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Characterizing co-continuous high density polyethylene/polystyrene blends

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Abstract

The lack of adequate characterization techniques has been a hindrance to the effective exploitation and study of co-continuous morphologies in polymer blends. In this paper we prepare co-continuous blends of high density polyethylene/polystyrene in order to compare various microstructural characterization techniques. The influence of a triblock copolymer interfacial modifier, hydrogenated styrene–ethylene–butadiene–styrene on the system has also been investigated. The surface area and pore dimensions of the blend system after solvent extraction of one of the phases have been measured using the BET nitrogen adsorption technique and mercury porosimetry, respectively. Image analysis was also carried out as a third source of microstructural information. It is shown that mercury porosimetry can lead to erroneous information while the BET method appears to be both rapid and consistent with SEM observation. The specific surface area of the compatibilized co-continuous blend system is five fold higher than that of its non-compatibilized counterpart, while the pore diameter of the extracted compatibilized blend is reduced five fold. Using the BET technique, it is possible to generate an emulsification curve in the co-continuous region, demonstrating the efficacy of the interfacial modifier in this complex system. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer blend; Co-continuity; Characterization

1. Introduction

The blending of two or more polymers to form a polymer blend is now an established route to developing new polymeric materials [1–5]. Most polymer blends are immiscible due to thermodynamic reasons [6,7], essentially related to the negligible entropy, and unfavorable enthalpy of mixing. Consequently, polymer blending usually leads to a heterogeneous system with a multiphase morphology. In a two phase blend, at low concentration, the predominant morphology is of the dispersed droplet/matrix type. The further addition of the minor phase will lead to a percolation point, and at higher concentrations phase inversion eventually occurs. At that point, the two immiscible phases co-mingle in such a way that each phase remains continuously connected throughout the bulk of the blend. This morphological structure is called dual phase continuity or co-continuity [8–11]. Solvent extraction of one of the components of a co-continuous blend results by definition in 100% removal.

Polymer blends with a co-continuous structure are of special interest for many types of applications, such as blends with barrier properties, conductive polymers and impact resistant materials [12–14]. The microstructure of the network is a critically important physical characteristic of such materials. Conventionally, for the droplet/matrix morphology, SEM combined with image analysis is an adequate approach to measure the domain size and distribution of the dispersed phase [15]. However, it becomes laborious at best and impossible at worst to examine the microstructure in the region of co-continuity by such a method. This is easily understood since the image analysis approach is based on the analysis of two-dimensional photomicrographs, while co-continuity is a complicated three-dimensional interpenetrating and intertwining structure. The lack of adequate characterization techniques has been a hindrance to the effective exploitation and study of co-continuous morphologies in polymer blends.

In this paper the BET method and mercury porosimetry will be compared as characterization techniques for analyzing co-continuous morphologies. Using the most appropriate technique, the efficacy of hydrogenated styrene–ethylene–butadiene–styrene (SEBS) copolymer

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Table 1
Characteristics of materials

	Polystyrene	Polyethylene	SEBS[a]
M_w	215,000	79,000	S = 7500, EB = 35,000
M_n	100,000	24,000	
Melt index (g/10 min)	8.0[b]	4.0[c]	–
Density (20°C) (g/ml)	1.04	0.962	1.000
Density (200°C) (g/ml)	0.974	0.754	–
Supplier	Dow	Dow	Shell

[a] 30%(wt) polystyrene.
[b] 200°C/5.0 kg.
[c] 190°C/2.16 kg.

interfacial modifier for the high density polyethylene/polystyrene (HDPE/PS) co-continuous blend system will also be investigated.

2. Experimental

2.1. Materials

The materials used in this study were PS (MFI = 8.0 g/10 min), HDPE (MFI = 4.0 g/10 min) and a hydrogenated tri block copolymer (styrene-ethylene-butadiene-styrene, SEBS containing 30 wt% polystyrene) as interfacial modifier. Characteristic properties of HDPE, PS and SEBS are given in Table 1.

2.2. Sample preparation

The above materials were dry blended and dried under vacuum at 90°C overnight. A typical blending experiment consists of the following steps. With the temperature of the mixing chamber initially set at 195°C and blades turning at 50 rpm, the resin mixture was fed into the chamber. Once all of the resin was added, the blend was allowed to mix for 5 min under a constant flow of dry nitrogen. Next, the melt was rapidly transferred to a press at 195°C under very low pressure for 2 min. The compression molded sample was held in the hydraulic press under the same pressure until the sample had cooled down to room temperature. Finally, the sample was extracted with tetrahydrofuran (THF) to remove the polystyrene phase.

2.3. Microscopy

Plane surfaces were prepared for each specimen using a microtome equipped with a glass knife. While cutting, the samples were held below −150°C to minimize surface deformation. The microtomed surfaces were coated with gold and palladium, and observed under a Jeol JSM 840 SEM at 10 and 15 kV.

2.4. BET measurement

A flowsorb 2300 BET instrument was used to measure the surface area of the specimen. Prior to testing, a given amount of nitrogen was introduced to the instrument through a septum to calibrate the system. Sample testing was conducted at liquid nitrogen temperature. In contrast to the conventional BET nitrogen adsorption technique, which requires vacuum apparatus, a dynamic BET technique [16,17] which does not use vacuum was employed in this study. The gas mixture, which is composed of nitrogen and helium, continuously passes through the sample cell. Nitrogen gas, as an adsorbate, flows into the sample chamber, and is adsorbed on the adsorbent (extracted blends where PS phase was removed), at the liquid nitrogen temperature. When the sample cell is immersed into and removed from the liquid nitrogen bath, adsorption and desorption of nitrogen gas, respectively, occur on the sample surface. The change in effluent gas composition during adsorption and desorption is sensed by a thermal conductivity detector. The BET technique measures the total volume of nitrogen gas adsorbed on the surface. The volume of gas required to form an adsorbed monomolecular layer, is estimated using Eq. (1) below [18],

$$\frac{p}{p^0\left[\mathrm{v}\left(1-\left(\frac{p}{p^0}\right)\right)\right]}=\frac{1}{\mathrm{v}_\mathrm{m}c}+\frac{c-1}{\mathrm{v}_\mathrm{m}c}\frac{p}{p^0}, \tag{1}$$

where, v_m is the volume of gas (at standard temperature and pressure (STP)) required to form an adsorbed monomolecular layer, v is the volume (STP) of gas adsorbed at experimental pressure, p. p^0 is the saturation pressure, i.e. the vapor pressure of liquefied gas at the adsorbing temperature and c is a constant related to the energy of adsorption.

The determination of surface area from the BET theory is a straightforward application of Eq. (1). Fig. 1 shows the experimental curves of the multiple point method (use of several experimental pressures) for three different HDPE/PS/SEBS blends with PS and SEBS extracted. A plot of $p/[p^0(\mathrm{v}(1-(p/p^0))]$ versus p/p^0 yields a straight line with the slope $(c-1)/(\mathrm{v}_\mathrm{m}c)$ and intercept $1/(\mathrm{v}_\mathrm{m}c)$. If $c \gg 1$, the intercept is assumed to vanish and then Eq. (1) reduces to:

$$\mathrm{v}_\mathrm{m}=\mathrm{v}(1-(p/p^0)). \tag{2}$$

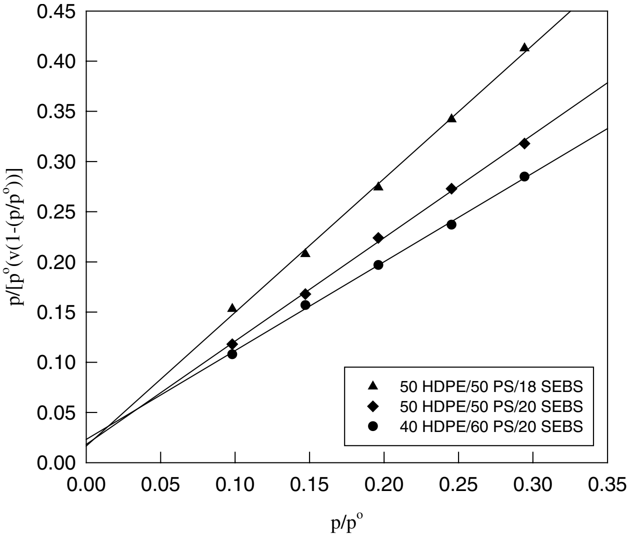

Fig. 1. BET multiple point method for the extracted ternary blend systems.

This simplified equation allows for the estimation of v_m using a single experimental pressure (single point method). The surface area, S, of the sample is then calculated from

$$S = v_m Na/V_M, \tag{3}$$

where, N is Avogadro's number, a is the area of one adsorbed nitrogen molecule (16.2×10^{-20} m^2), and V_M is the molar volume of the gas. The single point method offers the advantages of simplicity and speed with little loss in accuracy. The c value obtained in this study is 58, confirming the condition of $c \gg 1$ and that the use of the single point method approach is justified.

In order to obtain the morphological parameters (surface area and pore diameter) in the co-continuous region, it is assumed that: (1) the geometric shape of the pore is an interconnected cylinder; (2) the total volume of the pore is equal to that of the extracted phase; and (3) the total surface area is that of the pore wall. The total volume of the pore is

$$V = n\pi d^2 l/4, \tag{4}$$

where, n is the number of cylinders, d the diameter of the cylinder, l the length of cylinder and the total surface of the pore wall is

$$S = n\pi dl. \tag{5}$$

The pore diameter may be calculated from the following formula [19]

$$d = 4V/S. \tag{6}$$

2.5. Mercury porosimetry

The porosity of the samples was also estimated by mercury intrusion porosimetry (Poresizer 9320). This experimental method involves the evacuation of all gas from the volume containing the sample. Prior to the measurement, the samples were dried overnight under vacuum. Mercury is then introduced into a sample container while under vacuum. Finally, pressure is applied to force mercury into the porous sample. The mercury volume forced into the pores is usually monitored in a penetrometer, which is a calibrated precision stem of a glass cell, containing the sample and filled with mercury. As intrusion occurs, the mercury level in the stem varies. A means of monitoring both the applied pressure and the intruded volume are integral parts of all mercury porosimeters. The experimental data treatment is based on the Washburn equation [20]

$$Pr = -2\sigma \cos \theta, \tag{7}$$

where, P is the applied pressure, r is the radius of the pore, σ is the interfacial tension and θ is the contact angle. A mercury contact angle of 140° and an interfacial tension of mercury of 480 mN/m were used for all measurements. Analysis of the pore size and size distribution from mercury intrusion porosimetry is described in Section 3.

3. Results and discussion

3.1. System without interfacial modifier

Fig. 2 shows the SEM micrographs of HDPE/PS samples (PS from 30 to 60% volume fraction). The PS was extracted from the blends. The morphological structure changes distinctly with composition. With increasing PS composition, the dispersed phase becomes more and more continuous due to coalescence. An interpenetrating structure occurs at a concentration of 50% PS (confirmed by extraction experiments), and at this composition, it becomes difficult to distinguish the dispersed phase from the matrix. According to Mekhilef et al. [21], the morphology at this composition demonstrates a coarsening effect upon annealing, but maintains the co-continuous type morphology.

Table 2 lists both the pore size and specific surface area data of the samples analyzed by the BET technique. The specific surface area depends on the blend composition and ranges from 0.32 to 0.82 m^2/g. The pore size of the sample is in the dimension range of 5.4–7.3 μm, which depends on the amount of PS.

Table 3 lists the pore diameters of the extracted non-compatibilized network measured by the BET technique, mercury porosimetry and image analysis, respectively. It can be seen that the BET results correlate well with the

Table 2
Specific surface area and pore diameter of extracted non-compatibilized blends using the BET technique

	Specific surface area (m^2/g)	Pore diameter (μm)
HDPE/PS:70/30	0.32	5.4
HDPE/PS:60/40	0.43	6.2
HDPE/PS:50/50	0.63	6.4
HDPE/PS:40/60	0.82	7.3

Table 3
Pore size of non-compatibilized HDPE/PS blends measured by three different techniques

	Image analysis		BET technique (μm)	Mercury porosimetry (μm)
	d_v (μm)	d_n (μm)		
HDPE/PS:60/40	15.0	7.2	6.2	0.6
HDPE/PS:50/50	17.3	7.6	6.4	1.3

number average diameter measured by image analysis. The correlation of the BET data to the number average diameter is expected since the BET technique measures a surface area parameter (monolayer adsorption of nitrogen on the HDPE surface). The smaller diameter fibers will dominate the surface area generation. Mercury porosimetry, on the other hand, yields significantly smaller values. This is likely due to the creation of tiny pores in the material that result from the uneven distribution of the high operating pressure. Clearly, mercury porosimetry is not an effective technique for this non-compatible system.

3.2. System with interfacial modifier

Fig. 3 shows the SEM micrographs of HDPE/PS/SEBS networks (polystyrene concentration varied from 30 to 60% volume fraction). The PS is extracted from the blends. In contrast to Fig. 2 the morphological structure of compatibilized samples changes only slightly with composition. Nevertheless, as shown in Fig. 4 the specific surface area of the compatibilized network as measured by the BET technique increases with increasing PS composition. Comparing that data with Table 2, it can be seen that the specific surface area of the compatibilized 50HDPE/50PS

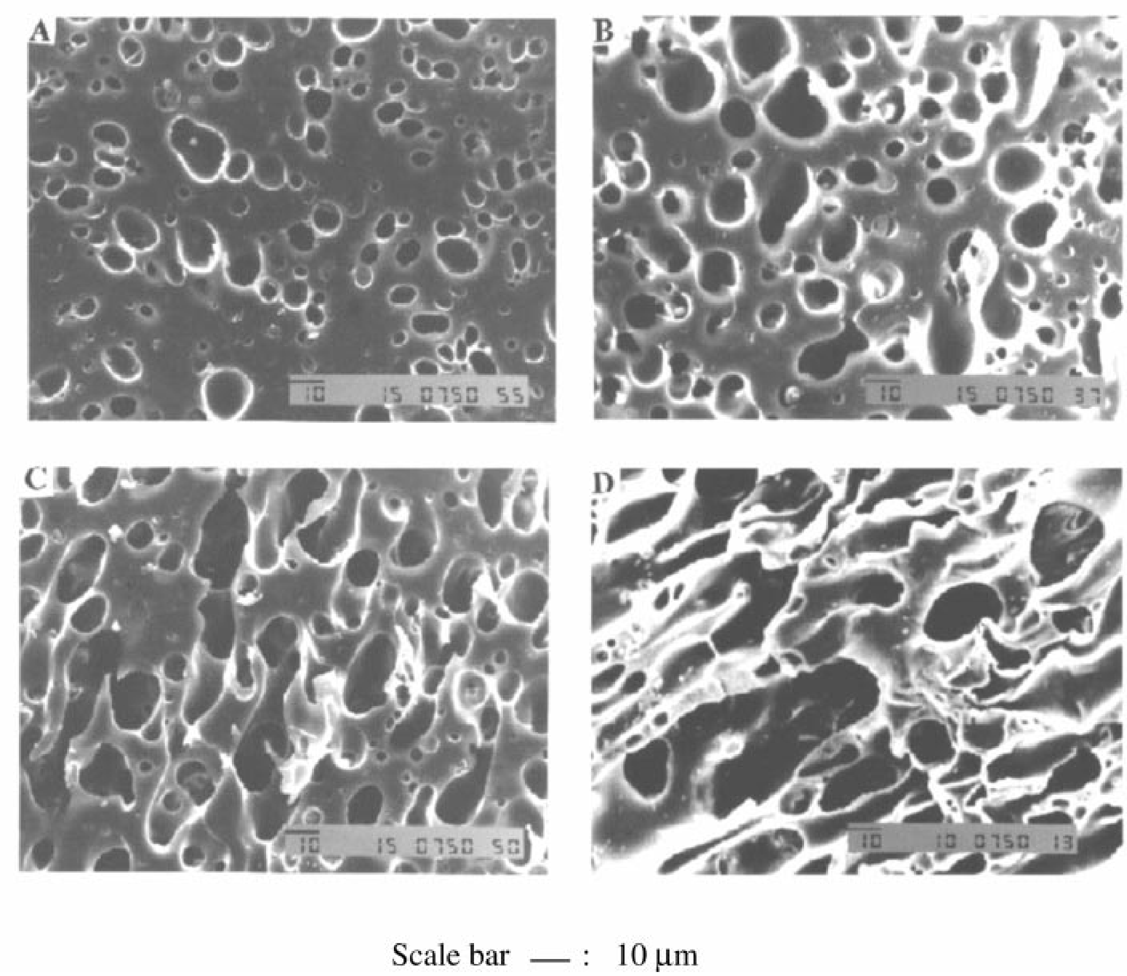

Fig. 2. Morphology evolution of non-compatibilized HDPE/PS blends with composition: (A) 30 PS/70 HDPE; (B) 40 PS/60 HDPE; (C) 50 PS/50 HDPE and (D) 60 PS/40 HDPE.

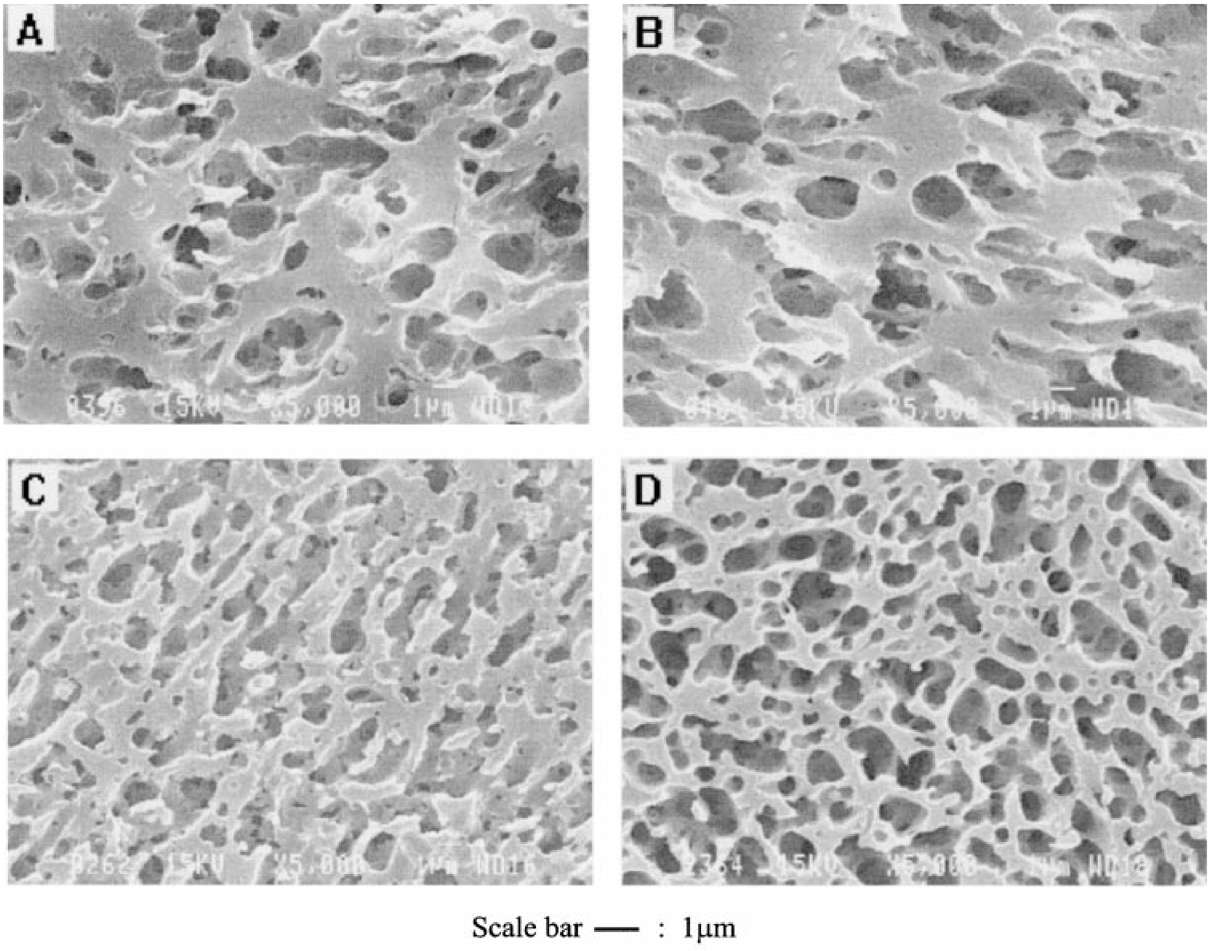

Fig. 3. Morphology evolution of compatibilized HDPE/PS blends with composition. 20% SEBS interfacial modifier based on the minor phase was added. (A) 30 PS/70 HDPE/20 SEBS; (B) 40 PS/60 HDPE/20 SEBS; and (C) 50 PS/50 HDPE/20 SEBS and (D) 60 PS/40 HDPE/20 SEBS.

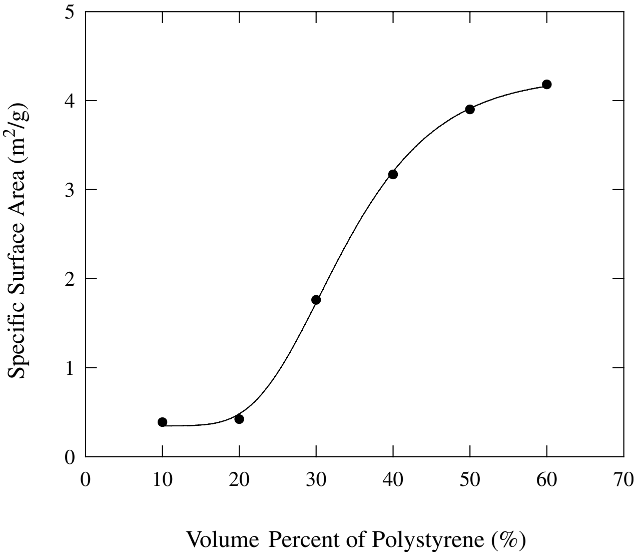

Fig. 4. Effect of PS composition on the specific surface area for compatibilized blends. 20% SEBS interfacial modifier based on the minor phase was added.

blend is five fold higher than its non-compatibilized counterpart. Also, Tables 2 and 4 demonstrate that the pore size of the compatibilized 50HDPE/50PS blend was reduced by a factor of five compared to the non-compatibilized blend. Table 4 also shows that a similar pore size is maintained with increasing PS composition for the compatibilized system which indicates that the porous volume increases without influencing pore diameter. Bourry and Favis [22] also found that addition of an interfacial modifier did not change the d_n pore size between 30 and 50% PS. The effect of composition on morphology is greatly suppressed by the presence of interfacial modifier. This observation is also consistent with previous work on the compatibilization of dispersed particles. The addition of interfacial modifier significantly reduces the interfacial tension between HDPE and PS [21]. The copolymer locates at the interface between HDPE and PS, and there is miscibility of styrene block units with polystyrene on the one hand, and the miscibility of the hydrogenated ethylyene-butadiene blocks with polyethylene, on the other. This effect allows for the stabilization of the phase morphology, and diminishes

Table 4
Pore size of extracted compatibilized blends measured by BET and mercury porosimetry, respectively

Pore size of extracted polymeric blend (μm)		
	BET nitrogen adsorption	Mercury porosimetry
HDPE/PS/SEBS:70/30/20	1.4	1.0
HDPE/PS/SEBS:60/40/20	1.5	1.2
HDPE/PS/SEBS:50/50/20	1.3	1.0
HDPE/PS/SEBS:40/60/20	1.3	1.5

coalescence. The morphology of this compatibilized blend is thus very stable, and only slight coarsening occurs even after a long annealing time [21].

The pore size and distribution of the samples were also estimated by mercury porosimetry, and all the pore size and distribution curves of the compatibilized samples are virtually identical. Fig. 5 illustrates the pore size and distribution curve from mercury porosimetry of the compatibilized 50HDPE/50PS blend. Table 4 compares the pore diameters of the compatiblilized blends as estimated by the BET technique and mercury porosimetry. It is interesting to note that the data from the two different techniques are similar. It seems that for a more homogeneous morphology, as is the case of compatibilized blends, mercury porosimetry can also be used to obtain morphological data. In such a case, the operational pressure is more evenly distributed in the system, and the risk of deforming the morphological structure during testing is reduced. Another possibility is that tiny pores are being created during the mercury porosimetry experiment, but since they are close to the actual pore sizes, they do not affect the measurement results. In any case, the overall results of this study clearly point to BET as the most reliable method. Although the micrographs in Fig. 3 are too complex to analyze with high accuracy, it can be seen that the SEM pore size is in a range consistent with the values reported in Table 4.

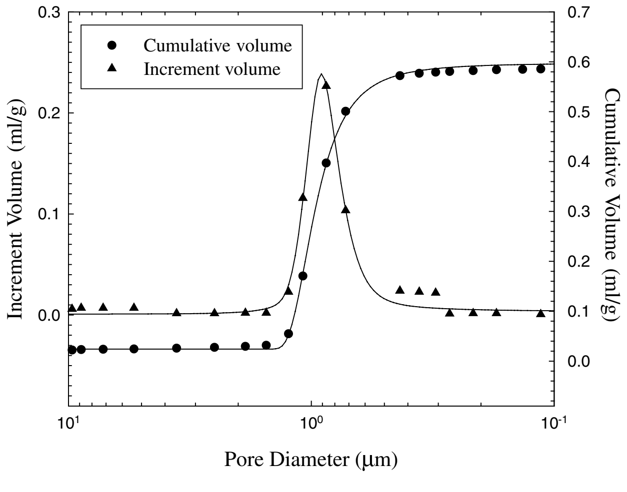

Fig. 5. Pore size distribution of the extracted compatibilized blend (50 HDPE/50 PS/20 SEBS) measured by mercury porosimetry.

3.3. Emulsification effect in the co-continuous region

Having determined the applicability of the BET technique, it was then desired to use it to examine the effect of an interfacial modifier on the microstructure of a co-continuous polymer blend. It is apparent from the previous discussion that the addition of SEBS as an interfacial agent results in a substantially finer network in the co-continuous region. The morphology evolution of the porous network (HDPE/PS: 50/50) due to the addition of interfacial modifier can be demonstrated through SEM observation by comparing Figs. 2C and 3C.

The relation of the specific surface area and pore size of the network as measured by BET to the amount of SEBS is depicted in Fig. 6 (HDPE/PS: 50/50). The specific surface area of the network increases sharply in the range of 3–10 parts of SEBS modifier (based on the amount of HDPE). However, the specific surface area of the network reaches a plateau value at about 15 parts of SEBS. The use of morphology data to study emulsification phenomena has been reported for matrix/dispersed phase morphologies in several different systems [23–26]. In those papers the dependence of the particle diameter with interfacial modifier concentration is taken as an indication of the efficacy of

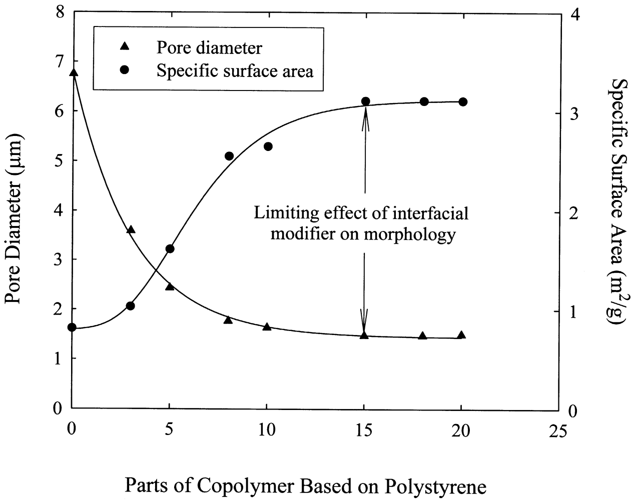

Fig. 6. Effect of copolymer compatibilizer concentration on the specific surface area and pore size of extracted co-continuous blends (HDPE/PS: 50/50). The amount of SEBS added is based on the PS phase.

the modifier in emulsifying the interface. So far, however there is little information reported on emulsification in the region of co-continuity, due to the difficulty of analyzing this type of complex morphology. The emulsification curve of the co-continuous region shown in Fig. 6 demonstrates that the tracking of surface area via the BET technique provides a powerful tool for analyzing the efficacy of interfacial modifiers at emulsifying co-continuous morphologies. The possibility now exists to study the relative efficacy of different modifiers and aspects such as areal density at the interface, modifier architecture and molecular weight on the emulsification of these morphologically complex systems. This subject will be studied in detail in upcoming work.

4. Conclusions

In this study, PS extraction followed by the use of a BET nitrogen adsorption technique is found to be an effective route to analyze the microstructure of highly continuous HDPE/PS polymeric blend networks. The specific surface area and the average pore size can be obtained in this way. It is shown that mercury porosimetry can lead to erroneous results. The emulsification of the co-continuous morphology with added SEBS interfacial modifier has also been studied quantitatively with the BET technique. It is shown that the tracking of surface area via BET provides a powerful quantitative tool for analyzing the efficacy of interfacial modifiers at emulsifying co-continuous morphologies.

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