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Influence of a low molecular weight anhydride on the morphology of PSU/PA-alloys

Piyada Charoensirisomboon[a], Martin Weber[b,*]

[a]National Metal and Materials Technology Center, 73/1 Rama VI Road, Rajdhevee, Bangkok 10400, Thailand
[b]BASF Aktiengesellschaft, Polymer Research Laboratory, Plastics ZKT-B1, Ludwigshafen D-67056, Germany

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Abstract

In order to develop a new polymeric material with a nice combination of high heat resistance, chemical resistance and flow, polysulfone (PSU)/polyamide blends have been investigated. The incompatibility of these polymers can be overcome by the addition of functionalized PSU, especially anhydride terminated PSU (PSU–PhA). Since PSU–PhA sometimes contains traces of low molecular weight compounds, the influence of such reactive impurities was investigated with phthalic anhydride (PhA) as model compound. Solvent extraction and electron microscopy results suggested that the amount of in situ created PSU–PA-copolymers is significantly reduced by the addition of PhA during the extrusion process resulting in a coarsening of the morphology. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Reactive blending; Emulsifier; Morphology

1. Introduction

Reactive compatibilization is very often used to obtain blends with desirable properties [1]. The process is based on in situ formation of block or graft copolymers at the interface between the different phases during melt mixing by coupling reactions of functionalized components [2–4]. The presence of copolymers at the interface is believed to play dual roles in promoting mixing [5–10]. One is to reduce the interfacial tension and hence to promote droplet breakup. The other is to provide the steric hindrance between dispersed particles and thus to suppress droplet coalescence.

For use in the reactive compatibilization, polymers must offer reactive functional groups. Generally, one component polymer contains reactive groups inherent in chains, such as polyamide (PA), while the other has no inherent functionality. Reactive groups can be incorporated into the other constituent by chemical modification. This chemical modification may be carried out in solution, in melt, or even in solid state [11–13].

Recently, polysulfone (PSU)/PA blends have been studied to develop a new polymeric material with a nice combination of high heat resistance, chemical resistance, and flow [14–18]. The incompatibility of these polymers can be overcome by the addition of functionalized PSU, especially anhydride terminated PSU (PSU–PhA). The coupling reaction between the amine groups of PA and phthalic anhydride (PhA) of PSU–PhA during melt mixing forms the PSU–PA copolymer at the interface [16]. However, as a consequence of the synthesis procedure, it has been found that PSU–PhA sometimes contains traces of free low molecular weight anhydride as impurity. This free anhydride may participate in the coupling reaction during melt processing and affect the obtainable morphology of the blends. Possible coupling reactions taking place during melt processing of PA/PSU–PhA containing small amounts of free low molecular weight anhydride are schematically shown in Fig. 1. If the coupling reaction between PA and PSU–PhA predominates (route 1), the normal compatibilization effect by in situ formed copolymers at the interface is expected. On the other hand, if the coupling reaction between PA and free anhydride is preferable and takes place first (route 2), the amount of copolymers generated at the interface would be reduced. Consequently, a lower amount of in situ formed copolymer at the interface acting as polymeric emulsifier to suppress particle coarsening may result in bigger dispersed phase size in the blend, compared with the normal reactive blend.

It is a purpose of this paper to investigate the effect of reactive low molecular weight compounds, PhA, on the blend morphology. Melt blending of PSU–PhA, non-reactive

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* Corresponding author. Tel.: +49-621-60-78298; fax: +49-621-60-20313.

E-mail address: martin.weber@basf-ag.de (M. Weber).

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PSU, and small amount of PhA with PA at 70/30 ((PSU + PSU–PhA)/PA) was carried out using a batch mixer. By ^{19}F NMR it was shown that the PSU–PhA used in the study had no trace of free anhydride. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed to reveal the morphology of the blends. Digital image analysis was applied to analyze SEM and TEM micrographs. Solvent extraction was carried out to evaluate the extent of interfacial reaction.

2. Experimental section

2.1. Materials

The PSU and PA used were commercial polymers of BASF AG, Ultrason® S2010 and Ultramid® T, respectively. PSU is a condensation product of Bisphenol-A and 4,4′-dichlorodiphenylsulfone. PA is a partially aromatic polyamide consisting of units derived from ϵ-caprolactam, hexamethylene diamine, and terephthalic acid. Melting temperature of this PA is about 290°C. Number average molecular weight (M_n) and weight average molecular weight (M_w) were determined by gel permeation chromatography (GPC) at 25°C. Carrier solvent/standard sample used for GPC were tetrahydrofuran/polystyrene for PSU and hexafluoropropylalcohol/poly (methyl methacrylate) for PA. The amount of amino groups was determined by titration.

PSU–PhA was prepared by the addition 4-fluorophthalic anhydride to the as-polymerized solution of PSU. The polymer was isolated by precipitation in water and then extracted three times with hot water. The amount of anhydride end-groups in weight percent was determined by FT-IR. By ^{19}F NMR it was shown that the sample used for this study contains no free 4-fluorophthalic anhydride. Detail of preparation procedure has been given elsewhere [14,19]. Characteristics of the materials used are summarized in Table 1 and their chemical structures are shown in Fig. 2.

Table 1
Characteristics of polymers used

Nomenclature	M_n [a]	M_w [a]	η^{*} [b]	Functionality [c]
PA	13,000	35,000	1500	50
PSU	12,000	30,000	1700	0
PSU–PhA	9600	33,570		162

[a] By GPC measurement (g/mol).

[b] Complex melt viscosity at 310°C, frequency range 10–50 rad/s (Pa s).

[c] Content of functional group (μmol/g).

2.2. Melt mixing

To remove absorbed moisture, all polymers were vacuum dried at 80°C over night before blending. A mixture of non-reactive PSU and reactive PSU was melt blended with PA at 70/30 (PSU/PA) wt. ratio using a batch mixer, Haake Rheomix 600 at 315°C. All materials were fed to the mixer in pellet form. The rotation speed was fixed at 50 rpm. At this rotor speed, the maximum drag flow, shear rate in the mixer is 65 s^{-1}. This can be calculated on the basis of the rotor speed and the minimum gap between the rotor tip and the mixing chamber wall. The mass of material charged to the mixer always was 50 g. The mixing proceeded for 8 min. The composition of the prepared blends are given in Table 2.

2.3. Morphology analysis

The morphology was observed with both TEM and SEM. For TEM observations, the quenched specimen was cryomicrotomed at −45°C by ultramicrotome (Reichert Ultracut-S). The ultrathin section of ca. 60 nm thickness was mounted on 200 mesh copper

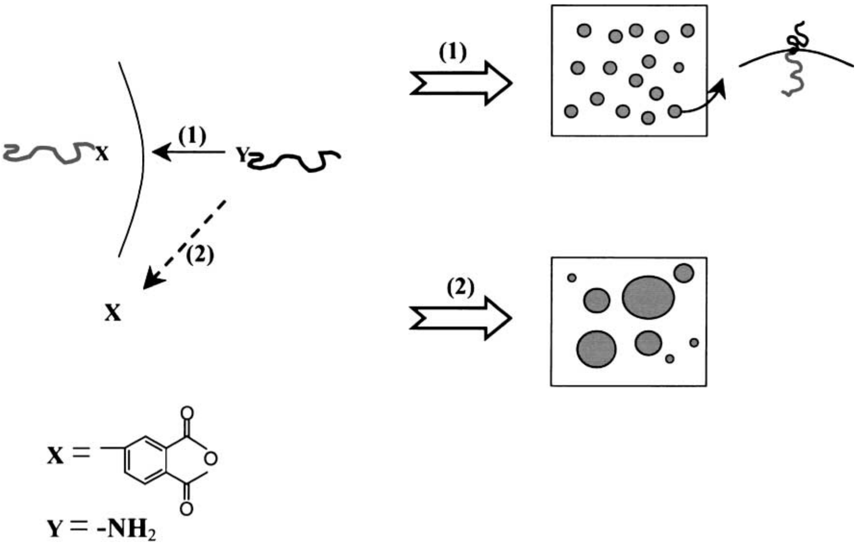

Fig. 1. Schematic representation of possible coupling reactions that may take place during melt processing of PA/PSU–PhA and small amounts of free PhA.

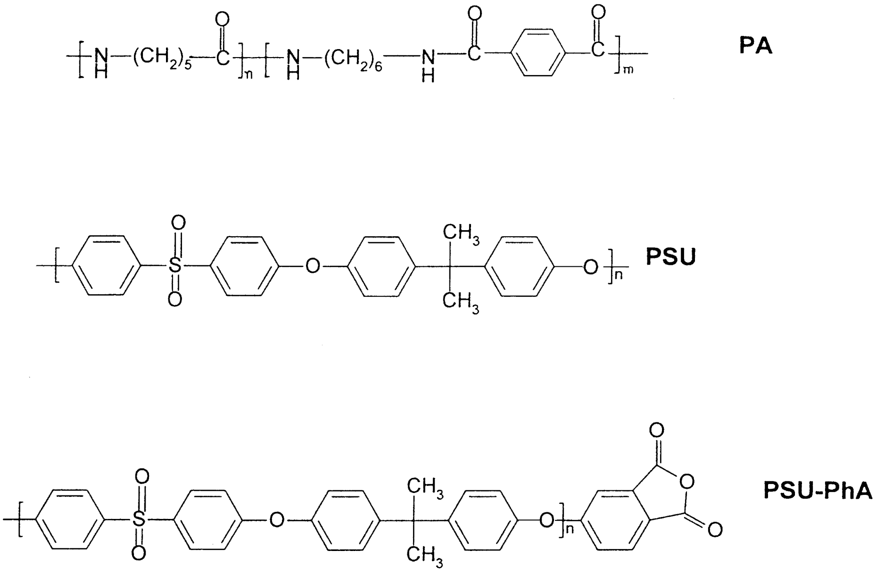

Fig. 2. Chemical structures of polymers used.

grid and exposed to the RuO_4 vapor for 20 min. The two-phase morphology was observed by transmission electron microscope (Zeiss EM 902) at an accelerating voltage of 100 kV.

For SEM observations, the specimen was stained with RuO_4 at room temperature for 4 h to render better contrast between PSU and PA. A stained specimen was cryomicrotomed at −65°C to ensure a flat surface. After deposition of a carbon layer, SEM observation was performed by a scanning electron microscope (Hitachi S 4000) at the accelerating voltage of 12 kV under backscattered electron mode. Note that the mentioned technique for SEM observation provides enough contrast; therefore, the reliable results on the two-phase morphology with domain size of a few to sub-micrometers can be obtained [20–21].

SEM pictures were digitized. The area of each individual particle was directly determined using an appropriate software (analySIS 3.0, GmbH). The diameter of dispersed particle D_i was calculated by $D_i = 2(a_i/\pi)^{1/2}$, assuming the circular shape of the particle. Then, we obtained an average: $D_{\mathrm{EM}} = \sum_{i=1}^{N} D_i^3 / \sum_{i=1}^{N} D_i^2$ when N was 300–600 in a SEM picture.

2.4. Extraction procedure

About 5 g of each blend was immersed in 100 ml of *N*,*N*′-dimethylformamide (DMF) for the extraction of the PSU matrix phase. After 24 h, the suspension was separated into two phases by centrifugation at 14,000 rpm for 30 min. The transparent top phase (PSU in DMF) was collected. The bottom phase, insoluble materials (unreacted PA and PSU–PA copolymers), was dried and further extracted with formic acid (HCOOH), which acts as a selective solvent for the PA. The insoluble material was again separated and counted as in situ formed copolymers.

2.5. Thermal analysis

In a differential scanning calorimeter (DSC), a Universal V2.4F TA Instruments, neat polymer or blend specimen packed in aluminum pan was heated at a heating rate of 20°C min^{-1} under nitrogen atmosphere. Each sample was heated to 350°C to erase thermal history of specimens then cooled to 0°C and reheated to 350°C. The glass transition temperature (T_g) reported here are obtained at the middle point from the second heating.

Table 2
Experiment runs

Code	Blend composition (wt%)				$[NH_2]$:[PhA-PSU]:[PhA-free][a]
	PA	PSU	PSU–PhA	PhA	
Blend 1	30	70	–	–	
Blend 2	30	60	10	–	1:1.1
Blend 3	30	60	10	0.25	1:1.1:1
Blend 4	30	60	10	0.50	1:1.1:2

[a] Stochiometric ratio calculated from functionality of PA, PSU–PhA, and PhA.

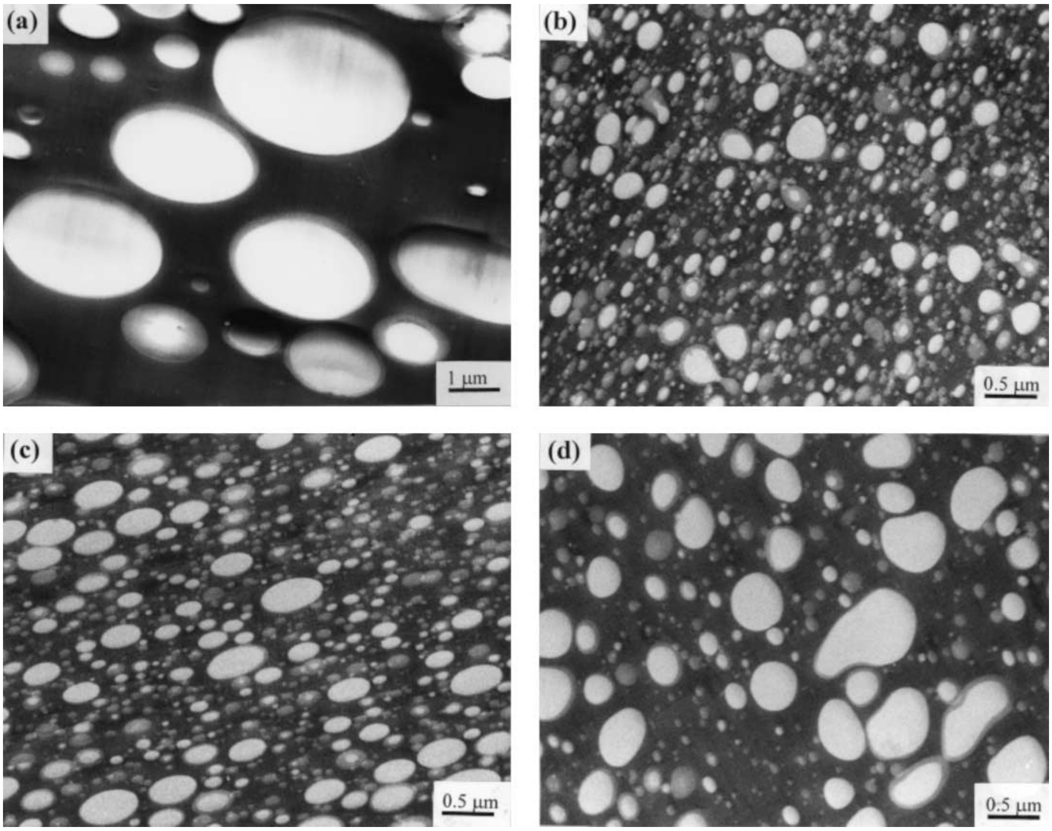

Fig. 3. TEM micrographs (RuO_4 stained) of the blends after mixing at 315°C for 8 min. (a) Blend 1, (b) Blend 2, (c) Blend 3, and (d) Blend 4.

3. Results and discussion

Fig. 3 shows TEM micrographs of blends after 8 min mixing. The dark region corresponds to the PSU phase stained by RuO_4. It can be seen that the normal reactive system[1] (Blend 2, Fig. 3b) yields finer particles than the non-reactive system (Blend 1, Fig. 3a). These are expected results, since the reactive system is known to generate the PSU–PA copolymer, which acts as emulsifier to provide entropic repulsion between neighboring particles and hence retard the particle-coarsening during melt blending.

To see the effect of small molecular weight compounds on the morphology of the reactive blends, small amounts of PhA were added to Blends 3 and 4. If PhA groups of PSU–PhA react predominantly with the amine group of PA, the morphology of Blends 3 and 4 would remain similar to the Blend 2 (without free PhA). However, if the free PhA participates in coupling reactions with the amine groups of PA, a lower amount of PSU–PA copolymer would be formed at the interface and thus the morphology of Blends 3 and 4 may be different from Blend 2. From TEM micrographs in Fig. 3, the later appears to be the case as a difference in the morphology between the reactive system without free PhA, Blend 2, (Fig. 3b) and the reactive systems containing free PhA, Blends 3 and 4 (Fig. 3c and d) was observed. The normal reactive system Blend 2 has a rather narrow particle size distribution with many particles sizing 85–95 nm and a small numbers of co-existing sub-μm particles. However, when the small amount of free PhA was introduced to the blend, number of sub-μm to μm particles increases as shown in Fig. 3c and d. Furthermore, in Fig. 3b–d, an effect of loaded amount of PhA on the morphology (the dispersed phase sizes and their distribution) could also be demonstrated. The higher amount of PhA leads to a greater population of the μm-order particles.

TEM results imply that the added free-PhA participated in the coupling reaction during melt mixing. In the case of Blend 3, the amount of free PhA loaded is roughly equal to the amount of PhA attached on PSU–PhA chains (see Table 2). Therefore, one may anticipate an equal possibility in reaction between amino groups of PA chains and free PhA or PSU–PhA. Some amino groups may react with free PhA and the others may react with PSU–PhA. On the other hand, in Blend 4, the amount of loaded free-PhA is one time larger than the amount of PhA from PSU–PhA (see also Table 2). The reaction between the free PhA with the amino groups of PA may take place first and consume some amino groups of PA. This may reduce the possibility of the coupling reaction between the amino groups of PA with the PSU–PhA to generate copolymer at the interface.

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[1] The Blend systems containing PSU–PhA, which can react with PA, are called the reactive system. These are Blends 2–4 in this study (see also Table 2).

Table 3
Results of solvent extraction

Blend	DMF-extraction		HCOOH-extraction		Total insoluble part
	Soluble part (wt%)	Insoluble part (wt%)	Soluble part (wt%)	Insoluble part (wt%)	
1	70.2	29.8	99.3	0.7	0.2
2	63.8	36.2	54.2	45.7	16.5
3	66.8	33.2	57.1	42.9	14.2
4	67.6	32.4	64.2	35.8	11.6

Consequently, the lower amount of copolymer at the interface to retard particle coalescence finally may result in the bigger dispersed phase size and broader particle size distribution; i.e. the μm PA particles seen in Fig. 3d may not be covered by the copolymer.

In order to provide a rough idea about the amount of PSU–PA copolymers formed during the mixing, the solvent extraction was employed to the blends as explained in Section 2. The non-reactive PSU and PSU–PhA as a major component can be dissolved in DMF. Likewise, unreacted PA can be dissolved selectively in formic acid. The PSU–PA copolymer formed during melt mixing should not be soluble in DMF or formic acid. This fraction is an insoluble residue in the extraction procedure. The results of extraction are summarized in Table 3. In the case of the non-reactive system Blend 1, only a small amount of insoluble residue was observed, indicating no copolymer formation has taken place. In the Blends 3 and 4 containing the free added-PhA a lower amount of insoluble residue than in the normal reactive Blend 2 was detected, suggesting the reduced formation of PSU–PA copolymer during melt blending, as expected from the TEM results. Note that DSC results of insoluble materials of Blends 2–4 showed two T_gs at ca. 106 and 180°C corresponding to the T_gs of PA and PSU–PhA component polymers, respectively, confirming the copolymer formation as well. Furthermore, the extent of compatibilization of this PA/PSU blend series was investigated also using their heat capacity increment at the T_g. It was found that the heat capacity varies with the extent of compatibilization. More details and results of the analysis will be reported separately [22].

To check whether or not the in situ created PSU–PA copolymers act as emulsifier to stabilize the morphology against coalescence, the blends were annealed at 315°C for 30 min under nitrogen flow atmosphere. After annealing, the blends were quenched into dried ice and examined for morphological changes by SEM. Fig. 4 shows quantitative image analysis of the morphologies before and after annealing in terms of particle size distribution and Table 4 summarized also the results of image analysis in terms of the D_{EM} and standard deviation (S_{av}). In Fig. 4, it can be seen that the center of particle size distribution of the specimens after annealing shifted to the bigger particle size, suggesting that the particle coarsening took place during annealing. The smallest shift and S_{av} were found in the Blend 2, the normal reactive system. This may be due to the emulsifying effect provided by the in situ formed copolymers locating at the interface to retard the particle coarsening. On the other hand, in the Blends 3 and 4, it can be seen that by annealing the shape of particle size distribution clearly changed from log-normal distribution (Fig. 4c$_1$ and d$_1$) to bi-modal distribution (Fig. 4c$_2$ and d$_2$). Particularly, in Blend 4, the center of particle size distribution is significantly shifted to the bigger particle-diameter side and the average particle size D_{EM} increases from 0.4 to 2.14 μm, the same order as in a case of the non-reactive blend. The results suggested insufficient coverage of the interface by the in situ formed copolymer to prevent particle coarsening. This may be caused by the lower amount of copolymer at the interface due to the effect of added free PhA on the coupling reaction as discussed earlier.

Table 4
Results of image analysis (S_{av} is the standard deviation of number average particle diameter)

Code	Before annealing		After annealing	
	D_{EM} (μm)	S_{av}	D_{EM} (μm)	S_{av}
Blend 1	2.74	1.1	3.45	1.0
Blend 2	0.13	0.06	0.23	0.06
Blend 3	0.23	0.12	0.45	0.26
Blend 4	0.40	0.32	2.14	0.96

4. Conclusions

In this study, the effect of a reactive low molecular weight compound, PhA, on the morphology of PA/PSU alloys was investigated. When PSU–PA copolymers are formed in situ by the coupling reaction at the interface, they act like typical emulsifiers and provide a finer particle size and better morphological stability, compared to the non-reactive system. On the contrary, it was found that the reactive low molecular weight compound, PhA, could participate in the coupling reaction with amino groups of PA chains and consequently lead to a reduced amount of in situ formed copolymers at the interface. The blends with less in situ formed copolymer showed worse morphological stability under static annealing than the normal reactive blend, without loaded PhA.

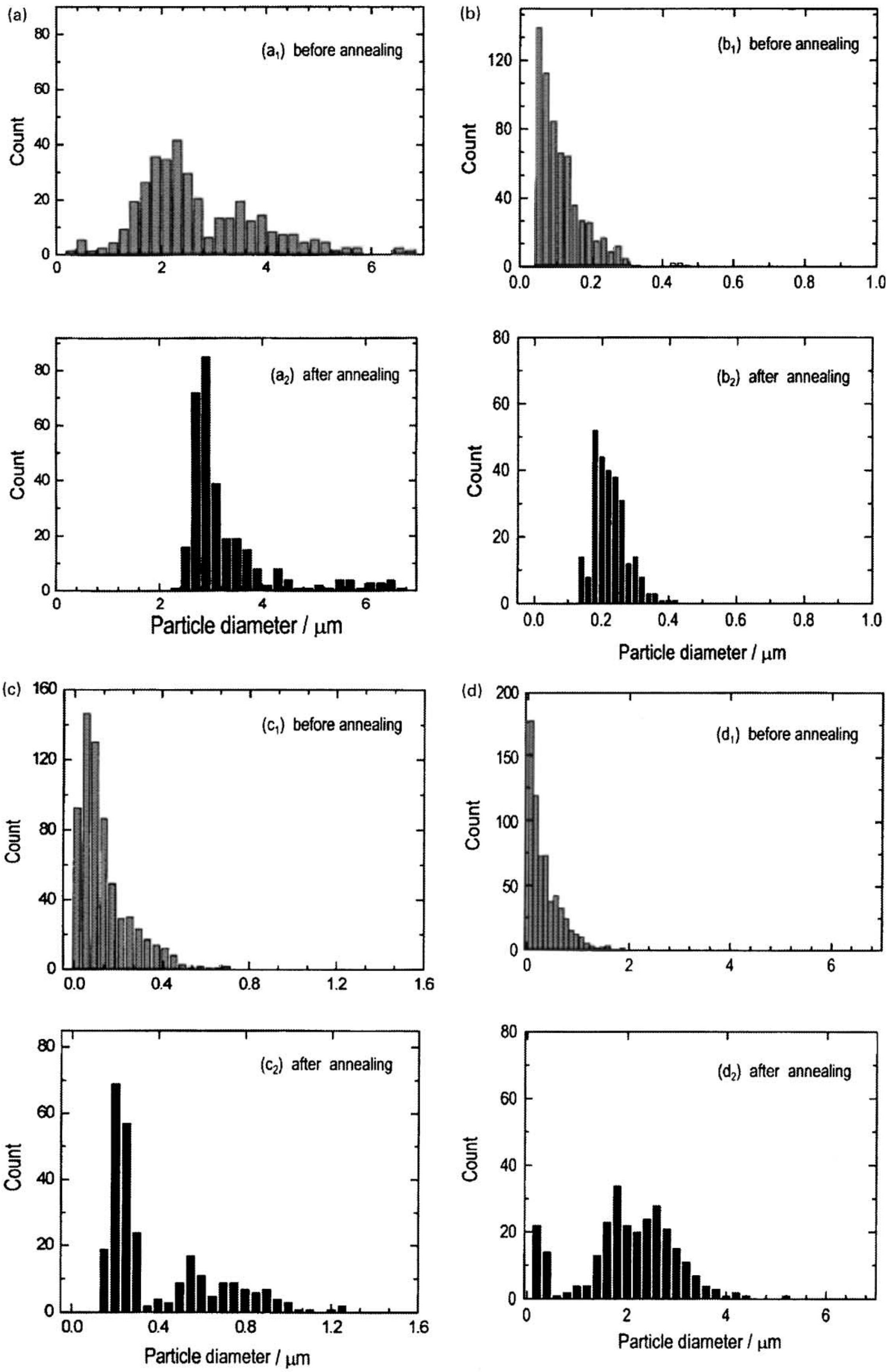

Fig. 4. Comparison of particle size distributions of equivalent diameter obtained by image analysis of SEM micrographs of Blend 1 (a_1, a_2), Blend 2 (b_1, b_2), Blend 3 (c_1, c_2), and Blend 4 (d_1, d_2).

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