

EFFECT OF COMPOSITION AND PROCESSING CONDITION ON MICROSTRUCTURAL PROPERTIES AND DURABILITY OF FLUOROPOLYMER/ACRYLIC BLENDS

Li-Piin Sung^{a*}, Xiaohong Gu^a, Derek L. Ho^a, Forrest. A. Landis^b and Diep Nguyen^c

^a National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA

^b Pennsylvania State University, York, PA, USA

^c Illinois Institute of Technology, Chicago, IL, USA

Abstract Fluoropolymer blends have been widely used as binders for exterior coatings because of their excellent resistance to ultra-violet (UV) radiation as well as to many corrosive chemical agents. It is known that the fluorinated component usually has a lower glass transition temperature and easily crystallizes in the final structure depending upon the blend composition and sample annealing condition. We investigated the effect of blend composition and annealing process (slow and fast cooling) on the surface morphology and microstructure a poly(vinylidene fluoride)/poly(methyl methacrylate) (PVDF/PMMA) blend before and after UV exposure. Surface and subsurface microstructures were studied by atomic force microscopy (AFM) and laser scanning confocal microscopy (LSCM). Bulk microstructure of PVDF-coatings before and after UV exposure were characterized using small angle neutron and light scattering. Higher PVDF content and a slow cooling process result in larger spherulite crystallite structure and rougher surface morphology. Significant ordering in the spherulite crystallite structure has been observed on the surface and the bulk films after UV exposure.

Keywords: AFM; Confocal microscopy; Crystallinity; Surface morphology; Small angle scattering; UV exposure.

INTRODUCTION

Poly(vinylidene fluoride) (PVDF)-based coatings are increasingly used for protecting outdoor structures. These coatings exhibit excellent chemical resistance, outstanding gloss retention, good flexibility, and a high resistance to chalking and cracking during weathering^[1–3]. However, the chemical inertness of PVDF prevents good adhesion to substrates and also makes it difficult to disperse pigments. Other disadvantages of PVDF coatings, such as inability to obtain a glossy finish, high melt viscosity, inferior scratching and marring resistance and high cost, make it necessary to introduce a secondary polymer component to optimize the performance of PVDF materials^[1]. The most widely used class of polymers is acrylic resin, such as poly(methyl methacrylate) (PMMA) and its copolymers. These polymers have not only good compatibility with PVDF but also provide good adhesion, mechanical properties, weatherability and optical clarity.

The preparation methods and the process conditions used strongly influence the microstructure and morphology of these coatings and, hence, their durability. It is also known that the fluorinated component has a lower glass transition temperature and easily crystallizes in the final structure depending upon the blend composition and sample annealing condition used. Typical PVDF paint binder compositions consist of 70%–80% (by mass) PVDF resin, and 20%–30% of a miscible acrylic co-resin (*e.g.*, a methyl methacrylate-ethyl acrylate copolymer^[1]). Coating grade PVDF resin is semicrystalline with a melting temperature, T_m , of

* Corresponding author: Li-Piin Sung, E-mail: li-piin.sung@nist.gov

Invited lecture presented at the International Symposium on Polymer Physics, 2008, Xiamen, China

Received August 19, 2008; Revised September 23, 2008; Accepted September 23, 2008

about 178°C. The glass transition temperature, T_g , of PVDF is -30°C and the T_g of acrylic resins is between 60°C and 100°C. Both T_g s are much lower than T_m of the PVDF. As the coating is baked above T_m , the resin components form a miscible alloy and, upon cooling, form a film comprised of a complex mixture of crystalline and amorphous regions^[4]. This physical blending produces a PVDF/acrylic mixture on a macro-molecular scale. Recent research efforts^[2, 5-7] have focused on improving the blending methods to form a more uniform blend of PVDF/acrylic on micro-molecular scale. The process is based on incorporating the acrylic with the fluoropolymer in the emulsion polymerization stage. This process has been reported to produce water-borne coatings with significantly improved properties.

In this paper, we investigate the effect of blend composition and annealing/cooling process (slow and fast cooling) on the surface morphology and microstructure of a PVDF/PMMA-poly(ethyl acrylate) copolymer (PMMA-co-PEA) blend. Surface morphology and bulk microstructure of the blend before and after UV exposure over a wide range of length scales were characterized for various processing conditions and blend compositions. Atomic force microscopy (AFM) and laser scanning confocal microscopy (LSCM) were used to characterize surface and near surface morphology. Small angle neutron scattering (SANS) was performed to determine the microstructure of PVDF-rich micro-domains in the blend films and the cross-polarized (Hv) small angle light scattering (SALS) was carried to determine the size of spherulites in the blend films.

EXPERIMENTAL*

Materials and Sample Preparations

The PVDF/PMMA-co-PEA blend films of different compositions were prepared in the following steps: (1) PMMA-co-PEA solutions in toluene were thoroughly mixed with homopolymer PVDF powders (Arkema Inc.) to provide desired blends by gradually adding isophorone solvent under electric stirring. PVDF and PMMA-co-PEA (PPG Industries, Inc.) blend ratios (by mass) were 70/30, 60/40, 50/50, and 30/70, respectively. (2) The mixtures were cast on glass plates by a drawdown technique, yielding a dry film thickness of approximately 75 μm . (3) After heating at 246°C for 10 min in an air-circulating oven, coated glass plates were removed from the oven and cooled to ambient temperature (24°C). After immersing in boiling water for 10 min, the films were readily peeled from the glass plates. To achieve different annealing/cooling processing conditions, the final cooling temperature at step 3 was varied. The “RT-cooled” condition involved slow cooling at room temperature in air (24°C); the “water-cooled” condition involved fast cooling by quenching specimens into a water bath (16°C). In the “oven-cooled” condition, specimens were left in the oven after the oven was shut off. Therefore, the water-cooled condition had the highest cooling rate and the oven-cooled condition clearly the lowest.

Ultra-violet (UV) Exposure Experiment

The specimens were characterized before and after exposure to UV light at 50°C and 9% relative humidity (RH) for 6 months. The radiation source of UV light was supplied by a 1000 W xenon arc solar simulator, which provides infrared-free, near ambient temperature (24°C) radiation with wavelengths between 275 nm and 800 nm. The physical and chemical changes of PVDF/PMMA-co-PEA blend films were measured as function of UV exposure time, and the experimental results were reported elsewhere^[8, 9]. In this report, we reported the results of surface morphology and microstructure changes of the exposed samples in 2-month and 6-month exposure time, and compared to the results of the unexposed samples.

Atomic Force Microscopy (AFM)

A Dimension 3100 Scanning Probe Microscope from Digital Instruments was operated in tapping mode to characterize the surface morphology of PVDF/PMMA-co-PEA blend films before and after UV exposure. Commercial silicon microcantilever probes were used. Topographic and phase images were obtained simultaneously using a resonance frequency of approximately 300 kHz for the probe oscillation and a free-

* Certain instruments or materials are identified in this paper in order to adequately specify experimental details. In no case does it imply endorsement by NIST or imply that it is necessarily the best product for the experimental procedure.

oscillation amplitude of (62 ± 2) nm. The set-point ratio (the ratio of set point amplitude to the free amplitude) ranged from 0.60 to 0.80.

Laser Scanning Confocal Microscopy (LSCM)

LSCM (Zeiss LSM510) was used to characterize the surface/subsurface morphology of PVDF/PMMA-co-PEA blend films. The laser wavelength used in this study was 543 nm. Details on instrument specifications and measurement protocols are given elsewhere^[10, 11]. LSCM images presented here are two-dimensional (2D) intensity projections, which are effectively the sum of all the light backscattered by different planar layers of the film. The pixel intensity level represents the total amount of backscattered light. Approximately 6 to 10 micrographs were obtained for each sample, with representative images reported here.

Small Angle Neutron Scattering (SANS)

Small angle neutron scattering measurements were performed at the NIST Center for Neutron Research using the 30 m SANS instrument with a combination of various wavelengths and a special focusing neutron optics-device to achieve the wide range of size scale from 1 nm to 500 nm^[12]. The scattered intensity was corrected for background and parasitic scattering, placed on an absolute level using a calibrated secondary standard and circularly averaged to yield the scattered intensity, $I(q)$, as a function of the wave vector, q , where $q = (4\pi/\lambda)\sin(\theta/2)$ (θ is the scattering angle, and λ is the incident wavelength of the neutron). Since the fluoropolymer has a higher neutron scattering cross section than the acrylic, the scattered intensity is proportional, in the first order, to differences in the fluoropolymer local concentration within the sample. The estimated extended uncertainties ($k = 2$) in the SANS data presented in this paper are smaller than the size of symbols in all figures.

Small Angle Light Scattering (SALS)

Small angle light scattering with cross-polarized configuration was used to study the crystal morphology in the polymer blend. A linearly polarized (vertically) He-Ne laser with a wavelength of 633 nm laser was scattered by the sample, and the scattered light was then filtered with an analyzed polarizer perpendicular to the polarization direction of the incident light. The scattered pattern was imaged on a screen behind the analyzer and recorded with a high-resolution CCD camera (Princeton Instruments, model RTD/CCD-1300Y), with a q range spanning from $0.05 \mu\text{m}^{-1}$ to $2.0 \mu\text{m}^{-1}$. The cross-polarized (Hv) scattered pattern exhibits a symmetrical four-lobed pattern, indicative of a spherulitic crystalline morphology.

RESULTS AND DISCUSSION

Microstructure and Surface Morphology of PVDF/PMMA-co-PEA Blends

PVDF has a low glass transition temperature ($T_g \approx -30^\circ\text{C}$) and a high melting temperature ($T_m \approx 178^\circ\text{C}$); and easily forms a crystalline structure depending upon the composition and annealing conditions. Figure 1(a) shows the small angle neutron scattering (SANS) results on the PVDF/PMMA-co-PEA (70/30) blends prepared under three different cooling/annealing conditions. Note that the SANS scattered intensity is proportional, in the first order, to differences in the fluoropolymer local concentration within the blended films. The SANS data show that there is a higher degree of ordered crystallinity (a well-defined peak)^[13]. A peak in the scattering profile at scattering wave vector q ($q = q_{\text{peak}}$) indicates the existence of fluoropolymer-rich micro-domains or lamellae structures with characteristic average distance, $d = 2\pi/q_{\text{peak}}$, between the domains or lamellae. The corresponding characteristic distance, d , for three conditions are (25 ± 1.5) nm (oven-cooled), (16.5 ± 1.0) nm (RT-cooled), and (13.6 ± 1.0) nm (water-cooled), respectively. This result shows that the growth rate of the crystalline structure under the oven-cooled condition is the greatest. Figure 1(b) shows the size of spherulites can be as large as $60 \mu\text{m}$, which is 2–3 times the spherulite size observed under the RT-cooled condition at larger size scales.

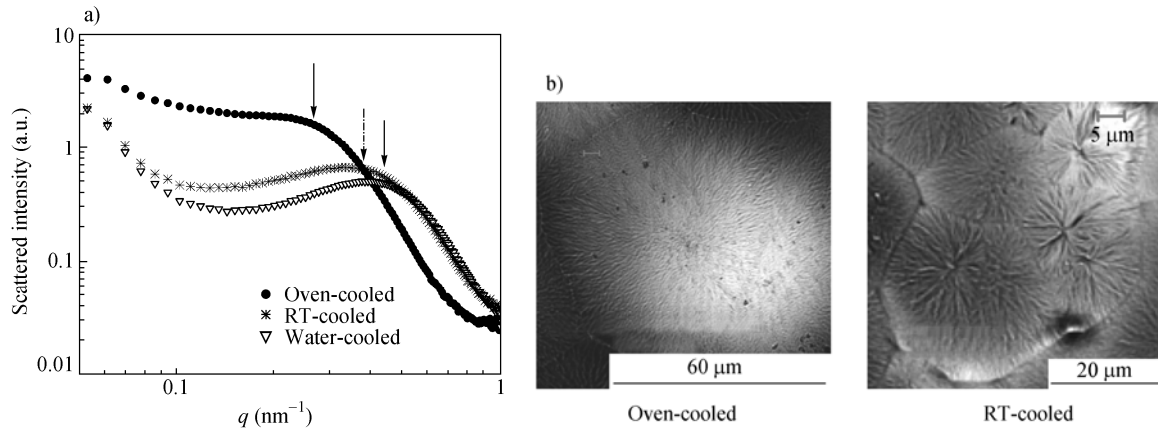


Fig. 1 (a) SANS intensity profiles of the 70/30 PVDF/PMMA-co-PEA blend films at three different processing conditions as indicated in the legend. The arrows indicate the position of q_{peak} . The error bars are smaller than the symbols in the graph; (b) LSCM images show the surface morphology of the oven cooled and RT cooled samples. Note that the two images in (b) are not at the same scale, and the size bar is indicated in each image.

The microstructure of PVDF/PMMA blends also depends on the processing conditions and the blend composition. Figure 2(a) displays LSCM images of surface morphology of PVDF/PMMA-co-PEA blend films for four compositions: 100/0, 70/30, 60/40, and 50/50, respectively. The samples studied in this section were prepared under the RT-cooled condition. Figure 2(b) shows, for 70/30 and 60/40 blends in a higher magnification, the typical spherulite structure in which aggregates of crystalline lamellae have grown from a common center in the radial direction. The crystallite structures almost completely cover the surfaces of 100/0 and 70/30 blends; however, there was no distinguishable spherulite morphology observed on the surface of the 50/50 blend at this size scale. Moreover, the size of spherulites and overall surface roughness decreases as the mass fraction of PVDF component decreases. For example, the size of the spherulites on the surface of the 60/40 and 50/50 blends drops significantly compared to the 70/30 samples. Small crystallites are not visible in the LSCM image of the 50/50 blend, are clearly seen in the AFM image presented later in Figure 4. This change may be attributed to the substantial reduction of the crystallization rate of PVDF with the higher level of amorphous PMMA-co-PEA copolymer in the blend^[14]. Previous study on PVDF/PMMA blends has shown that, as the concentration of PMMA increased from 0% to 50%, the growth rate of PVDF spherulites decreased more than 100 times due to changes in melt viscosity completed to the wide variation of T_g of the mixtures^[5]. Differential scanning calorimetry (DSC) analysis revealed that the 70/30 PVDF/PMMA-co-PEA blend has a T_g of 49°C and T_m of 157°C; for the 50/50 blend, T_g is 53°C and T_m is 149°C. The increase in T_g and the decrease in T_m with higher contents of acrylic copolymer are believed to influence the crystallization rate of PVDF and, hence, the crystallite structures (size and distance between and the lamellae) and the overall crystallinity of the blends.

The LSCM images provide information on the surface morphology and spherulite structure on and near the surfaces of the blend films. To determine the size of spherulites of the blend films, small angle light scattering (SALS) experiments were performed. Figure 3 displays the corresponding cross-polarized (Hv) SALS patterns for 100/0 and 60/40. The 100/0 blend exhibits a smaller, intense (in terms of scattered intensity) four-lobed pattern near the center (scattering wave vector $q = 0$), while the 60/40 blend has a larger, weaker scattering profile. The size of the spherulites, L^* , can be estimated from the peak intensity position, $q^*(I_{\text{max}})$, of each lobe (see the lines along 45°, 135°, 225°, 315° as indicated in the figure) using $L^* = 2\pi/q^*(I_{\text{max}})$. The average spherulite sizes for 100/0 and 60/40 blends were estimated to be $(50 \pm 5) \mu\text{m}$, and $(14.8 \pm 6) \mu\text{m}$, respectively. This result is consistent with the surface morphology information, and provides direct evidence that the spherulite structures exist on the surface as well as throughout the entire film.

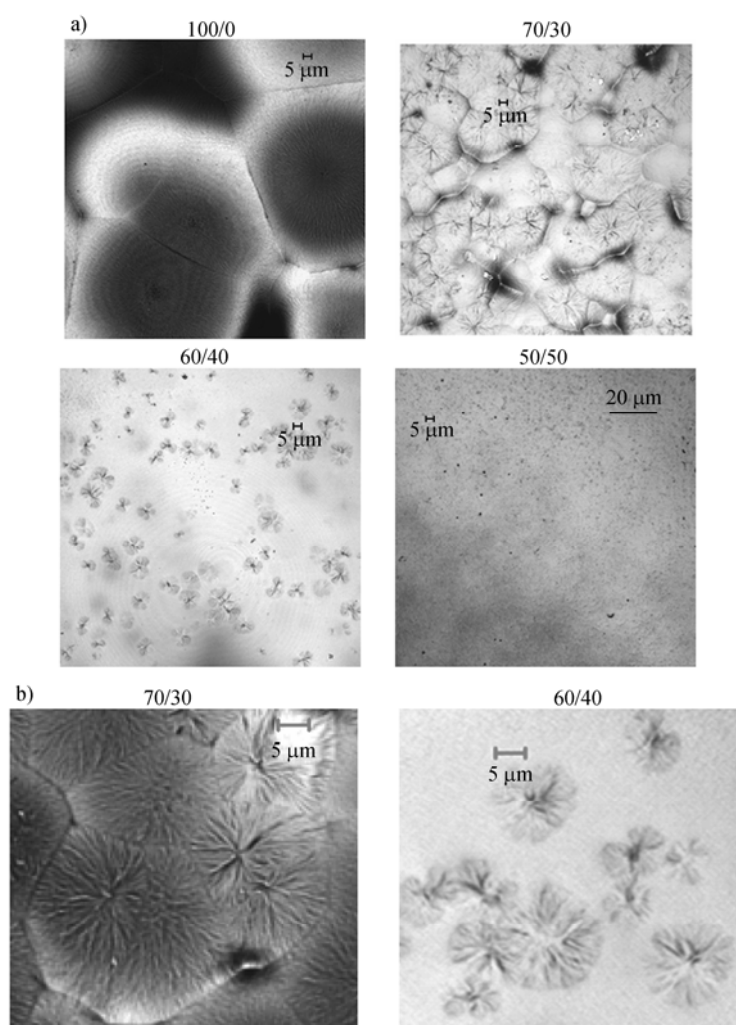


Fig. 2 (a) LSCM images of four different PVDF/PMMA-co-PEA blends: 100/0, 70/30, 60/40, and 50/50, respectively; (b) LSCM images at high magnification for the surface of the 70/30 and 60/40 blends. Samples were prepared under RT-cooled condition.

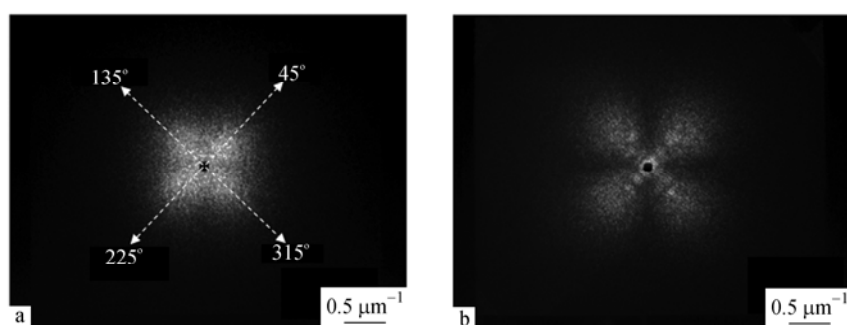


Fig. 3 2D SALS intensity profiles of the 100/0 (a) and 60/40 (b) PVDF/PMMA-co-PEA blend films, corresponding to Fig. 2. The size bar is indicated in each image.

LSCM and SALS results provide surface morphology and microstructure information on the micron scale and larger. To investigate the spatial arrangement of crystalline lamellae within the spherulites on the surface

and in the bulk film, AFM and SANS techniques are most suitable for the study. Figure 4 displays AFM images of PVDF/PMMA-co-PEA for three compositions, 70/30, 60/40 and 50/50, respectively. The height images show topographical features, but note that the phase images in tapping mode AFM often provide better microstructural information than the topographic images. For the 70/30 blend, the surface ($50\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$) appears rough with large, circular spherulite morphology, which is especially obvious in the phase image. At higher magnification ($1\text{ }\mu\text{m} \times 1\text{ }\mu\text{m}$), the phase image reveals branched lamellae structures. Some particle-like features are found to be dispersed in the radiating branches or aggregated in the boundaries between the crystallites (images are not shown here). We believe that the particle-like structure is mainly PMMA-co-PEA materials, because they were rejected into the inter-lamellae regions or the fronts of the spherulites during PVDF crystallization^[15–17].

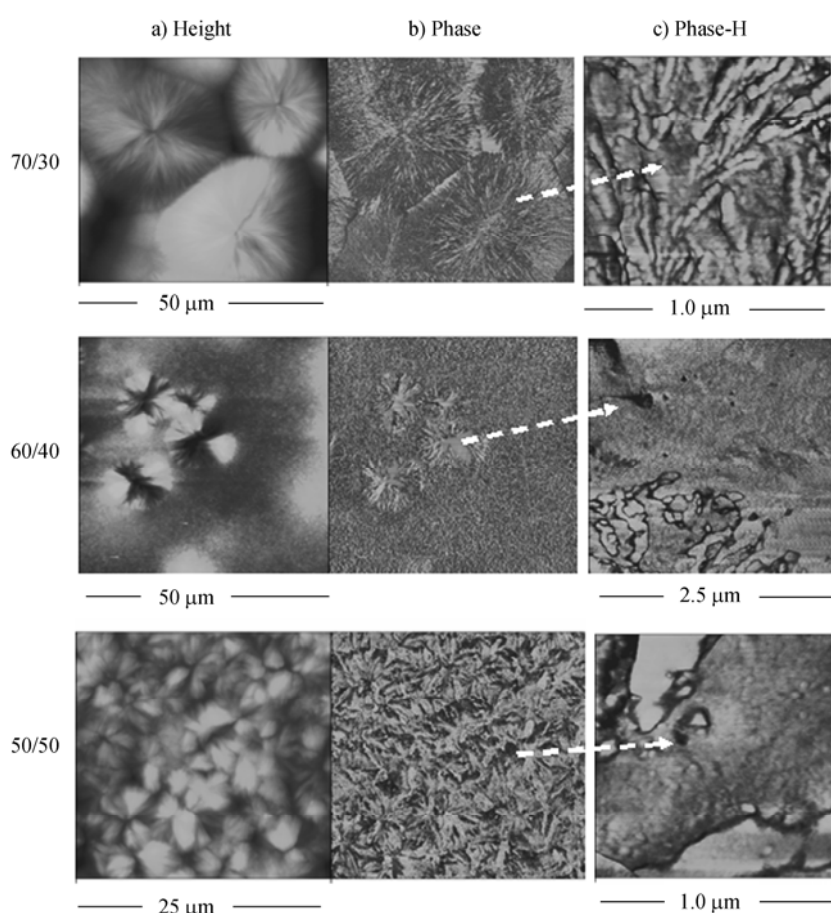


Fig. 4 AFM (a) height, (b) phase, and (c) phase-H images of the surface of the PVDF/PMMA-co-PEA blends. The length scale is indicated in each image; Samples were prepared under RT-cooled condition.

For the 60/40 blend, the surface ($50\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$) appears smoother and contains smaller spherulites. There are no distinguishable lamellae structures in the phase image at higher magnification. For the 50/50 blend, a smaller measured area ($25\text{ }\mu\text{m} \times 25\text{ }\mu\text{m}$) is needed to obtain better structural images. The surface is mostly covered with the crystallites (both in height and phase images). This crystallite morphology is much smaller ($3\text{--}5\text{ }\mu\text{m}$) than that observed on the surface of the 70/30 blend. More particle-like structures are observed in the high magnification phase images. Note that we did not observe any particular structure in the LSCM images in Fig. 2(a). This implies these crystallites don't have strong optical contrast against the neighboring amorphous materials, and the surface of the blend is reasonably smooth thus appearing featureless in the LSCM images.

It should be mentioned that, even at high magnification, we did not observe the fine fibrils and lamellae

structures that were reportedly found in the AFM images of the pure crystallized PVDF film^[18]. However, the SANS results, as shown in Fig. 5, indicate the existence of PVDF-rich microstructure (randomly distributed lamellae structure in a three dimensional bulk film). As mentioned previously, SANS measures the “spacing” between lamellae structures or PVDF-rich domains. By fitting the scattered intensity, $I(q)$, to a Guinier approximation: $I(q) \approx I(q = 0)\exp(-q^2 R_g^2)$ ^[13], the radius of gyration, R_g , of PVDF-rich domain can be determined. The values of R_g are (2.5 ± 0.09) nm for the 70/30 blend, (7.6 ± 0.08) nm for the 50/50 blend, and > 25 nm for the 30/70 blend. Here the radius of gyration, R_g , which is proportional to the correlation length of PVDF concentration fluctuations, increases as the PVDF content decreases. This result implies that the distance between lamellae structure increases with a higher acrylic copolymer (PMMA-co-PEA) content. Therefore, we believe that the microstructures of the PVDF spherulites in the bulk of the blends have been modified due to the presence of the acrylic copolymer. Additionally, the incorporation of the acrylic copolymer in the crystals may have blurred the fine structure of PVDF during AFM imaging.

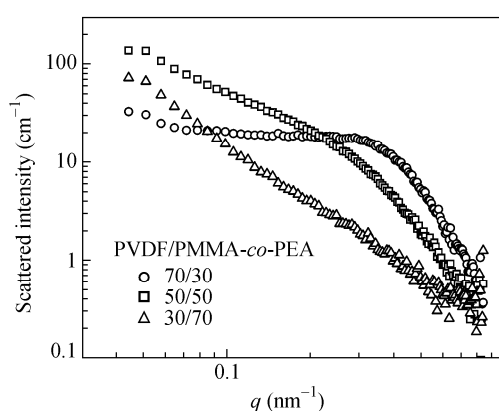


Fig. 5 SANS intensity profiles of PVDF/PMMA-co-PEA blends at three different blend compositions: 70/30, 50/50, and 30/70. The error bars are smaller than the symbols in the graph; Samples were prepared under RT-cooled condition.

UV Exposed PVDF/PMMA-co-PEA Blends

Figure 6 shows the results of SANS analysis of 70/30 PVDF/PMMA-co-PEA blends prepared by two different processing methods for unexposed (fresh) and exposed to UV radiation for 2 months. For both conditions, the scattered intensities of exposed samples decrease in the q range of 0.2 nm^{-1} and 0.5 nm^{-1} , but the q_{peak} positions are not significantly changed. The water-cooled samples (fast cooled, small crystallites) exhibit smaller changes

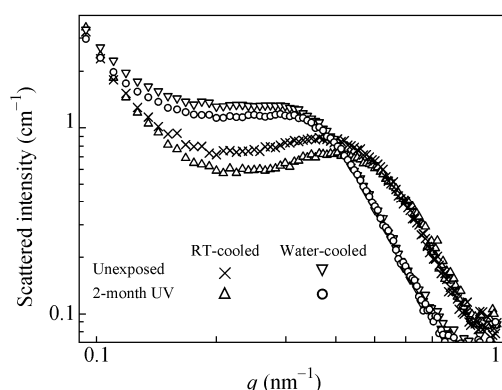


Fig. 6 SANS intensity profiles of the 70/30 PVDF/PMMA-co-PEA blends before and after a 2-month UV exposure at two cooling conditions: RT-cooled and water-cooled as indicated in the legend. The error bars are smaller than the symbols in the graph.

in intensity profiles compared to that of the RT-cooled samples. This implies that the fast cooled samples had better UV resistance. Furthermore, a sharper peak was observed in the RT-cooled sample, and indicating more ordering in the size distribution of the PVDF-rich domains of slow cooled samples and more organized lamellae structures.

Evidence for the increased ordering of the PVDF-rich domain can be also seen in the AFM images of the UV-degraded surface of the blend films. Figure 7 displays the AFM images of 2-month exposed PVDF/PMMA-co-PEA blends for three compositions, 70/30, 60/40 and 50/50, respectively. The samples studied in this section were prepared under the RT-cooled condition. For the surface of the 70/30 blend, there is no obvious change in the topography after UV exposure (Fig. 7a). However, the phase images, especially the ones observed at higher magnification ($1\ \mu\text{m} \times 1\ \mu\text{m}$, Fig. 7c), have revealed that the microstructure of the spherulite has changed substantially after 2 months of UV exposure. The distinct lamellae arrangements are clearly seen on the exposed sample, while blurred branches with some amorphous particles shown on the unexposed sample. The changes in the 60/40 and 50/50 blends are dramatically different compared to Fig. 4(c), in which no noticeable lamellae features were observed. As shown in the last two images in Fig. 7(c), the crystallites distinctly stand out on the sample surface, resulting in a much rougher surface than the unexposed one. Combining the attenuated total reflection-FTIR spectroscopy (not represented here)^[8, 9] and AFM results, it is reasonable to conclude that such morphological changes are due to a degradation of the acrylic copolymer on the surface of the blend films during UV exposure. The higher the content of acrylic copolymer on the sample surface, the more pronounced the observed changes.

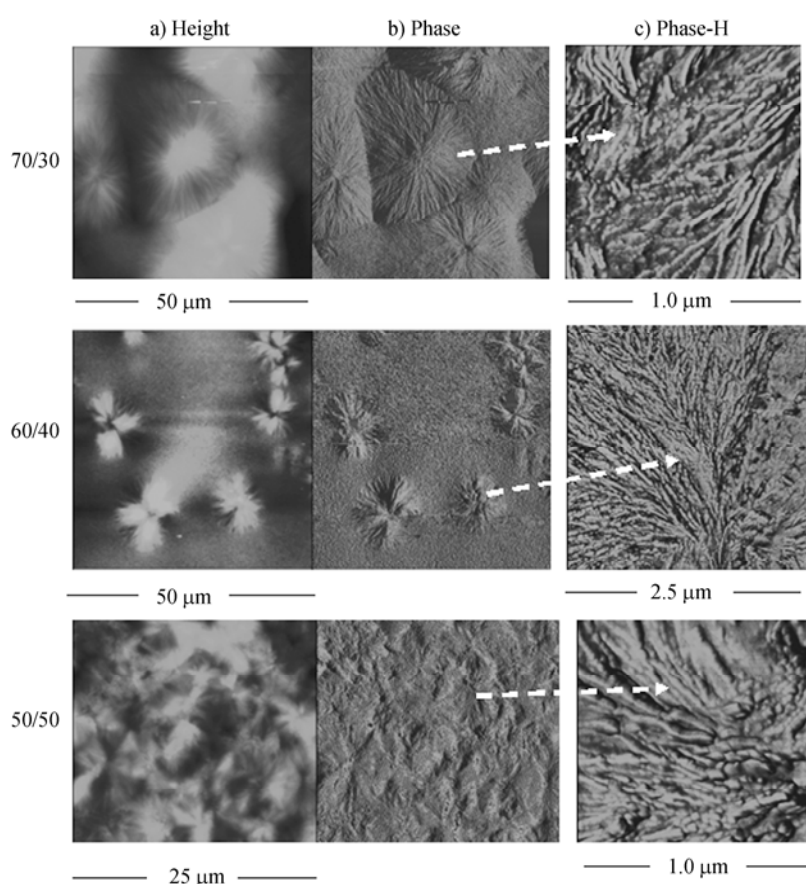


Fig. 7 AFM (a) height, (b) phase, and (c) phase-H images at higher magnification for surface of the PVDF/PMMA-co-PEA blends after a 2-month UV exposure
The length scale is indicated in each image.

As mentioned previously, the fine lamellae structure in the spherulites are clearly observed in the phase image of the exposed samples (Fig. 7c) as compared to the unexposed ones. The erosion of the acrylic copolymer during UV irradiation leads to the exposure of the PVDF crystallites, revealing the detailed crystalline information without interference from the acrylic materials. However, it is also possible that the crystallite structure has been modified by exposure. Previous studies have shown that PVDF can undergo recrystallization, increase or decrease its crystallinity when exposed to ionizing irradiation, γ -ray/UV exposure or thermal annealing^[19–21]. Changes depend on radiation wavelength, the intensity and duration, temperature and environment. In this study, the UV exposure was performed at 50°C, 9% RH using a UV source with wavelengths ranging from 275 nm to 800 nm. The exposure temperature was close to the glass temperature of the PVDF/PMMA-co-PEA blends (for example, T_g of 50/50 blend film is 53°C), and was much higher than T_g of PVDF (–30°C). The effect of the annealing and the UV irradiation may cause local movement, chain rearrangement, and even the recrystallization of PVDF in the blends. Therefore, the microstructural changes observed in the AFM images might not only be due to the degradation of acrylic copolymer in the blends^[8, 9], but may also involve certain microstructural modifications in the PVDF crystalline regions.

LSCM and SALS experiments were carried to investigate the surface morphology and microstructure of PVDF/PMMA-co-PEA blends at larger size scales. Figure 8 displays the LSCM 2D projection images for the three PVDF/PMMA-co-PEA blends after a 6-month UV exposure. Compared to Fig. 2(a), the surface roughness is increased and more distinguishable, and larger crystallite structures are observed in all three blends after UV exposure. For the 50/50 blend, the smooth and featureless surface (Fig. 2a) becomes a surface filled with small crystallites as seen in LSCM images (Fig. 8). LSCM and AFM provide evidence of the effect of UV radiation on the surface morphology. To understand the effect of UV irradiation on the entire bulk films, SANS and SALS were used. Figure 9 shows the cross-polarized (Hv) SALS scattered intensity profiles as a function of scattering wave vector, q , for unexposed and the 6-month UV-exposed 60/40 blend. The 2D SALS scattering images of a four-lobed pattern is also displayed in the insert of the Fig. 9. The scattered intensity is an averaged value of the intensities along the lines of each lobe. The 2D SALS image of the UV-exposed sample exhibits much higher intensity in the pattern than the unexposed sample. The overall scattering intensity increases as shown in the graph, however, the peak intensity position, $q^*(I_{\max})$ remains the same after UV exposure. This implies that the average size of spherulites does not change after UV exposure but the contrast in crystallites and neighboring amorphous materials has increased. This is direct evidence of the ordering of PVDF crystallites during UV irradiation. Thus, the UV irradiation may cause local movement, chain rearrangement, and even the recrystallization of PVDF in the blends.

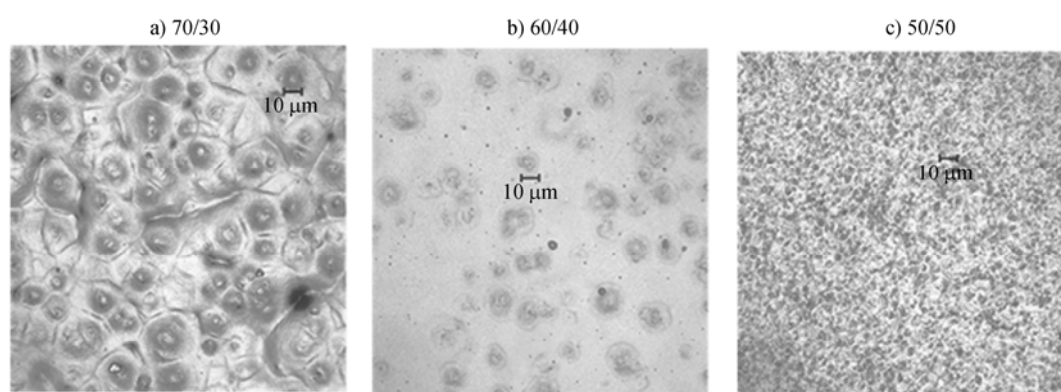


Fig. 8 LSCM images of the PVDF/PMMA-co-PEA blends after a 6-month UV exposure

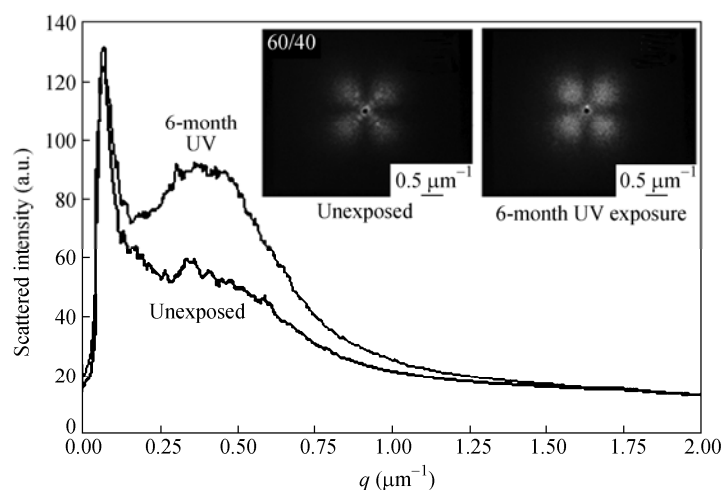


Fig. 9 SALS intensity profiles as a function of scattering wave vector of the 60/40 PVDF/PMMA-co-PEA blend films before and after a 6-month UV exposure
The error bars are smaller than the width of the line in the graph; The 2D SALS images are also represented in the insert; The size bar is indicated in each image.

CONCLUSIONS

The effects of processing conditions and blend composition on the surface morphology and microstructure of PVDF/PMMA-co-PEA blend films before and after UV exposure have been investigated by combining the surface analysis techniques, AFM and LSCM, and bulk microstructure characterization tools, SANS, and SALS, which cover a wide range of length scales (1 nm to 1 mm). The size of the spherulite structures and surface morphology of the blends depends strongly on processing conditions and blend composition. Higher PVDF content and slower cooling process result in a larger spherulite crystallite structure and rougher surface morphology. After UV exposure, significant surface degradation of PMMA-co-PEA copolymer was observed. The surfaces of the blends having greater than 60% mass fraction of PVDF show little change in the morphology after UV exposure. But lower PVDF contents exhibited a much rougher surface due to a larger amount of the erosion of the acrylic copolymer. Additionally, substantial change in the microstructure of the spherulites has been observed after UV exposure. Well-organized lamellae structures are clearly observed in the AFM phase image as well as in the cross-polarized (Hv) SALS profile of the exposed samples as compared to the unexposed ones. This change may be due to the erosion of PMMA-co-PEA copolymer on the sample surface and the microstructural modification of the crystallites in the PVDF spherulites.

REFERENCES

- 1 Iezzi, R.A., "Fluoropolymer coatings for architectural applications", In "Modern Fluoropolymer: High Performance Polymers for Diverse Applications", ed. by Scheirs, J., John Wiley & Sons Ed, New York, 1997, Chap. 14, p.271
- 2 Iezzi, R.A., Gaboury, S. and Wood, K.A., Prog. Org. Coat, 2000, 40: 55
- 3 Scheirs, J., Burks, S. and Locaspi, A., TRIP (Trends in Poly Sci), 1995, 3: 74
- 4 Bernstein, R.E., Crua, C.A., Paul, D.R. and Barlow, J.W., Macromolecules, 1977, 10: 681
- 5 Wang, T.T. and Nashi, T., Macromolecules, 1977, 10: 421
- 6 Wood, K.A., Cypcar, C. and Hedhli, L., J. Fluorine Chem., 2000, 104: 63
- 7 Sung, L., Vicini, S., Ho, D.L., Hedhli, L., Olmstead, C. and Wood, K.A., Polymer, 2004, 45(19): 6639
- 8 Gu, X, Sung, L., Ho, D.L., Michael, C.A., Nguyen, D., Jean, Y.C. and Nguyen, T., "Proceedings of the FSCT-ICE 80th

- Annual Meeting Technical Program”, Federation of Societies for Coatings Technology, Blue Bell, PA, USA, 2002
- 9 Gu, X., Michaels, C.A., Nguyen, D., Jean, Y.C., Martin, J.W. and Nguyen, T., *Appl. Surf. Sci.*, 2006, 252: 5168
 - 10 Corle, T.R. and Kino, G.S., “Confocal Scanning Optical Microscopy and Related Imaging Systems”, Academic Press, San Diego, CA, USA, 1996
 - 11 Sung, L., Jasmin, J., Gu, X., Nguyen, T. and Martin, J.W., *JCT Research*, 2004, 1(4): 267
 - 12 Choi, S.M., Barker, J.G., Glinka, C.J., Cheng, Y.T. and Gammel, P.L., *J. Appl. Cryst.*, 2000, 33: 793
 - 13 Higgins, J.S. and Benoit, H.C., “Polymers and Neutron Scattering”, Clarendon Press, Oxford, UK, 1994
 - 14 Saito, H., Okada, T., Hamane, T. and Inoue, T., *Macromolecules*, 1991, 24: 4446
 - 15 Kalivianakis, P. and Jungnickel, B.J., *J. Polym. Sci. Polym. Phys.*, 1998, 36: 2923
 - 16 Brau, D., Jacobs, M. and Hellmann, G.P., *Polymer*, 1994, 35: 706
 - 17 Briber, R.M. and Khoury, F., *Polymer*, 1994, 28: 38
 - 18 Magonov, S. and Godovsky, Y., *American Laboratory*, 1999, 31(8): 52
 - 19 Biswas, A., Gupta, R., Kumar, N., Avasthi, D.K., Singh, J.P., Lotha, S., Fink, D., Paul, S.N. and Bose, S.K., *Appl. Phys. Lett.*, 2001, 78: 4136
 - 20 Pae, K.D., Bhateja, S.K. and Gilbert, J.R., *J. Polym. Sci., Polym. Phys.*, 1987, 25: 717
 - 21 Katan, E., Narkis, M. and Siegmman, A., *J. Appl. Polym. Sci.*, 1998, 70: 1471