removed from the system.

## 3.3 Control of the pore size by annealing

In the case of an application field such as tissue engineering, the optimal pore size of the scaffold to host the cell growth ranges from several to hundreds of microns depending on cell type [12]. In order to examine the potential of the current system to achieve larger pore sizes, annealing was undertaken. This strategy has been successfully used for unimodal porous polymers generated from single co-continuous polymer blends. It has been shown that the pore size can be controlled over two orders of magnitude from submicron to hundreds of microns [17, 19, 21, 22, 30, 36, 37] by varying annealing temperature and time. Fig. 4 shows the pore size evolution for the ternary PLA/HDPE/SEBS (50/25/25) blend annealed at 200°C for a period of 60 min (also see Fig. S2 in the Supporting Information). The pore sizes of the continuous PLA and SEBS phases grew quickly during the first 10 min from 3.3 to 8.4 µm and from 438 to 702 nm respectively after which the growth rates gradually decreased and very limited pore size increments were observed during the last 30 min (11.4 to 12.4 µm for larger pores and 959 to 1080 nm for smaller pores). These results indicate that the coalescence of these continuous phases was supressed. In fact the results in Fig. 4 resemble the coarsening profile of a compatibilized co-continuous binary system [38]. Non-compatibilized co-continuous systems typically follow a linear profile for phase growth [30, 38]. The different coarsening profiles during annealing can be explained by the balance between a capillary pressure effect and capillary instability phenomena [38].



Figure 4. Pore size evolution for the ternary blend (PLA/HDPE/SEBS 50/25/25) annealed at 200°C for a period of 60 min

An important factor to consider in the case of dual-continuous ternary polymer blends is the presence of two interfaces and the mutual effect of these interfaces on each other during the annealing process. For example, at the larger scale, the growth of the PLA phase, which is controlled by a capillary instability mechanism between PLA/HDPE, must be affected by the presence of SEBS and its effect on HDPE. In this way the very low interfacial tension between HDPE and SEBS has a cascade effect on the PLA/HDPE phase growth. Thus, although the PLA/HDPE system is a high interfacial tension, PLA phase growth shows a behavior that is similar to that of a partially compatibilized system.

Veenstra *et al.* reported a limited non-linear coarsening process for long time annealing in cocontinuous polymer blends and they attributed the slow-down or even cessation of the phase growth to the high viscosity, more importantly, the yield stress originating from the physical cross-links of the SEBS copolymer phases [39, 40]. In this context, Elmendorp proposed an approximation to explain the effect of a yield stress on limiting the breakup of a polymer thread within another polymer matrix [41]. In that process, the breakup is driven by the pressure difference along the distorted thread. The thread will not even break up for the systems where the pressure difference cannot overcome the yield stress. This is also a potential explanation for the non-linear coarsening behavior results in this work since both SEBS and the blend of HDPE/SEBS (50/50) show high viscosities and yield stresses at the low shear rates (Fig. 1) associated with annealing. In other studies, Macosko and co-workers also observed an initial linear growth followed by a slower coarsening rate in different binary blend systems of polyethylene/polystyrene, polypropylene/polystyrene and polystyrene/styrene-acrylonitrile [42, 43]. In their model, they consider that the excess interface free energy that drives the coarsening process is proportional to both interfacial area and interface curvature and the decrease in the coarsening rate is owing to the reduction of the interface curvature during annealing with respect to the viscous force.

The blend of PLA/HDPE/SEBS with a volume fraction of 50/40/10 was also examined using the annealing conditions of 220°C and 60 min. The smaller pore size in this ternary system remains the same at 1.3 µm while the larger pore size was doubled compared to the blend of 50/25/25 (30.9 *vs.* 16.5 µm) under the same conditions (Fig. 5: *a*, *b* and d). Using the mutually dependent interfacial argument developed above, the reduction of the interfacial area between HDPE/SEBS with a decreasing amount of SEBS would be expected to reduce the "cascade effect" between the interfaces of different scales. This would lead to a higher coarsening rate of the PLA phase. It is less likely, but also possible, that the increased PLA coarsening could also be explained by the reduction in the yield stress and viscosity of the HDPE/SEBS system owing to the lower

concentration of SEBS. By increasing the PLA phase to 60%, while maintaining the volume ratio of HDPE/SEBS (i.e., HDPE/PLA/SEBS 60/32/8), the larger pore diameter further increases to 70  $\mu$ m without notably affecting the smaller pore size (increased to 1.38  $\mu$ m) (Fig. 5: *c* and d). This increment is mainly due to a composition effect. The above observation also indicates that the composition has a significant effect on the phase size for the high interfacial tension system, but has little influence in the case of low interfacial tension, which has been demonstrated previously [18, 21]. The continuity of the PLA and SEBS phases were also examined for all the ternary blends after annealing and was found to be 102 ~ 105%.



Figure 5. Morphology of the annealed ternary blends PLA/HDPE/SEBS with volume fractions: a) 50/25/25, b) 50/40/10, and c) 60/32/8; d) pore size distribution of the blends after anealed at 220°C for 60 min and the small pore region is further shown in the inserted image.

## 4. Conclusion

We have demonstrated a novel technique to prepare dual-continuous hierarchically porous polymers with two distinct pore size scales from an A/B/C-B-C ternary polymer blend. PLA/HDPE/SEBS was used as a model system and after extraction of PLA and SEBS, hierarchically porous HDPE was generated with a large pore size scale of several microns and a smaller pore size of hundreds of nanometers. By varying the composition in annealing, the size of the larger pores can be tailored independently of the smaller ones. With the conditions used in this study, the smaller pores can be maintained constantly at around 1.3  $\mu$ m while the larger pores can be controlled from 16.5 to 70  $\mu$ m, a 4-fold difference, with the potential to increase even more at longer annealing times. This strategy provides a promising technique to fabricate fully interconnected dual-continuous porous materials of highly controlled microstructure.

#### Acknowledgment

The authors would like to thank Sylvie St-Amour from FPInnovations for the assistance in the MIP tests and Willard McLean and Yonghua Zhou from Kraton for providing the SEBS and the information on the polymer. Jun Wang would like to acknowledge the China Scholarship Council (CSC) for a scholarship. Benoît H. Lessard would like to thank the Natural Sciences and Engineering Research Council (NSERC) for a scholarship.

## References

[1] Bruck H. Implantable Biomedical Devices and Biologically Inspired Materials. In: Sharpe WN, Jr.,

editor. Springer Handbook of Experimental Solid Mechanics: Springer US, 2008. pp. 891-928.

- [2] Lakes R. Nature 1993;361(6412):511-515.
- [3] Godin B, Tasciotti E, Liu XW, Serda RE, and Ferrari M. Accounts of Chemical Research 2011:44(10):979-989.
- [4] Wang D-W, Li F, Lu GQ, and Cheng H-M. Carbon 2008;46(12):1593-1599.
- [5] Hasegawa G, Morisato K, Kanamori K, and Nakanishi K. Journal of Separation Science 2011;34(21):3004-3010.
- [6] Lin Y-G, Hsu Y-K, Chen S-Y, Chen L-C, and Chen K-H. Journal of Materials Chemistry 2010;20(47):10611-10614.
- [7] Li Y, Fu ZY, and Su BL. Advanced Functional Materials 2012;22(22):4634-4667.
- [8] Yun H-s, Kim S-e, and Hyeon Y-t. Chemical Communications 2007;0(21):2139-2141.
- [9] Roohani-Esfahani SI, Lu ZF, and Zreiqat H. Materials Letters 2011;65(17-18):2578-2581.
- [10] Ko Y-G, Kawazoe N, Tateishi T, and Chen G. Journal of Biomedical Materials Research Part B: Applied Biomaterials 2010;93B(2):341-350.
- [11] Li X, Wang X, Chen H, Jiang P, Dong X, and Shi J. Chemistry of Materials 2007;19(17):4322-4326.
- [12] Yang SF, Leong KF, Du ZH, and Chua CK. Tissue Engineering 2001;7(6):679-689.
- [13] García Cruz DM, Gomes M, Reis RL, Moratal D, Salmerón-Sánchez M, Gómez Ribelles JL, and
- Mano JF. Journal of Biomedical Materials Research Part A 2010;95A(4):1182-1193.
- [14] George PA, Quinn K, and Cooper-White JJ. Biomaterials 2010;31(4):641-647.
- [15] Singh R, Lee PD, Jones JR, Poologasundarampillai G, Post T, Lindley TC, and Dashwood RJ. Acta Biomaterialia 2010;6(12):4596-4604.
- [16] Dorj B, Park J-H, and Kim H-W. Materials Letters 2012;73(0):119-122.
- [17] Sarazin P and Favis BD. Biomacromolecules 2003;4(6):1669-1679.
- [18] Li JM, Ma PL, and Favis BD. Macromolecules 2002;35(6):2005-2016.
- [19] Sarazin P, Roy X, and Favis BD. Biomaterials 2004;25(28):5965-5978.
- [20] Sarazin P and Favis BD. Polymer 2005;46(16):5966-5978.
- [21] Yuan ZH and Favis BD. Biomaterials 2004;25(11):2161-2170.
- [22] Virgilio N, Sarazin P, and Favis BD. Biomaterials 2010;31(22):5719-5728.
- [23] Li J and Favis BD. Polymer 2001;42(11):5047-5053.
- [24] Elemans PHM, Janssen JMH, and Meijer HEH. Journal of Rheology 1990;34(8):1311-1325.

[25] Virgilio N, Desjardins P, L'Esperance G, and Favis BD. Macromolecules 2009;42(19):7518-7529.

[26] Biresaw G and Carriere CJ. Journal of Polymer Science Part B: Polymer Physics 2002;40(19):2248-2258.

- [27] Torza S and Mason SG. Journal of Colloid and Interface Science 1970;33(1):67-83.
- [28] Veenstra H, van Lent BJJ, van Dam J, and de Boer AP. Polymer 1999;40(24):6661-6672.
- [29] Ravati S and Favis BD. Polymer 2010;51(16):3669-3684.
- [30] Yuan ZH and Favis BD. Aiche Journal 2005;51(1):271-280.
- [31] Favis BD and Chalifoux JP. Polymer 1988;29(10):1761-1767.
- [32] Pagnoulle C and Jerome R. Polymer 2001;42(5):1893-1906.

[33] Martin P, Maquet C, Legras R, Bailly C, Leemans L, van Gurp M, and van Duin M. Polymer 2004;45(10):3277-3284.

- [34] Le Corroller P and Favis BD. Polymer 2011;52(17):3827-3834.
- [35] Pitet LM, Amendt MA, and Hillmyer MA. Journal of the American Chemical Society 2010;132(24):8230-8231.
- [36] Bramfeldt H, Sarazin P, and Vermette P. Journal of Biomedical Materials Research Part A 2009;91A(1):305-315.
- [37] Yao DG, Zhang W, and Zhou JG. Biomacromolecules 2009;10(5):1282-1286.
- [38] Yuan ZH and Favis BD. Journal of Polymer Science Part B-Polymer Physics 2006;44(4):711-721.
- [39] Veenstra H, Van Dam J, and de Boer AP. Polymer 2000;41(8):3037-3045.
- [40] Veenstra H, Van Dam J, and de Boer AP. Polymer 1999;40(5):1119-1130.
- [41] Elmendorp JJ. Polymer Engineering & Science 1986;26(6):418-426.

[42] Pyun A, Bell JR, Won KH, Weon BM, Seol SK, Je JH, and Macosko CW. Macromolecules 2007;40(6):2029-2035.

[43] Lopez-Barron CR and Macosko CW. Soft Matter 2010;6(12):2637-2647.