Small-Angle X-ray Scattering Study of Modified Porous Suspension–Poly(vinyl chloride) Particles

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ABSTRACT: Small-angle X-ray scattering (SAXS) was applied to investigate the microstructure of unmodified and modified porous commercial suspension-type poly(vinyl chloride) (PVC) particles. The modified PVC particles were prepared by an *in situ* stabilizer-free polymerization/crosslinking of particles absorbed with a monomer/crosslinker/peroxide solution. The modifying polymers include styrene with or without divinyl benzene (DVB) as a crosslinker and methyl methacrylate (MMA) with or without ethylene glycol dimethacrylate (EGDMA) as a crosslinker. The SAXS method was used to highlight the effect of polystyrene (PS) on the microstructure of PVC particles and to evaluate the characteristic lengths, both in the PVC/PS and the PVC/XPS (PS crosslinked with 0 and 5% DVB, respectively) systems. A model is suggested, where during the synthesis modification process, swelling of PVC by styrene and styrene polymerization occur simultaneously. PVC swelling by styrene causes destruction of the PVC subprimary particles, whereas styrene polymerization leads to phase separation resulting from incompatibility of the polymers. It was further suggested that because of PVC swelling by styrene, structure of the subprimary particles is lost. Therefore the characteristic lengths of PVC/PS and PVC/XPS, as calculated from the SAXS measurements, were attributed to the size of the phase-separated PS and XPS inclusions, respectively. The SAXS method also shows that PMMA and XPMMA do not influence the PVC microstructure. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 95: 1024–1031, 2005

Key words: SAXS; poly(vinyl chloride) (PVC); blends; polystyrene; polymethyl methacrylate

INTRODUCTION

A focal point of polymer science and technology is the tendency to shift from wholly new polymers to modification or blending of the existing polymers. There are several methods for preparation of polymer blends, including mechanical hot melt mixing, casting from a common solvent, and *in situ* polymerization. *In situ* polymerization is the polymerization of one monomer in the presence of another polymer,[1] which can be performed by reactions in the melt, in solution, in a seeded latex, or in the solid phase.[2] *In situ* polymerization in the solid state (usually powder or granular material) is advantageous because of its low cost and the large variety of possible modifications, compared to polymerization in solution or in the melt.[3]

In situ polymerization/crosslinking of a given monomer within an uncrosslinked polymer leads to formation of a semi-interpenetrating polymer network (semi-IPN).[4] With two miscible polymers the interpenetration occurs on a molecular level. A major parameter making the networks in IPNs more miscible appears to be the presence of crosslinks, which hinder phase separation.[5,6] Semi-IPNs, including poly(vinyl chloride) (PVC) with given crosslinked polymers, can improve important properties of the neat PVC, such as impact strength, and also make it an interesting absorbent of halogenated organic compounds from water.[7]

A previous publication[8] dealt with modified porous semi-IPN PVC particles prepared by an *in situ* stabilizer-free polymerization/crosslinking process of a monomer/crosslinker/peroxide solution absorbed in the porous commercial suspension-type PVC particles. The monomer/crosslinker pairs selected to modify the PVC particles were styrene/divinyl benzene (DVB) (XPS) and methyl methacrylate (MMA)ethylene glycol dimethacrylate (XPMMA). Scanning electron microscopy (SEM) observations and dynamic mechanical thermal analysis (DMTA) measurements[8] have shown that the structure of polystyrene (PS) and poly(methyl methacrylate) (PMMA)–modified PVC particles has been modified. Based on porosity measurements before and after modification, it was concluded that both styrene and MMA mainly polymerize within the PVC particles' bulk and the remaining amounts in the pores. SEM observations revealed that the small amount of styrene polymerized within the pores partly fills them, whereas the small amount of MMA polymerized within the pores polymerized as a

crust on the PVC pore surfaces.[8] Because the SEM resolution is limited, it is of interest to investigate smaller structural differences, on a colloidal scale, as reported in this study, based on small-angle X-ray scattering (SAXS) studies.

The few scattering studies of PVC that were reported in the literature mainly deal with the crystalline of this polymer, which has been reported as 0 to 20%.[9] Ballard et al.[10] characterized plasticized PVC using SAXS and small-angle neutron scattering (SANS) and found a crystallinity degree of about 15%.[10] Wenig[11] concluded from wide-angle X-ray scattering (WAXS) experiments that suspension-type PVC powder pressed into a thin film at 160°C had 8% crystallinity. Wenig[11] and Walsh et al.[9] reported a lamellar thickness of 10.5–11.6 nm from SAXS measurements. Upon annealing, the crystallites become sufficiently organized to give a broad Bragg scattering peak also corresponding to a period of about 10 nm.[12] However, Straff and Uhlmann[13] were unable to find peaks in the SAXS pattern of unplasticized PVC and thus claimed that PVC had no crystallinity.[13]

The current research is aimed at studying the structure of unmodified and modified PVC particles, on a colloidal scale. In a previous publication it was concluded that SAXS results were unsatisfactory for PVC because of the combination of poor electron density contrast and high absorption of X rays.[12] Also, the use of SAXS analysis of polymeric materials (such as PVC), characterized by a degree of crystallinity less than 20%, is difficult even in more transmitting materials. In spite of these difficulties, the SAXS results described in the following reveal valuable structural information.

EXPERIMENTAL

Materials

Suspension porous PVC particles (Epivyl 40, K value 67; Frutarom, Haifa, Israel), 100–150 μm diameter, were used as received. The crosslinking agents DVB (divinyl benzene) solution containing 50% ethylvinylbenzene (Riedel-de Haën, Seelze, Germany) and EGDMA (ethylene glycol dimethacrylate, practical grade; Fluka, Buchs, Switzerland) were used as received. Styrene (Riedel-de Haën) and MMA (Merck, Darmstadt, Germany) monomers were washed for removal of the inhibitor with a 5% sodium hydroxide aqueous solution, followed by rinsing with water until neutralization was achieved. Benzoyl peroxide (BP; Merck) was purified by recrystallization from hot ethanol. Water was deionized and distilled.

Preparation procedure of the modified PVC

PVC particles were modified by XPS (polystyrene crosslinked with 0 and 5% DVB) and XPMMA (poly-methyl methacrylate crosslinked with 0 and 5% EGDMA), using BP as an initiator (0.5%). The PVC/modifying monomer mass ratio was 75/25. The polymerization/crosslinking reaction was carried out in a glass reactor, immersed in a water bath at 80°C. The reactor was fitted with a Teflon blade agitator, nitrogen bleed, dropping funnel, and condenser. Distilled water (800 g) and PVC particles (75 g) were charged to the reactor and stirred. A monomer, crosslinker, and BP solution (25 g) was placed in a dropping funnel and continuously added to the reactor over a period of 30 min, with stirring at room temperature, for complete absorption of the monomer solution in the particles. The temperature was then elevated to the polymerization temperature, 80°C, which was subsequently maintained for 4 h. The resulting modified PVC particles were filtered and dried.

Characterization

A JSM 5400 scanning electron microscope (SEM; JEOL, Tokyo, Japan), at an accelerating voltage of 10 kV, was used to observe the particles' freeze-fractured surfaces. Samples were prepared by embedding PVC particles in an epoxy matrix and fracturing at liquid nitrogen temperature. All samples were gold sputtered before observation.

The dynamic mechanical properties of compression-molded specimens (at 150°C) were measured by a dynamic mechanical thermal analysis system (ARES system; Rheometric Scientific, Piscataway, NJ), in the torsion mode. The frequency used was 1 Hz, and heating was carried out in an inert nitrogen atmosphere at a rate of 3°C/min.

SAXS measurements were performed with Cu–K$_\alpha$ radiation (sealed-tube generator) using a compact Kratky camera (Anton Paar GmbH, Graz, Austria) having a linear position-sensitive detector system with phase-height discrimination (Raytech, France) coupled to a multichannel Nucleus analyzer (GMI Inc., Albertville, MN). The entrance slit to the collimation block was 20 μm, and the slit length delimiters were set at 15 mm. The sample to detector distance was 26.4 cm. Three types of samples were examined: samples of PVC particles were suspended in water and injected into a 2.0 mm diameter glass capillary that was sealed with epoxy glue. Compression-molded films (0.4 mm thickness) were prepared by pressing PVC particles between two Mylar sheets at 150°C, followed by cooling the pressed films at room temperature for 15 min. The films were taped to a sample holder. PVC powder was taped directly to a sample holder. The sample temperature was kept constant at 25°C by means of a temperature controller (Anton Paar). The scattering curves were corrected for sample absorption and a constant background, determined using a Porod plot, was subtracted. The correction for the effects of the

geometry of a slit-collimated incident beam (desmearing) was performed using the program ITP (indirect Fourier transformation procedure).[14]

DATA ANALYSIS

In a SAXS experiment, the X-ray intensity $I(h)$ is measured as a function of the scattering vector h, defined as

$$h = (4\pi/\lambda)\sin\theta \tag{1}$$

where 2θ is the scattering angle and λ is the X-ray wavelength. For an overall isotropic system, the scattered intensity $I(h)$ is given by[14]

$$I(h) = 4\pi \int_0^\infty P(r) \frac{\sin(hr)}{hr} dr \tag{2}$$

where r is the distance from an arbitrary reference point and $P(r)$ is the distance distribution function, defined as

$$P(r) = r^2 \int_0^\infty [\,\rho(r') - \bar{\rho}][\,\rho(r' + r)]4\pi r^2 dr \tag{3}$$

where $\rho(r)$ is the local electron density at distance r from an arbitrary reference point and $\bar{\rho}$ is the mean electron density.

The distance distribution function $P(r)$ may be used for a structural analysis because the dimensions of the structural units are directly evident from it.[14] Technically, it is possible to calculate $P(r)$ and correct the effects of the slit-collimated beam geometry (desmearing) simultaneously, using the ITP program.[14] It should be noted that the use of the ITP program is limited to those cases where the larger distance in the sample can be defined (e.g., dilute particulate systems). Although PVC cannot be assumed *a priori* to meet this criterion, the use of ITP can still be justified because of the low degree of PVC crystallinity that can be described as a dilute particulate system.

Another useful parameter is the integrated intensity (or the invariant) Q, which is a measure of the total scattering power of the sample and is defined as[15]

$$Q = \int_0^\infty h^2 dh I(h) \tag{4}$$

The invariant is sensitive to both changes in contrast (electron density differences) between the phases and to changes in their respective volume fractions.[15,16]

RESULTS AND DISCUSSION

The current study focuses on commercial porous suspension PVC particles, modified by a polymerization/crosslinking process.[7,8,17,18] These authors suggested a structural model schematically illustrated in Figure 1. Based on porosity measurements before and after modification, it was concluded that both styrene and MMA mainly polymerize within the PVC particles' bulk and the remaining amounts in the pores. SEM observations revealed that the small amount of styrene polymerized within the pores partly fills them, whereas the small amount of MMA polymerized within the pores appears as a crust on the PVC pore surfaces.[8] Polymerization within the bulk PVC particle yields a semi-IPN structure with interconnected phase-separated microdomains of the modifying polymer [Fig. 1(b) and (c)].

The dynamic mechanical properties of PVC are influenced by incorporation of PS and XPS but not by modifying with PMMA and XPMMA (Fig. 2). The lack of influence of PMMA and XPMMA on the dynamic mechanical properties is a reflection of the smaller amounts of PMMA and XPMMA incorporated within the PVC particles, compared to PS and XPS, because of low compatibility between PVC and PMMA.[8]

SAXS experiments were performed in an attempt to reveal structural details on a colloidal level. Four types of modified particles were examined, as summarized in Table I. After the polymerization-modification step, films were created from the recovered dry powder using compression molding, and X-ray scattering curves were recorded. Figure 3 summarizes the smeared background-subtracted SAXS curves measured for the compression-molded neat PVC, [PVC/PS], and [PVC/PMMA] films. The scattering curves obtained for the crosslinked systems (i.e., [PVC/XPS/5%DVB] and [PVC/XPMMA/5%EGDMA]) are compared to the scattering curve of the neat PVC in Figure 4. The corresponding distance distribution functions $P(r)$, normalized to a maximum value of 1, are shown in Figures 5 and 6.

As can be seen the $P(r)$ function of the compression-molded PVC films shows two peaks (at 3.4 and 29.9 nm), suggesting the existence of two characteristic lengths (Fig. 5). A geometric model that could account for two characteristic lengths was previously proposed for PVC.[11,12,19,20] According to this model, the inhomogeneity of PVC is attributed to crystalline regions embedded in an amorphous polymer matrix. Wenig[11] suggested that PVC is built of primary particles, which are further divided into subprimary particles. The subprimary particles, 23–24 nm in diameter, are actually lamellar stacks, which contain an average of two crystals per particle, each having a crystallite thickness of 11–11.6 nm. The subprimary particle's size, presented by the geometric model, is comparable
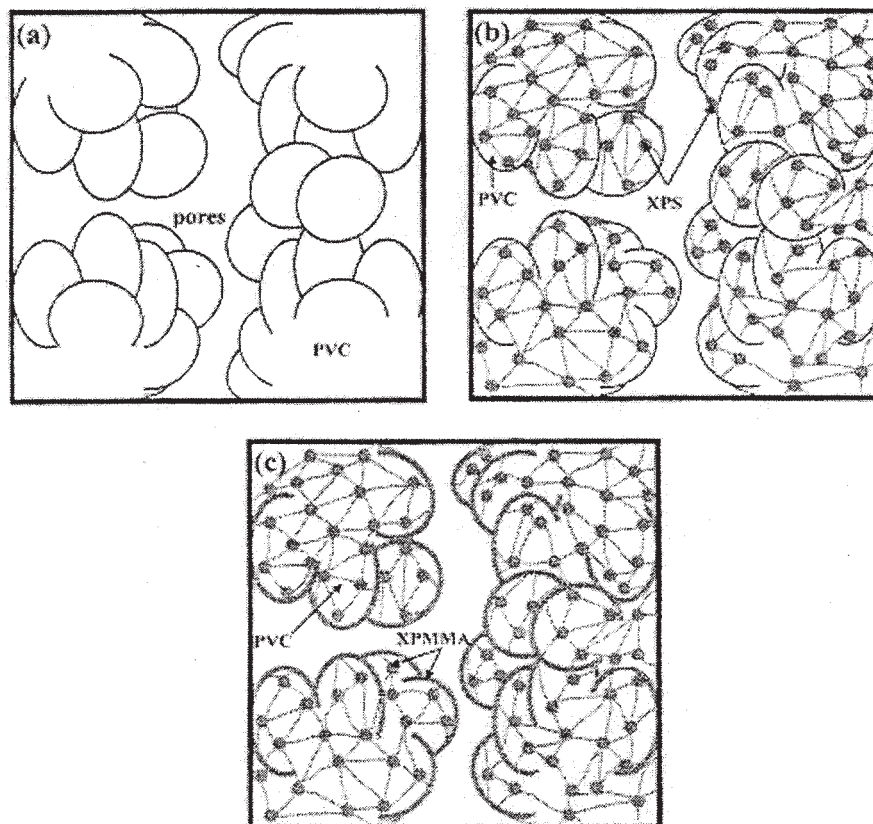
Figure 1 Schematic model describing the observed microtomed structure of (a) PVC, (b) PS modified PVC, (c) PMMA modified PVC.

with the compression-molded neat PVC characteristic length, 29.9 nm, as in Figure 5. Another model proposed to describe the PVC structure is the "fringed micelle" model.[19,20] Here the crystallites act as crosslinks, tied together by a three-dimensional network of tie molecules having a 10-nm spacing.[20]

Similarly to neat PVC, the $P(r)$ functions of the modified PVC, except to [PVC/PS], show two peaks, indicating again the existence of two characteristic lengths (Figs. 5 and 6). The peaks seen for the calculated $P(r)$ functions of compression-molded [PVC/XPS/5%DVB] films are 6.4 and 21.1 nm (Fig. 6). If these results are interpreted as before, attribution of the small-angle scattering to the PVC crystallinity gives a lamellar thickness much higher than that of the neat PVC lamellar thickness (3.4 nm), which is hard to justify. It is also possible to interpret the results by considering the possibility of XPS segregation; that is, that in addition to the PVC crystallinity, a second contribution to the SAXS signal arises from the contrast between colloidal XPS domains and PVC. During the modification process, swelling of PVC and polymerization/crosslinking of the modifying monomers occur simultaneously. These two processes have different effects on the microstructure: swelling eventually leads to the destruction of the subprimary parti-

cles, whereas polymerization/crosslinking leads to phase separation resulting from incompatibility of the polymers. Swelling continues until a higher degree of polymerization is reached and thus the structure of the subprimary particles may be completely lost. The characteristic length of [PVC/XPS] may reflect the size of the phase-separated XPS inclusions. The second peak in the $P(r)$ function of compression-molded [PVC/XPS/5%DVB], at 21.1 nm, which may represent the suspension-type PVC subprimary particles, is smaller than the characteristic length of compression-molded PVC film (29.9 nm), possibly because of dissolving the PVC subprimary particles' rim by the styrene before the polymerization/crosslinking occurs. For the [PVC/PS] system one characteristic length of 12 nm was obtained (Fig. 5), smaller than the size of the compression-molded PVC subprimary particles (29.9 nm). This length may be attributed either to phase-separated PS inclusions or to reduced-size subprimary PVC particles.

The calculated $P(r)$ functions for the compression-molded [PVC/PMMA] (Fig. 5) and [PVC/XPMMA/5%EGDMA] films (Fig. 6) reveal a different behavior. Unlike the PVC/XPS system, the location of the first peak in the $P(r)$ function, for both the uncrosslinked and the crosslinked systems, is similar to the one
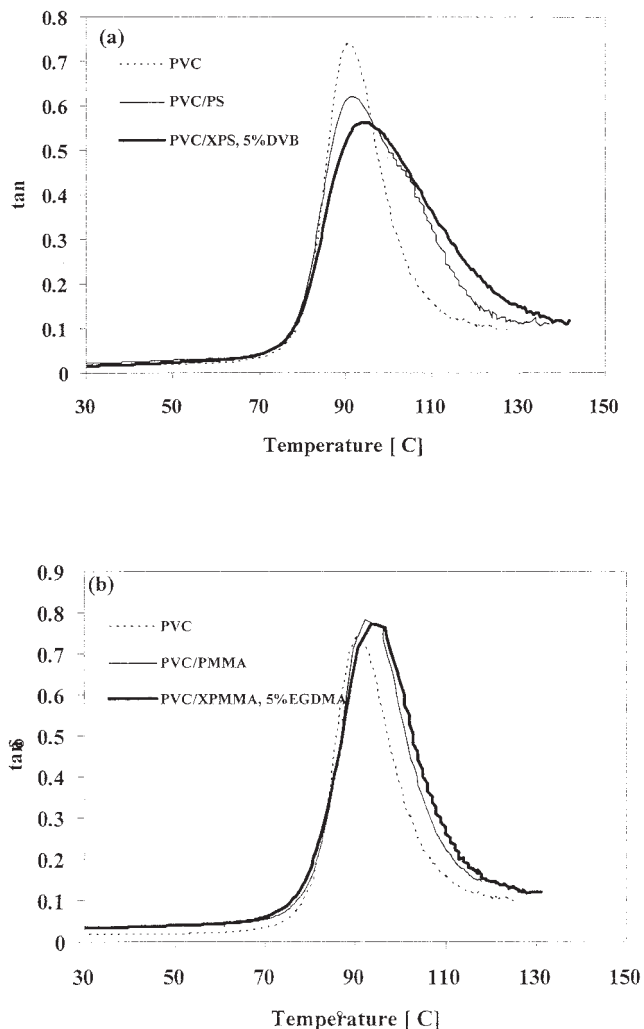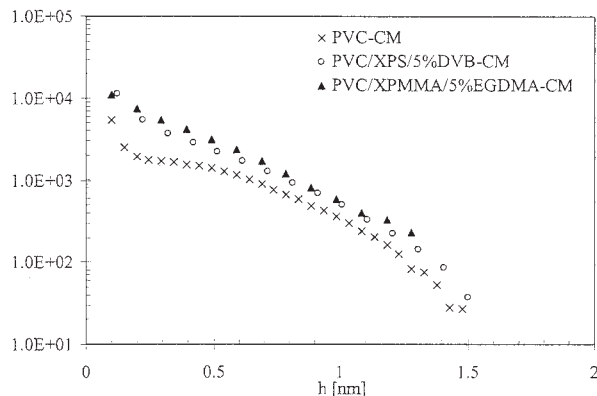
Figure 3 Scattering curves of compression-molded neat PVC, compression-molded [PVC/PS], and compression-molded [PVC/PMMA].

previously mentioned, MMA is less soluble in PVC than in styrene. Additionally, PMMA has a "crosslinked-like" behavior,[8] apparently resulting from the tendency of MMA to autoaccelerated polymerization[21] through reduced termination reactions,[3,22] leading to higher molecular weights. Thus, the swelling of the subprimary PVC particles is lower and phase separation does not occur, even in the absence of a crosslinker. The lack of influence of PMMA on the dynamic mechanical properties, attributed to the low compatibility between PVC and PMMA, supports this model [Fig. 2(b)].

To summarize, SAXS results are interpreted in terms of PVC crystallinity, whereas a different contribution from PS dissolving the PVC and XPS segregation was suggested for the [PVC/PS] and [PVC/XPS/5%DVB] systems. Yet, it should be noted that the SAXS data were obtained from samples that were subjected to two sequence steps: polymerization and compression molding. In an attempt to distinguish between the contribution of each step, SAXS experi-
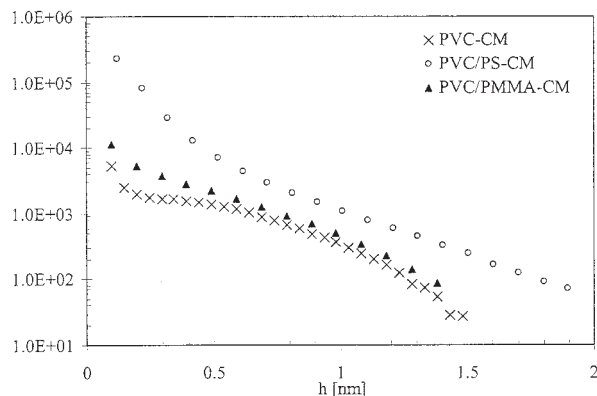

Figure 2 Tan δ of compression-molded (a) PVC, [PVC/PS], and [PVC/XPS, 5% DVB]; (b) PVC, [PVC/PMMA], and [PVC/XPMMA/5%EGDMA].

observed in compression-molded neat PVC film (3.4 nm). Therefore, this peak may be interpreted as arising from the PVC crystallinity. The second peak in the $P(r)$ function of compression-molded [PVC/PMMA] and [PVC/XPMMA/5%EGDMA] films (19.8 and 14.6 nm, respectively), which may represent the suspension-type PVC subprimary particles, is smaller than the characteristic length of compression-molded PVC film, similar to the XPS-modified PVC system. As

TABLE I
Composition of Modified PVC Particles

No.	System	PVC/modifying polymer ratio (wt)
1	PVC/PS	78.8/21.2
2	PVC/XPS/5%DVB	75/25
3	PVC/PMMA	88.3/11.7
4	PVC/XPMMA/5%EGDMA	85/15

Figure 4 Scattering curves of compression-molded neat PVC, compression-molded [PVC/XPS/5%DVB], and compression-molded [PVC/XPMMA/5%EGDMA].
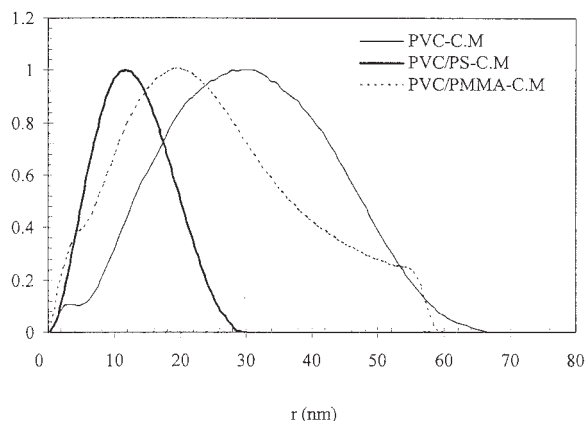
Figure 5 Distance distribution functions of compression-molded neat PVC, [PVC/PS], and [PVC/PMMA], calculated by the ITP method.

Figure 7 Scattering curves of neat PVC, [PVC/PS], and [PVC/PMMA].

ments were also performed using powders of neat and modified PVC particles, as obtained from the reactor. Figures 7 and 8 summarize the smeared background-subtracted SAXS curves measured for neat PVC, [PVC/PS], and [PVC/PMMA] particles and for neat PVC, [PVC/XPS/5%DVB], and [PVC/XPMMA/5%EGDMA] particles, respectively. The corresponding $P(r)$ curves are shown in Figures 9 and 10.

It seems initially that the differences between the scattering curves of the neat and the modified PVC are much less pronounced than the corresponding curves for the compression-molded samples (Figs. 3 and 4). The calculated $P(r)$ function of neat PVC particles (Fig. 9) shows a characteristic length of 20.0 nm. This characteristic length may represent the suspension-type PVC subprimary particles, as described by Wenig.[11] It should be mentioned, however, that this characteristic length might be influenced by the internal PVC particle's porosity.

It is worth noting that the second characteristic length, which may be interpreted as a reflection of crystallinity, is absent in the calculated $P(r)$ functions of neat and modified PVC particles (Figs. 9 and 10) and appears only after compression molding (Figs. 5 and 6). This observation agrees with previous reports showing that thermal treatments such as annealing enhance order and thus crystallinity.[11,12] Apart from that, the neat PVC and modified PVC particles show characteristic lengths similar to those of the corresponding compression-molded neat and modified PVC. XPS led to much smaller characteristic lengths than the characteristic length of neat PVC (20 nm) and higher than that of the PVC lamellar thickness (3.4 nm) and thus supported the model proposed for compression-molded [PVC/XPS/5%DVB] microstructure. PMMA and XPMMA seem not to affect the PVC particle's microstructure.

The calculated $P(r)$ function for [PVC/XPS/5%DVB] (Fig. 10) is broader than that for [PVC/PS] (Fig. 9). This is supported by the DMTA measure-
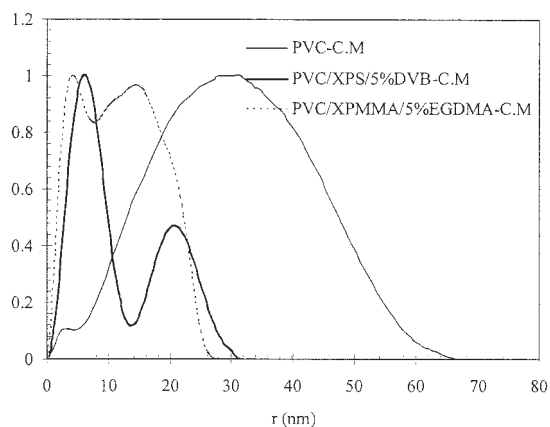

Figure 6 Distance distribution functions of neat PVC, compression-molded [PVC/XPS/5%DVB], and compression-molded [PVC/XPMMA/5%EGDMA], calculated by the ITP method.
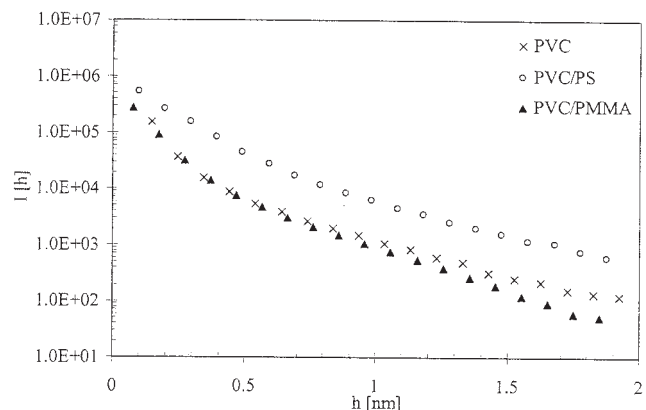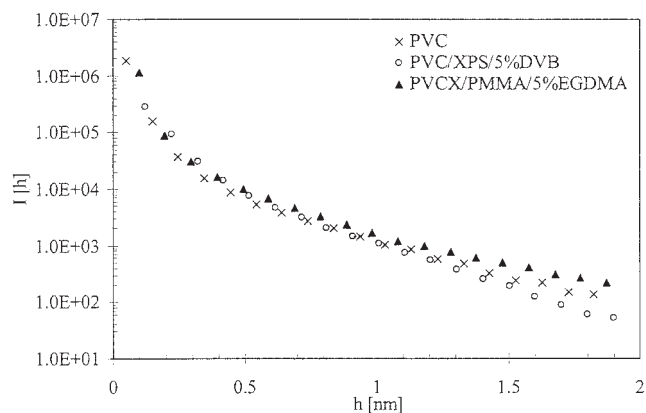

Figure 8 Scattering curves of neat PVC, [PVC/XPS/5%DVB], and [PVC/XPMMA/5%EGDMA].
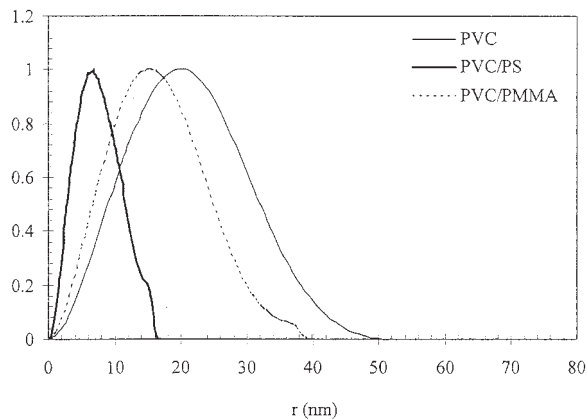
Figure 9 Distance distribution functions of neat PVC, [PVC/PS], and [PVC/PMMA], calculated by the ITP method.

Figure 11 Scattering curves of PVC immersed in styrene and methyl methacrylate.

ments (tan δ) showing that [PVC/XPS/5%DVB] is more heterogeneous than [PVC/PS] [Fig. 2(a)].

Another measure of the effect of the compression-molding process is the invariant [eq. (4)], an outcome of electron density differences. The invariant gave values of 9176 [esu^2/cm^6] for the neat PVC powder and 572 [esu^2/cm^6] for compression-molded neat PVC. Compression molding thus alters the PVC microstructure by blocking the voids and reducing their volume fraction. Thus, the significant reduction in the invariant values is expected.

Assuming that PVC does crystallize as a result of hot compression molding, it very likely should also do so (at various levels) after other treatments that promote segmental mobility, such as solvent treatment. To verify this assumption, SAXS patterns of PVC immersed in styrene and in MMA were measured. These experiments were conducted at room temperature be-
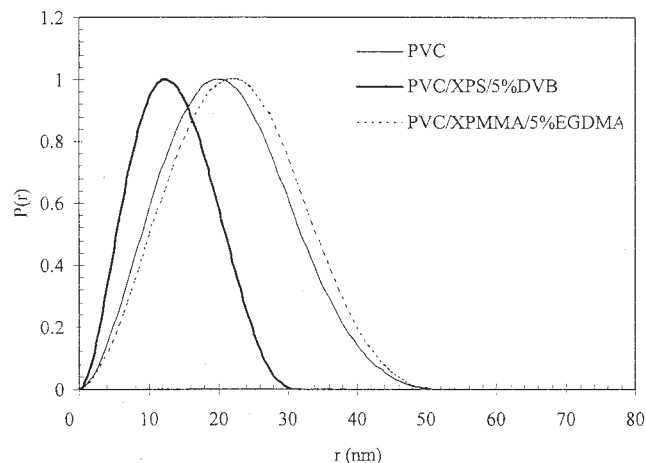
cause at a higher temperature PVC is completely dissolved in styrene. Figures 11 and 12 summarize the smeared background-subtracted SAXS curves measured for PVC particles immersed in styrene and in MMA and the corresponding $P(r)$ curves. Similarly to compression-molded PVC particles, two peaks are observed at 4.1 and at 19.1–19.9 nm. The appearance of the second peak in PVC immersed in styrene and in MMA, indicating PVC crystallinity, suggests that the monomers have acted essentially as plasticizers, enhancing segmental mobility and thus promoting PVC crystallization.[23–25] The similarity in the location of the first peak of PVC immersed in styrene and MMA indicates that the effect of these monomers on the lamellar thickness is similar. In a separate experiment, it was verified that neither MMA nor styrene polymerize under the irradiation field in the SAXS measurements, thus not affecting the observations.

The observation of a more enhanced first peak in the $P(r)$ function of PVC immersed in styrene, compared

Figure 10 Distance distribution functions of neat PVC, [PVC/XPS/5%DVB], and [PVC/XPMMA/5%EGDMA], calculated by the ITP method.
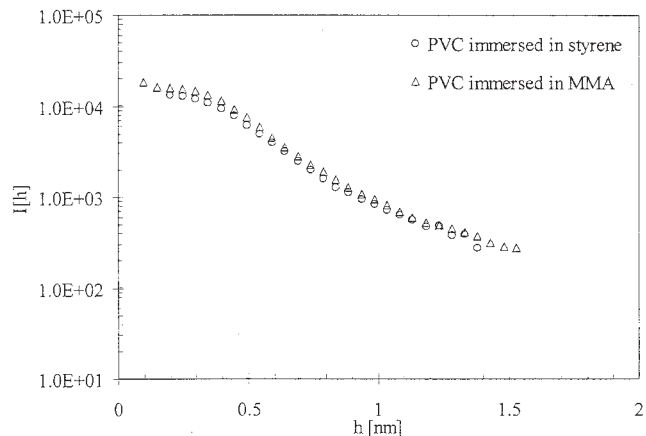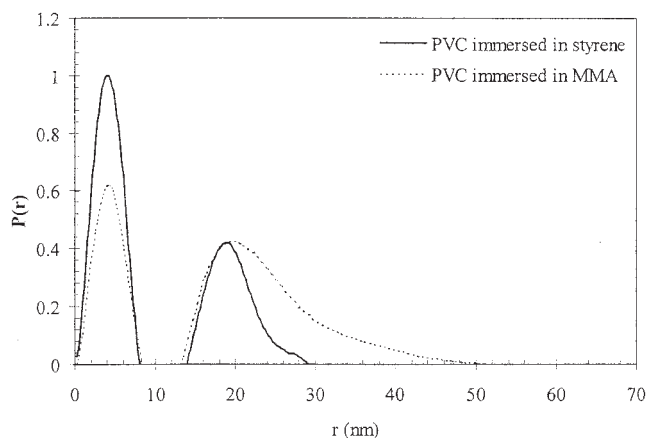

Figure 12 Distance distribution functions of PVC particles immersed in styrene and methyl methacrylate, calculated by the ITP method.

to PVC immersed in MMA, and a negligible one in compression-molded neat PVC, suggests that styrene generates a higher degree of crystallinity than MMA and much higher than compression molding. This is in accord with the relative solubility parameters of PVC, styrene, and MMA (19.2, 19.0, and 18.0 [$MPa^{1/2}$], respectively[26]); PVC indeed is more soluble in styrene than in MMA.

CONCLUSIONS

In summary, this article describes SAXS results for porous commercial suspension-type PVC particles modified by an *in situ* stabilizer-free polymerization/crosslinking of particles absorbed with a monomer/crosslinker/peroxide solution. The SAXS method appears to be a useful tool to study the effect of modifying PS on the PVC particle's microstructure and also the lack of influence of modifying PMMA on the PVC microstructure. This work shows that despite the limitations (poor electron density contrast, high absorption of X rays, and low crystallinity) SAXS may be used to characterize the structure of unmodified and modified PVC particles, on a colloidal scale.

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