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Miscibility of Branched Ethene Homopolymers with Iso- and Syndiotactic Polypropenes

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ABSTRACT: The melt miscibility of stereoregular polypropene with branched ethene homopolymers, prepared by Ni- and Pd-based catalysts, was investigated by means of transmission electron microscopy, atomic force microscopy, and differential scanning calorimetry. The number of branched C atoms per 1000 C atoms, referred to as degree of branching (DB), was varied from 6 to 112. Miscibility increases with increasing DB. Blends of branched ethene homopolymers and poly(ethene-*co*-1-octene) with isotactic (i-PP) and syndiotactic polypropylene (s-PP) were compared and show slightly improved miscibility for s-PP. For DBs of 98 and 112 partial miscibility with polypropene was found. The miscibility of polyethenes with longer branches resemble that of polyethene/1-octene copolymers, whereas short branched polyethenes behave more like polyethene/1-butene copolymers.

Introduction

Elastomeric ethene-*co*-1-olefin copolymers are blended together with polypropene (PP) in order to improve the impact resistance of PP.[1] It has been shown that highly compatible or partially miscible blends of i-PP with ethene-*co*-1-olefins exhibit attractive combinations of stiffness and toughness.[2−4] The compatibility and miscibility of polyolefin copolymers with PP depend on the molecular weight and strongly on the properties resulting from molecular microstructures, such as comonomer content, monomer structure, and comonomer distribution.[5−11] Several miscibility investigations of blends with copolymers synthesized using new types of single-site metallocene catalysts have been published.[12−14] These catalyst systems produce very uniform ethene-*co*-1-olefin copolymers with narrow molecular weight distribution ($M_w/M_n = 2$) and uniform comonomer incorporation.[15−17] It has been shown that i-PP exhibits a miscibility window with ethene-*co*-1-olefin copolymers.[18−22] The miscibility window was found for ethene/1-butene copolymers containing 88 wt % 1-butene and for ethene/1-octene containing 74 wt % 1-octene.[21,22] In contrast to i-PP, only partial miscibility was observed for syndiotactic polypropylene (s-PP). Yamaguchi and Miyata have shown that a ethene-1-hexene copolymer with a 1-hexene content of 57 mol % is miscible with i-PP but immiscible with s-PP.[23] For i-PP and s-PP a wide area of partial miscibility was observed, reaching from 1-olefin an incorporation in the copolymers of about 45 wt % up to 100 wt %. The area of partial miscibility becomes wider for poly-1-olefins with longer side chains.[12,13] For s-PP-blends partial miscibility was already observed for lower 1-olefin contents in the copolymer than for the corresponding i-PP blends.[12,13]

This study deals with the miscibility of high molecular weight, branched ethene homopolymers, synthesized by late transition metal catalysts, with i-PP and s-PP. From a synthetic point of view these branched polyethenes differ from the 1-olefin copolymers described above;[24,25] nevertheless, the short chain branching (mainly methyl, ethyl, propyl, and butyl branches) makes these polymers similar to ethene/1-olefin copolymers. Therefore, the aim of this paper is to compare the miscibility behavior of ethene/1-olefin copolymers with branched ethene homopolymeres. The bulk morphology of blends was observed by TEM and AFM. The mixing process of the branched polyethene with the highest miscibility was observed by investigating sandwich specimens annealed for different times.

Experimental Section

Materials. Highly branched ethene homopolymeres were synthesized by means of “chain walking” ethene homopolymerization using MAO-activated [diacetylbis(2,6-diisopropylaniline)palladium (methyl)(acetonitrile)]/(tetra(3,5-bis(trifluormethyl)phenyl) borate) as catalyst. Branched ethene homopolymeres with shorter side chains were synthesized using the MAO-activated catalyst system dibromo-[2,6-di-iso-Ph-DAD-(Me,Me)]nickel. A detailed description of the polymer synthesis is given elsewhere.[26] The characteristic data of the polymers are listed in Table 1.

Blend Preparation. PP blends with polyolefins of composition 70 wt %/30 wt % were prepared by mixing both components in a solution of xylene at 180 °C. The transparent hot solution was precipitated into cold acetone, filtered, and then dried in a vacuum oven for 2 days at 80 °C. The solvent free blends were then heated to 180 °C and annealed under vacuum for 5 h and then cooled from 180 °C down to room temperature using a cooling rate of 10 K min^{-1}.

Atomic Force Microscopy. AFM experiments were performed with a Nanoscope III scanning probe microscope. The height and phase images were obtained simultaneously while operating the instrument in the tapping mode under ambient conditions. Images were taken at the fundamental resonance frequency of the Si cantilevers which was typically around 300 kHz. Typical scan speeds during recording were 0.3−1 line/s using scan heads with a maximum range of 16 × 16 μm. The phase images represent the variations of relative phase shifts (i.e., the phase angle of the interacting cantilever relative to the phase angle of the freely oscillating cantilever at the resonance frequency) and are thus able to distinguish materials by their material properties (e.g., amorphous and crystalline polymers). The flat surfaces of the blend samples which were examined were obtained by cutting with a Diatome

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diamond knife at ≈ -120 °C using an ultramicrotome (Ultracut E, Reichert & Jung) equipped with a cryochamber.

Transmission Electron Microscopy (TEM). The TEM measurement were carried out with a LEO CEM 912 transmission electron microscope applying an acceleration voltage of 120 keV. The specimens were prepared using an ultramicrotome (Ultracut E, Reichert & Jung) equipped with a cryochamber. Thin sections of about 50 nm were cut with a Diatome diamond knife at −120 °C. The samples were stained with RuO_4.

Differential Scanning Calorimetry (DSC). DSC measurements were carried out with a Perkin-Elmer DSC 7 apparatus. The samples were cooled from the melt with a rate of 10 °C min^{-1} and then heated to 180 °C with a heating rate of 20 K/min.

Results and Discussion

Figure 1a shows the crystallinity of the branched polyethenes vs the degree of branching. The degree of branching (DB) is number of branched C atoms per 1000 C atoms. As expected, the crystallinity decreases from 60% for linear polyethene to nearly 0% for brPE112 (“112” means 112 branched C atoms per 1000 C atoms). Figure 1b,c shows a comparison between the branched polyethenes and ethene/1-olefin copolymers. It is interesting to see that the decrease of T_m and T_g of the branched polyethene is similar to the decrease shown for the ethene/1-olefin copolymers. For small DBs the branched PE behaves more like ethene/1-butene copolymers. For the highest degree of branching [brPE112] it resembles strongly on ethene/1-octene with high 1-alkene content. For blend studies branched ethene homopolymers and ethene/1-octene copolymers containing similar polyethene sequence length were selected. The miscibility of polyolefins is affected by the chain flexibility.[27,28] The chain flexibility is associated with glass temperature T_g. The similarity of the T_g values of brPE and the ethene/1-olefin copolymers indicates similar miscibility. From that point of view brPE112 should behave like a poly(ethene-*co*-1-octene) copolymer with high 1-octene content, whereas the other branched polyethens with low DB should resemble poly(ethene-*co*-1-butene).

AFM has been proven to be a powerful tool for the investigation of polymer blends. This method offers the possibility to distinguish between immiscible blends (phases divided by sharp interfaces) and miscible blends (no phases visible) but allows also the differentiation between partially miscible blends (mixed phases) and highly compatible immiscible blends (phases with irregular formed interfaces but without mixing of the polymers).[28]

Figure 2a shows the AFM phase-mode image of a s-PP/brPE6 (70/30 wt %) blend. s-PP forms the matrix and brPE6 the dispersed phase. Both polymers are crystalline. Therefore, the phase contrast between the phases is weak, but the phases can be clearly distinguished by the different lamellar morphologies of the polymers. The lamellaes of brPE6 are much thicker than the s-PP lamellae. The interface between the phases is sharp. The blend appears to be completely immiscible. Also, the blends with brPE4, brPE8, brPE11, and brPE31 were found to be immiscible. Figure 2b shows the 70/30 wt % blend based on brPE98. For this degree of branching the morphology of the blend has changed: The branched polyethene is nearly amorphous. The phases can be distinguished by the huge phase contrast between amorphous and crystalline material. The blend system is partially miscible in the melt. A clear indication for this behavior is s-PP lamellae growing into the brPE98 phase. This morphology was formed upon cooling from the melt, when the s-PP solved in the brPE98 phase crystallizes. In this case the surrounding s-PP matrix acts as a nucleating surface at the interface. Figure 2c depicts an AFM micrograph of the s-PP/brPE112 (70/30 wt %) blend. This blend is also partially miscible in the melt, but the miscibility is increased significantly when compared to that of the s-PP/brPE98 blend. The amount of s-PP solved in the brPE phase is higher, and it could be expected that the system is very near to a completely miscible blend system. After the

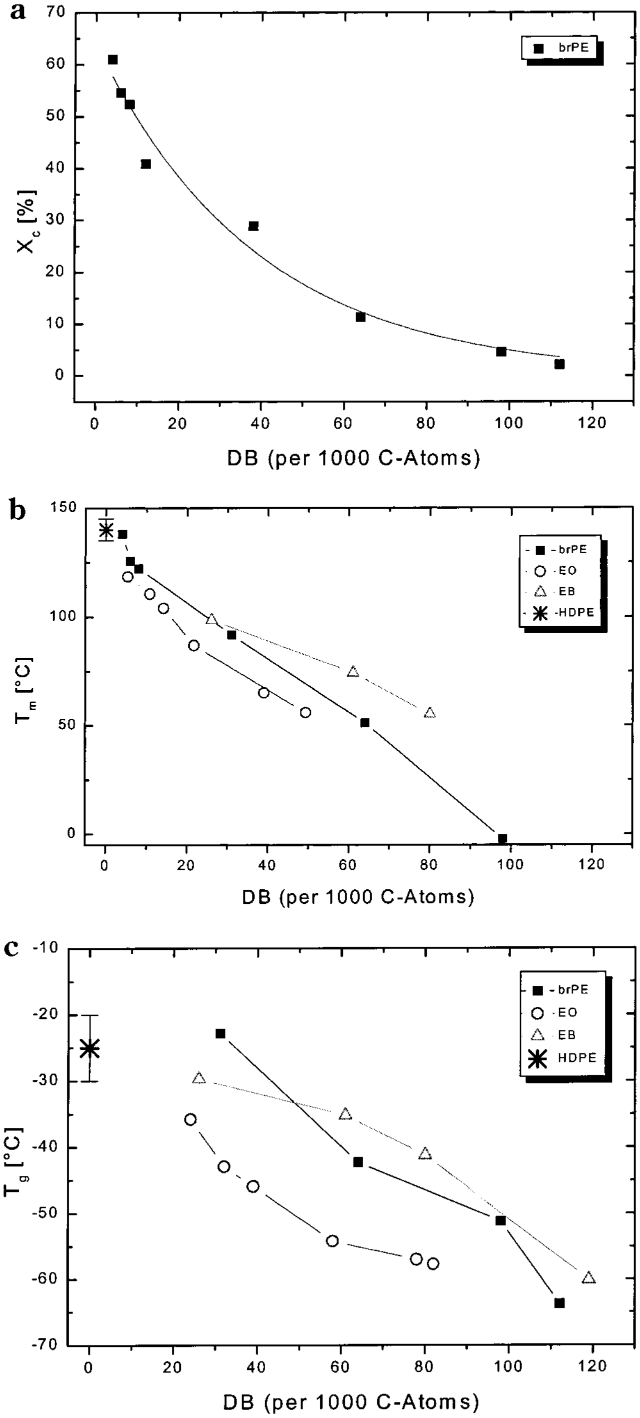

Figure 1. (a) Crystallinity of the branched polyethenes vs the degree of branching. (b, c) Comparison between T_m (b) and T_g (c) values of branched polyethenes and ethen-*co*-1-olefin copolymers.

Table 1. Data of the Polymers under Investigation

	M_n [g/mol]	M_w/M_n[a]	DB[b]	DB[b] eq 1	T_g[c] [°C]	T_m [°C]	X_c [%]	cat.
brPE 4	57 500	3.38	4	8		138	61	DHN[d]
brPE 6	39 800	4.17	6	12		125	55	DHN[d]
brPE 8	44 000	3.50	8	16		122	52	DHN[d]
brPE 11	30 300	2.90	11	22	−18	92	41	DHN[d]
brPE 31	$>10^7$	2.00	31	79	−42	51	29	DHN[d]
brPE 98	409 600	2.40	98	217	−51		5	DMN[e]
brPE 112	180 000	2.03	112	710	−63		2	DMPN[f]
PEO 55	105 100	2.1	69	819	−64			MBI[g]

[a] Determined by means of SEC (PE standards). [b] Determined by means of ^1H NMR and ^{13}C NMR. [c] Determined by means of DSC at a heating rate of 10 °C/min. [d] Dibromo-[2,6-di-iso-Ph-DAD(H,H)]nickel. [e] Dibromo-[2,6-di-iso-Ph-DAD(Me,Me)]nickel. [f] [Diacetyl-bis(2,6-diisopropylaniline)palladium (methyl)(acetonitrile)]/(tetra(3,5-bis(trifluormethyl)phenyl) borate). [g] *rac*-Dimethylsilylenbis(2-methylbenz-[*e*]indenyl)zirconium(IV) dichloride.

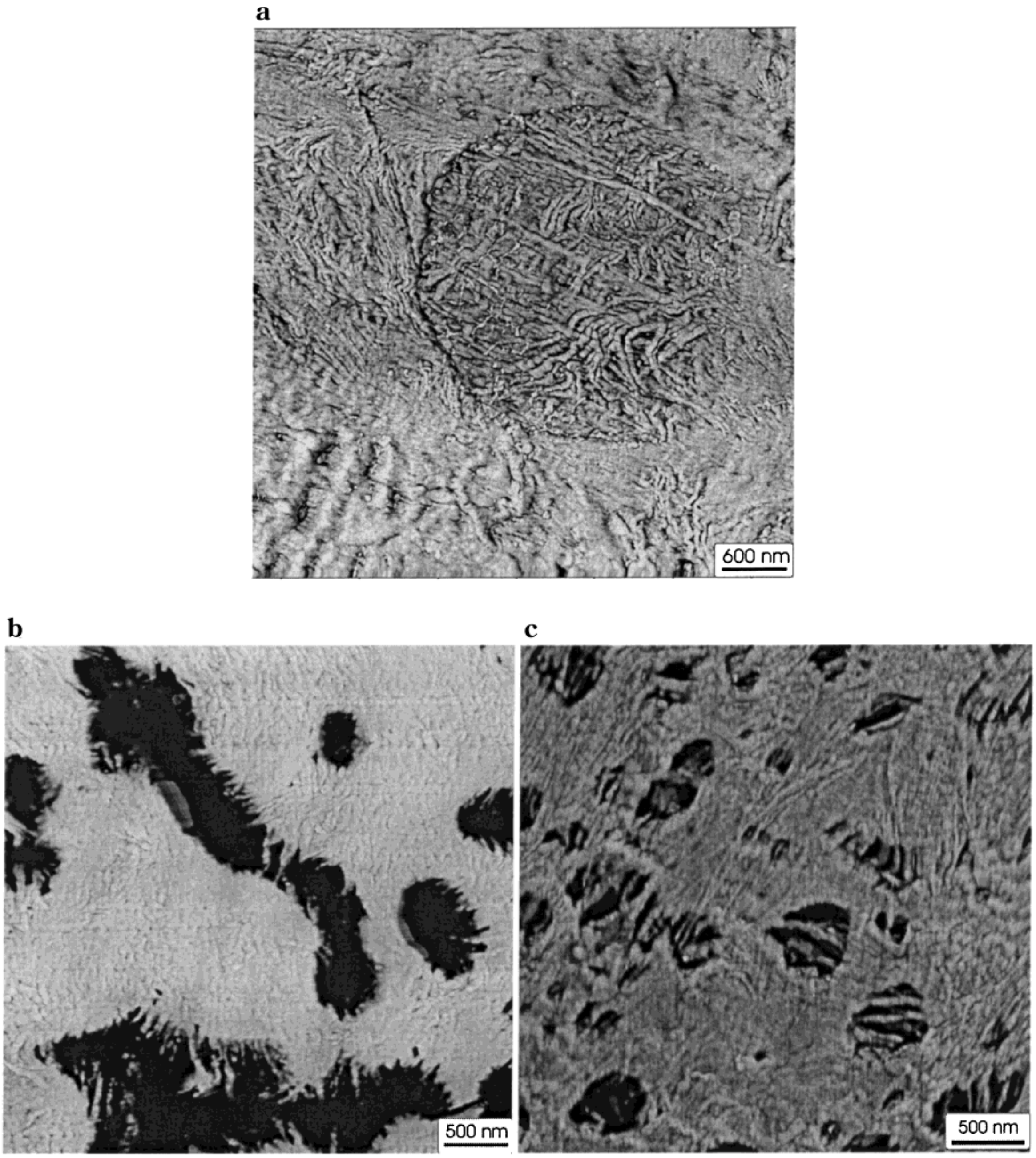

Figure 2. (a) AFM phase-mode image of the immiscible blend system 70/30 wt % s-PP/brPE6. (b, c) AFM phase-mode image of partially miscible 70/30 wt % s-PP/brPE98 blend (b) and of the blend with the highest miscibility s-PP/brPE112 (c).

crystallization large amounts of crystalline s-PP can be found inside the polyethene phases, mainly in the form of fibrils. In contrast to brPE98, the s-PP lamellae are able to grow through the whole phases. Although the molecular weight distribution for these branched polyethenes is relatively narrow (2.4 for brPE98/2.03 for brPE112), it should have an influence on the miscibility behavior. It is known that lower molecular weight polymers are more miscible than those with higher molecular weights.[28] Most likely poor partial miscibility

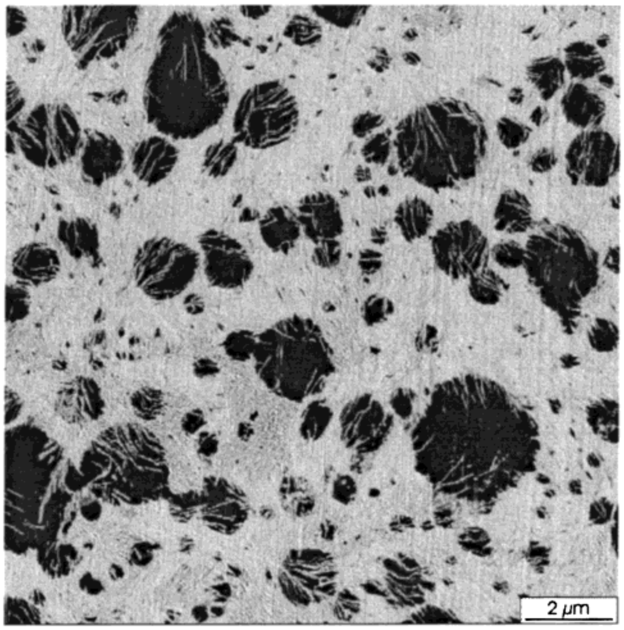

Figure 3. AFM phase mode image of the 70/30 wt % s-PP/PEO 55 blend.

means that only low molecular weight fractions were dissolved, and vice versa high partial miscibility means that even higher molecular weights fractions are able to mix.

Comparing the blends of s-PP and brPE98 and brPE112, a different miscibility behavior can be observed. Although the degree of branching is similar for both polymers, brPE112 shows a better miscibility in the melt than brPE98. The difference might be the result of two different catalyst systems used for the synthesis of the respective polymers. Using the catalyst DMN (dibromo-[2,6-di-iso-Ph-DAD(Me,Me)]nickel), short side chains [mainly methyl and ethyl] were formed. This catalyst was used for the synthesis of brPE98. The catalyst DMPN [diacetylbis(2,6-diisopropylaniline)palladium(methyl)(acetonitrile)]/(tetra(3,5-bis(trifluormethyl)phenyl)borate)] used for the synthesis of brPE112 results in high numbers of longer side chains (38 methyl, 23 ethyl, 2 propyl, 9 butyl, 3 pentyl, 35 hexyl or longer plus 3 branch of a branch).[26] As known, the miscibility of ethene-rich copolymers with i-PP or s-PP increases for a given degree of branching with the length of the side chain.[12,13] Therefore, it is interesting to compare the miscibility of the branched polyethene with s-PP with common s-PP/poly(ethene-*co*-1-octene) blends. As shown by Thomann et al., no miscibility window was found for the s-PP/poly(ethene-*co*-1-octene) system, but a maximal partial miscibility for blends with poly(ethene-*co*-1-octene) (PEO55) with 55 wt % 1-octene in the copolymer. Figure 3 shows the AFM micrograph of a s-PP/PEO55 (70/30 wt %) blend. The blend exhibits a miscibility with s-PP which is much better than the miscibility of brPE98, but very similar to brPE112, with large numbers of s-PP lamella inside of the ethene-*co*-1-octene phases. Especially the smaller phases, with a size similar to the phases of brPE112 shown in Figure 2b, exhibit a nearly identical morphology.

To discuss the relation between structure and miscibility of 1-olefine copolymers and branched polyethenes, it is not sufficient to compare only the number of branching points. As shown by Mäder et al.,[16] it is important to take the length and type of side chains into account. Equation 1 was found to give the best results (e.g., there is a clear correlation between T_g values and the degree of branching (SCBCmc).

$$\mathrm{SCBCmc} = (\mathrm{SC} + \mathrm{BC})/(1000\mathrm{MC}) \qquad (1)$$

with BC = number of branching points, SC = number of side chain C atoms, and MC = C atoms of the polyethene backbone. A simple calculation of the number of branching points of PEO55 with brPE98 and brPE112 gives incomparable results with the lowest number of branching points for PEO55. Weighting the type and length of the side chains with eq 1 gives a good explanation for different miscibility behavior of brPE98 and brPE112. Equation 1 gives comparable SCBCmc values of 710 for brPE112 and 819 for PEO55 and a significantly different SCBCmc of 217 for brPE98. This shows that PEO55 is very similar to brPE112 but differs significantly from brPE98. This difference is the result of a different catalyst system used leading to large amounts of long and branched side chains in brPE112 and mainly short side chains in brPE98 as determined by NMR. It can be concluded that the miscibility of branched polyethenes and poly(ethene-*co*-1-olefine) with s-PP is very similar, if the number and the type of side chains are taken into account correctly.

Partial miscibility could be observed by diffusion investigations at the interface of sandwich specimens. Figure 4 depicts AFM images of two-layer sandwich specimens of s-PP and brPE112 annealed in the melt for different times, cooled to room temperature, and cryosectioned with a microtome. Figure 4a shows the sandwich specimen after a annealing time of only 5 min. Nearly no diffusion is visible. After longer annealing times a diffusion of the branched polyethene in the s-PP can be observed. Figure 4b shows the morphology after an annealing time of about 10 h. The area of diffusion appears phase separated after cooling the sample to room temperature. This effects is caused by a demixing which appears upon slow cooling. Quenching experiments on similar samples have shown that the mixed interphase is homogeneous and could be frozen in without visible macrophphase separation.[12,13] Within the brPE112-rich phases s-PP fibrils can be observed. After an annealing time of 48 h the diffusion area has a thickness of about 55 μm (Figure 4c). A large number of small brPE112 phases can be found inside the s-PP layer. The amount of branched polyethene decreases with increasing distance from original interface, but it is relatively constant in the first 15 μm. It could be assumed that the amount of branched brPE112 found in this region is close to the maximum amount of brPE112 soluble with s-PP in the melt. From the size and the number of the brPE112 phases this maximum value could be calculated to about 20 wt % of brPE112. The increase of the thickness of the mixed interface is linear and found to be 1.1 ± 0.08 μm/h. In the right part of Figure 4c some spherulite boundaries were marked with white lines. Obviously, the brPE content in the center of the spherulite is significantly lower than in the exterior areas of the spherulite. This effect is caused by an exclusion of the brPE112 out of the spherulite during the crystallization. This exclusion leads to the formation of spherulite boundaries enriched with branched polyethenes and therefore to an mechanical weakening of the boundaries. To avoid this effect, the use of nucleating agents could be suggested.

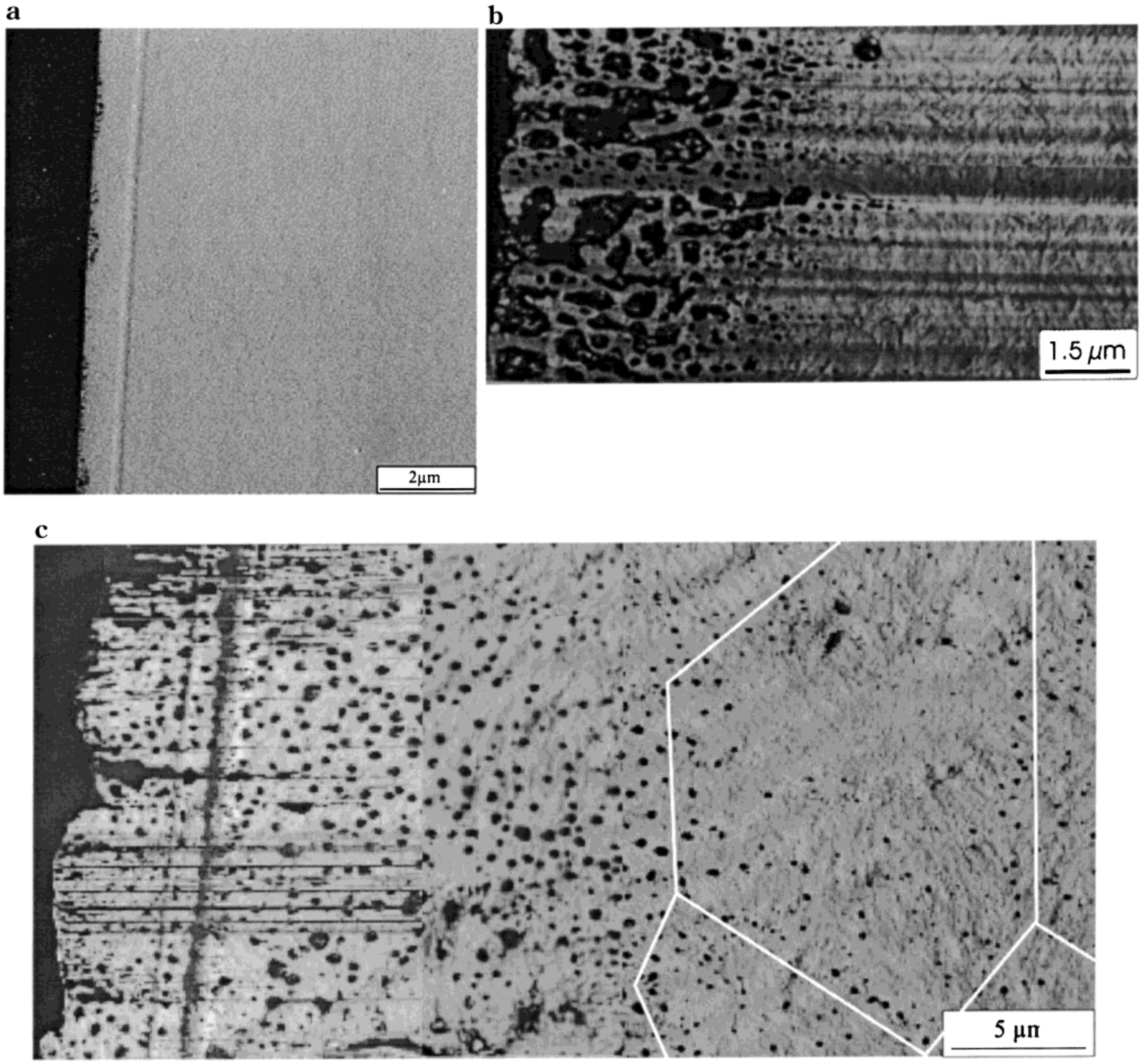

Figure 4. Sandwich specimens of brPE112 and s-PP annealed for different times at 180 °C: (a) annealing time (t_a) = 5 min, (b) t_a = 10 h, (c) t_a = 48 h.

Recent investigations have shown that the 1-olefin content in 1-olefin copolymers at which partial miscibility can be observed is lower for s-PP than for i-PP.[12,13] To see whether this is effect is also present for the branched polyethene, a 70/30 wt % blend of i-PP and brPE112 was investigated by TEM. Figure 5 shows the TEM image of this blend. It is also partially miscible, but the amount of i-PP included into the brPE112 phases is significantly lower than for s-PP. It resembles more on the miscibility behavior of the s-PP/brPE98 blend shown in Figure 2b. Therefore, it could be concluded that the difference in the miscibility behavior between s-PP and i-PP found for poly-1-olefins is also present in blends with branched polyethenes.

Conclusion

Highly branched ethene homopolymers with a controlled degree of branching represent a new family of elastomers of industrial significance. The miscibility behavior of the branched polyethenes was found to be similar to that of poly(ethene-*co*-1-olefins). With increasing number and length of the branches the miscibility increases. Partially miscible blends were found for branched polyethenes with a degree of branching of 98 and 112. The miscibility of brPE112 is significantly higher than that of brPE98 due to the different length of the branches: brPE112 exhibits large branches which makes it similar to poly(ethene-*co*-1-octene), whereas brPE98 resembles more on poly(ethene-*co*-1-olefins) with shorter branches. Similar to the behavior of poly(ethene-*co*-1-olefins), a slightly better miscibility with s-PP in comparison to i-PP was found for the degrees of branching under inverstigation. Because of the their compatibility and partially miscibility, s-PP and i-PP blend systems with branched polyethenes might be of greater technical importance in the future.

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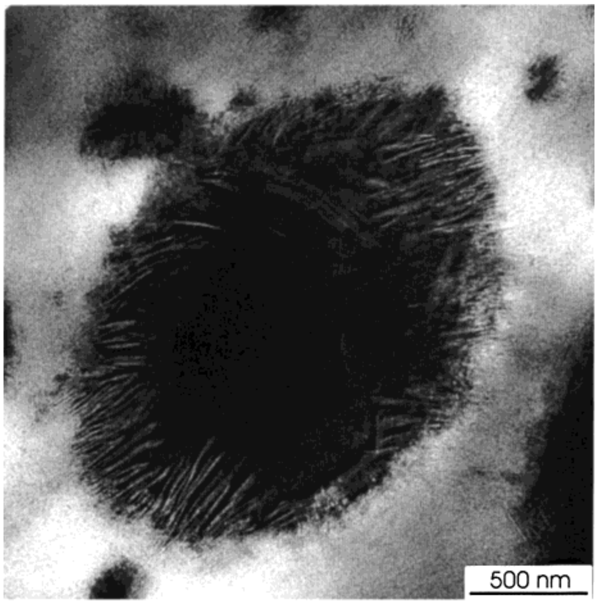

Figure 5. TEM image of a partially miscible 70/30 wt % i-PP/brPE112 blend.

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