

# Combination of Atomic Force Microscopy and Chemical Hydrolysis to Characterize Degradable Regions in Polymer Blends

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**ABSTRACT:** In this study, we demonstrate the usefulness of chemical-based method in combination with atomic force microscopy (AFM) to characterize the degradable regions in a wide range of polymer blends. This approach is based on selective hydrolysis of one of the components in a multiple-phase system, and the ability of AFM to provide nanoscale lateral information about the different phases in the polymer system. Composite films containing different percentage of hydrolyzable polymer were either melt processed or solution casted and then exposed to a hydrolytic acidic environment. Tapping mode AFM was used to analyze the samples before and after hydrolysis. Dramatic topographic changes

such as pits were observed on the acid exposed samples, indicating that the degradation was localized and the more susceptible component in the blend was hydrolyzed. Additionally, the progressive hydrolysis of the composites was studied by attenuated total reflection FTIR (ATR-FTIR) analyses to confirm the AFM results. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 726–733, 2006

**Key words:** tapping mode atomic force microscopy; degradable polymer blends; ATR-FTIR; selective hydrolysis; chemical method

## INTRODUCTION

The applications of polymer are diversified and require different levels of service performance. Long-term performance of polymer is required in aircrafts, automobiles, and electronics, while polymers with short service life are desired for many applications such as drug delivery system, filtration device, packaging, agricultural mulch film, degradable escape hatches for lobster pots, and nursery pots.

Development and use of degradable polymers will be of paramount importance in areas where polymers with short shelf life are required. Initial efforts to address the degradability of conventional recalcitrant polymeric material have focused on substituting a major portion of the nondegradable polymer by de-

gradable renewable polymer (i.e., starch, cellulose, lignin, poly(lactic acid), poly(hydroxy butyrate), and chitin), and/or degradable synthetic polymer (i.e., poly(vinyl alcohol), poly(caprolactone)).<sup>1–4</sup> Typically, the blends have starch particles dispersed in recalcitrant polymer matrix. Replacing some of the petroleum-derived synthetic polymer with renewable plant-based raw material (starch) is attractive, both economically and ecologically. The plant-based materials (e.g., starch) have been shown to readily degrade in biologically active environment to release nontoxic products.<sup>5</sup>

It is well known that starch granules are semicrystalline in which glucose particles are polymerized into amylose and amylopectin, forming closely packed structure. The diameter of the starch granule can range from 1 to 100  $\mu\text{m}$ , depending on the biological source, with typical corn starch granules falling between 5 and 20  $\mu\text{m}$ . The packing of amylose and amylopectin within the granules has been reported to vary among the starches.<sup>6–8</sup> Amylose is a linear polymer composed of glucopyranose units linked through<sup>1–4</sup>  $\alpha$ -D-glycosidic linkages, whereas the amylopectin is a highly branched polymer.<sup>9</sup> The crystallinity of starch is almost exclusively associated with the amylopectin component, while the amorphous regions are mainly represented by the amylose component.<sup>10,11</sup> Therefore, the starch with higher amylose content has lesser crystalline region and more amorphous region.<sup>12</sup>

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It has been suggested that the chemical and enzymatic reactivity and physicochemical properties of starch are strongly influenced by the structure of starch granules.<sup>13,14</sup> Acids such as HCl and H<sub>2</sub>SO<sub>4</sub> cause scission of the glucosidic linkages, thereby altering the native structure of the starch. The amorphous regions of the starch granule are more susceptible to acid hydrolysis than the crystalline regions. Evidence to suggest that indeed amorphous regions within the granule are preferentially attacked by acid comes from transmission electron microscopy observations of acid hydrolyzed starches.<sup>15</sup> Several hypotheses have been put forth to explain the slow hydrolysis rate of the crystalline parts of the starch granule, and they range from the difficulty of hydronium ions in accessing the dense packing of starch chains within the starch crystallites to the preferred conformation of the D-glucopyranosyl unit for the acid to perform chain scission.<sup>16,17</sup> Detailed review about the mechanism and effects of acid hydrolysis on structures and physicochemical properties of various starches can be found in Ref. 18.

In addition to starch structure, the extent of hydrolysis of starch can be controlled by the acid concentration, the reaction time, and the temperature. For example, when HCl concentration increased, it was noticed that more hydrogen ions would be available to access a greater proportion of amorphous and possibly crystalline regions, therefore, more degradation of amylose and amylopectin molecules would take place by concentrated HCl.<sup>13,14,18</sup> Since the primary objective of this study is to characterize degradable regions in starch-filled blends the hydrolysis study described deals with concentrated acid solution.

Although starch is a degradable additive in filled synthetic polymer system, over the last decade the overall degradability of the filled polymer system has been called into question. One way to enhance the degradability of the overall-filled polymer is to replace the nondegradable portion of the blend by other degradable polymers. By using suitable mixing and processing techniques, starch particles have been combined with poly(vinyl alcohol), poly(hydroxyl butyrate valerate), polylactic acid, and/or polycaprolactone to yield blends with a good degree of degradability.<sup>19–22</sup>

Generally at early stages of degradation, the polymeric material exhibits surface morphological changes before measurable changes in bulk properties are noticeable with time. For a heterogeneous polymer system, at early stages, the degradation is expected to start from the regions with more hydrolyzable or degradation-susceptible components. The micrometer or submicrometer length scale of the degraded regions in phase-separated polymer blends and the localized spatial distribution of these regions make the macro-

scopic techniques less valuable and the surface-averaged measurements less informative.

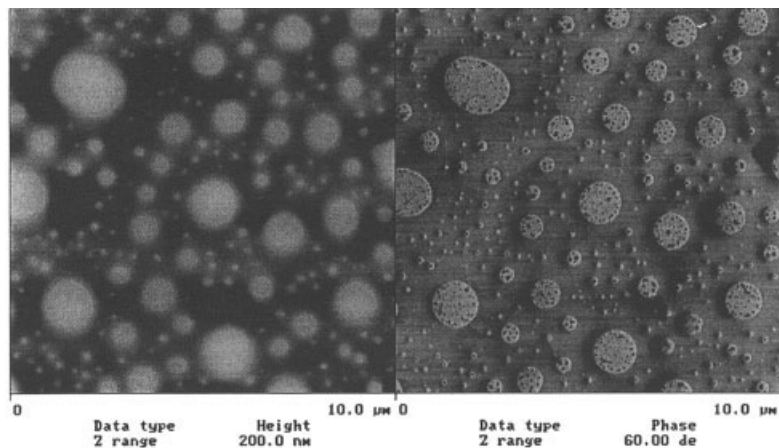
It is well known that AFM can provide direct spatial mapping of the surface topography of diverse regions in polymeric materials at nanometer resolution with minimal sample preparation.<sup>23–25</sup> In addition to surface topography mapping capability, phase images in tapping mode AFM often reflects differences in the properties of individual components of a heterogeneous polymer blend system. Our previous study had utilized a combination of phase imaging and nanoindentation capability of AFM to identify the multicomponents in a heterogeneous system based on their different local mechanical properties.<sup>26,27</sup> However, there is limited information available about the use of AFM to map individual phases in blends, where the individual components in blends differ in the extent of degradation. In an earlier paper, we had used a combination of chemical hydrolysis of polymer blend and AFM, to study the progressive degradation of the susceptible component in the blend.<sup>28</sup> We extend the work to characterize degradable regions in several polymer blend systems, particularly, in the corn starch based polymer blend, where the components of the blend show significant difference in the chemical characteristics and the degree of degradation.

A synthetic polymer blend system (polystyrene: poly(ethyl acrylate); PS : PEA), a partially renewable system (starch : polyethylene; S : PE) and a fully renewable system (starch : poly(hydroxy butyrate valerate); S : PHBV) were selected to study the usefulness of AFM to characterize regions in degradable polymer blend. Approximately the same locations of each sample were monitored with AFM at different exposure times. An inorganic acid has been chosen as the aggressive chemical medium so as to accelerate the hydrolysis/degradation of one of the components in a multicomponent polymer blend system without modifying the other component. AFM results are used along with results from attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) to assist in interpreting the composition of degradable regions in the blend system.

## EXPERIMENTAL

### Materials preparation

Poly(ethyl acrylate) (PEA) with  $M_w = 119,300$  and  $T_g = -30^\circ\text{C}$ , and PS with  $M_w = 250,000$  and  $T_g = 104^\circ\text{C}$  were acquired from the Aldrich Company. To prepare PEA : PS blend of 70% mass fraction and 30% mass fraction, a 2% mass fraction solutions of PS and PEA in toluene were mixed in appropriate amounts. The blend was casted into thin films by spin coating on silicon substrate, the details of which can be found elsewhere.<sup>28</sup> All of the cast films were conditioned for



**Figure 1** AFM topographic (left) and phase (right) image of PS : PEA (30 : 70 w/w) before exposure to HCl vapor. Contrast variations are 200 nm from white to black for the height images and 60° from white to black for the phase image.

24 h at  $24^{\circ}\text{C} \pm 2^{\circ}\text{C}$  before analysis. Some of the conditioned samples were analyzed using AFM, while the remaining samples were exposed to acid vapors and then analyzed using AFM and FTIR.

Polyethylene (PE) was placed in the bowl of Brabender processing equipment at  $170^{\circ}\text{C}$  and 110 rpm in order, for the polymer to melt. Corn starch (S) supplied by ADM Company was hand mixed with 2% vernonia oil by mass before the addition to PE melt. The starch–vernonia oil mixture was slowly added and blending was allowed to continue to mix in the processing unit for 5 min. Vernonia oil improved the mixing of starch and polymer and was noted at the interface of starch/polymer blend.<sup>29</sup> The blend of 60% mass fraction, S, and 40% mass fraction PE composite were then compression molded into thin films at 3500 psi by holding the sample at  $160^{\circ}\text{C}$  for 20 min, using a Carver Laboratory Press (Model 2518). Similarly, S:PHBV blend was also melt processed.

In addition to the renewable blend sample, films of PHBV and PE were also compression molded so that property changes in the starch-rich regions of the blend samples during hydrolysis could be compared with chemical property changes of films of PHBV and PE.

### Hydrolysis experiment

Acid was used to hydrolyze the degradable component in the blend. A 250 mL dessicator was initially filled with 100 mL of 2M HCl. The blend films were placed on a dessicator grid, which was kept several centimeters away from the acid solution. The hydrolysis experiment was conducted at  $24^{\circ}\text{C} \pm 2^{\circ}\text{C}$  for predetermined time intervals. At specified time intervals, PEA:PS, S:PE, and S:PHBV samples were removed from the dessicator for AFM and ATR-FTIR

characterizations. Care was taken to image the same region of the sample before and after exposure.

### Atomic force microscopy and ATR-FTIR analysis

A Dimension 3100 Scanning Probe Microscope from Digital Instruments was operated in tapping mode to characterize the morphology of blend and composite films. The same experimental procedure for AFM was carried out as those described in Refs. 26 and 27. ATR-FTIR analyses were performed using a diamond probe and dry air as purge gas. The collected ATR-FTIR spectra were the average of 256 scans at a resolution of  $4\text{ cm}^{-1}$  using liquid nitrogen cooled mercury cadmium telluride detector (MCT).

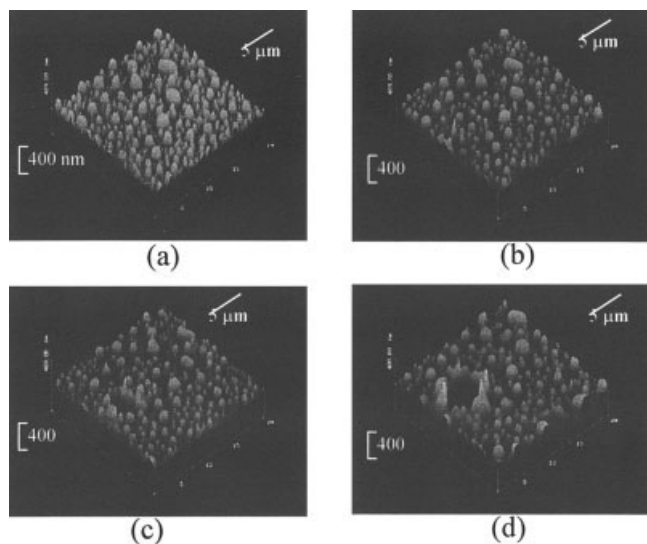
## RESULTS AND DISCUSSION

In this study, we demonstrate the usefulness of chemical hydrolysis and tapping mode atomic force microscopy (AFM) to identify different components in a wide range of degradable polymer blends and to study the early stages of their degradation. Among the systems selected for this study include solution casted PEA : PS, melt-casted S : PE, and melt-casted S : PHBV blends, where PEA and S are more acid hydrolyzable components in the blends. The morphological change at a fixed location of each sample was followed by AFM in tapping mode before and after the sample was exposed for specified time intervals.

### Characterization of PEA : PS blend

Figure 1 shows height image (left) along with the corresponding phase images (right) for a 70 : 30 PEA : PS blend film obtained by AFM under ambient conditions. The thickness of this film was  $150 \pm 20\text{ nm}$ , as





**Figure 2** 3D topographic image of PS:PEA (30:70 w/w) as a function of exposure time in HCl vapor (a) 0 h, (b) 0.5 h, (c) 3 h, and (d) 578 h.

measured by AFM. Both height and phase images show that phase separation has occurred and the circular domains are bright and elevated with respect to the matrix. However, it is difficult to identify the components based on the compositions of the domains or the matrix or based on the phase contrast of different regions in the phase images.<sup>27</sup>

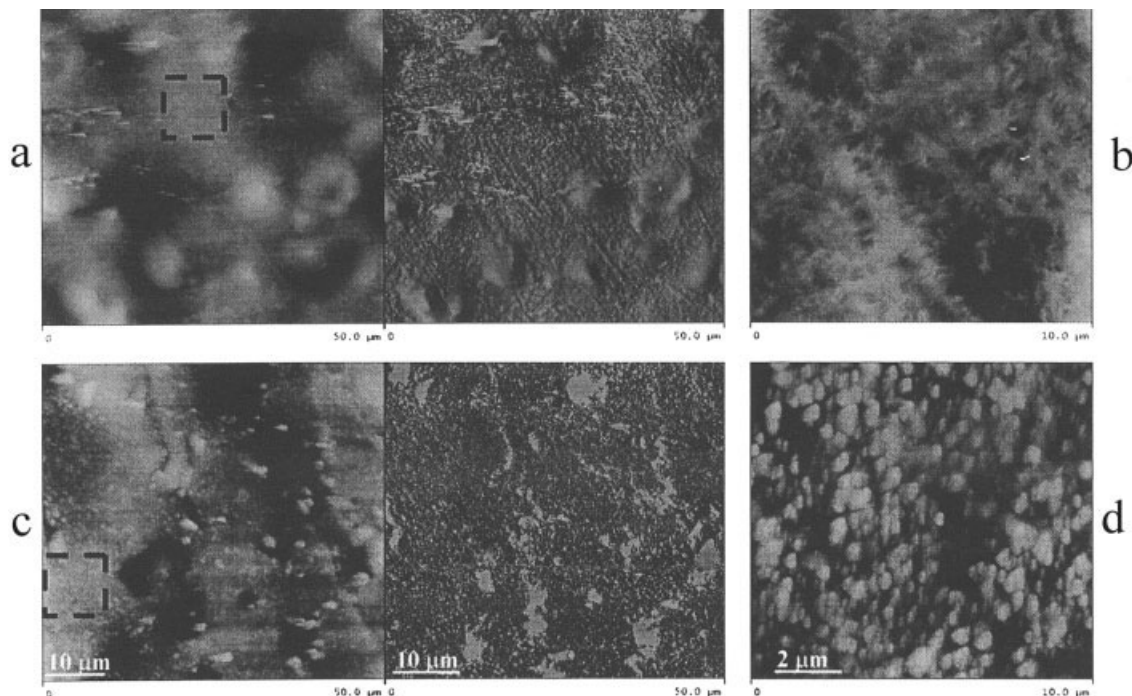
To establish that the elevated domains in blend are vastly different from the matrix region, inorganic acid medium was used to effectively hydrolyze the more degradable polymer in this synthetic polymer blend system. Since PEA is relatively a hydrophilic polymer compared with PS, it is expected that PEA regions in the blend will be more susceptible to acid environment. AFM images of the blend film that had been exposed to 2M HCl vapor were collected at several time intervals and three-dimensional topographic images were shown in Figure 2. During the initial phase of exposure (0.5 h) of the blend, the AFM topographic images showed a small amount of swelling of the matrix region in the blend. After 3 h of acid exposure, pits were observed to form locally at the matrix regions of the blend, pushing the domain particles around the pit towards the edge resulting in an elevated rim. However, other regions in the matrix were essentially unaltered at this stage. With prolonged HCl vapor exposure, the deepening and enlargement progression of the pit were observed, and a number of new pits appeared. The lateral dimension of one particular pit increased from tens of nanometers to several micrometers, and the depth of the pit was up to 150 nm. The results indicate that the pit has reached the bare silicon substrate, in which the entire 150-nm thick film has been removed.

To verify that the aforementioned morphological changes were indeed due to the hydrolysis of one of the components in the blend film, the morphology and composition of pure PEA film and pure PS film before and after acid exposure were studied by AFM and FTIR techniques. In contrast to generally smooth surface of exposed PS film, the AFM image of exposed PEA film showed isolated degradation pits.<sup>28</sup> The FTIR difference spectra between the PEA film before and after exposure also revealed the loss of the ester peak at  $1732\text{ cm}^{-1}$  and the growth of acid peaks at  $1710\text{ cm}^{-1}$ , whereas exposed PS film showed no obvious change in FTIR. Thus, PEA is indeed the more hydrolyzable component in the PEA : PS blend. It can be concluded that in 70 : 30 PEA : PS film, the hydrolyzed matrix was PEA-rich region and the domains were PS-rich. Through these results, we have demonstrated that in combination with the chemical hydrolysis, AFM is a valuable tool to identify the chemically heterogeneous regions in the polymer blend, and is a useful tool to study the early stages of degradation in synthetic polymer blends when exposed to aggressive environments.

#### Characterization of S:PE blend

The AFM/chemical modification approach was extended to study the early stages of degradation of partially renewable polymer blend and was used for identifying different phases in partially degradable 60 : 40 S : PE blend. In Figure 3, AFM height images (left) and the corresponding phase images (right) of the S:PE blend films unexposed (a) and exposed to HCl vapor for 7 days (c) were presented. Both the height and the phase images of the unexposed film exhibited that the domains with the asymmetric disc shape are dispersed in the matrix [Figs. 3(a) and 3(b)]. Sizes of these domains and the spacing between different domains are not regular in the melt-casted film with respect to the spin-cast film of PEA:PS presented previously. By analyzing the AFM phase images of several 50- $\mu\text{m}$  sized scans, the diameter of the domains is calculated as  $6.27 \pm 1.36\ \mu\text{m}$ . This value is in general agreement with the diameter of the starch granule reported in the literatures using SEM<sup>30</sup> or AFM.<sup>31</sup> A higher magnification of height image of a region in the matrix of the unexposed S : PE blend film was shown in Figure 3(b). Compared with the disc-like domains, the fine fibrillar structure was noticed in the matrix region, which is indicative of the semicrystalline PE.<sup>32</sup>

When PE:S blend was exposed to HCl vapor for 7 days, most of disc-like domains disappeared with the formation of holes at the same locations [Fig. 3(c)]. Note that the examined regions of the film before and after exposure to the acid environment were almost in the same location. The hole formation is consistent

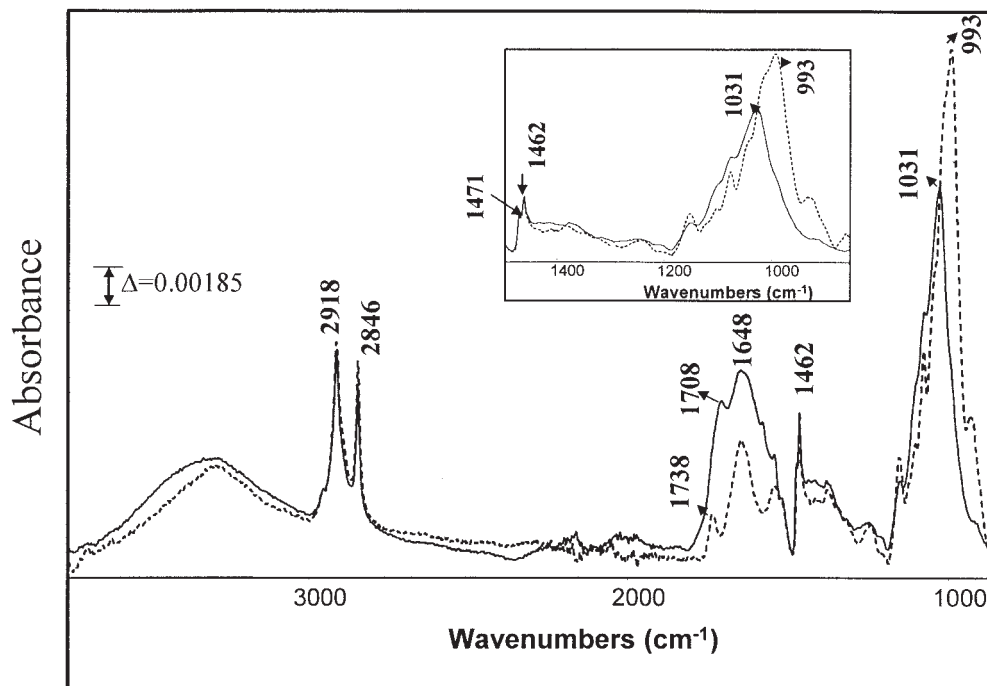


**Figure 3** Tapping mode AFM topographic and phase images of S : PE (60 : 40 w/w) film unexposed (a) and exposed to HCl vapor for 7 days (c). (b) and (d) represent the topographic images of the higher magnification of (a) and (c) in the squared regions, respectively. Color contrast from black to white represents a total range of 1000 nm in the height image of (a) and (c), 200 nm in (b) and (d), and 90° in the phase image.

with the previous *in situ* study of enzymatic degradation of starch by AFM.<sup>31</sup> It was proposed that the attack started from the weakest area of the surface and eroded a hole into the granule. We believe that such morphological changes are mainly a result of the chemical degradation of starch. Previous work<sup>33</sup> showed that the acid degradation of starch is dependent on the acid type. HCl was found to be one of most effective acids to degrade the starch. Substantial mass loss of starch was observed after HCl degradation,<sup>29</sup> along with significant molecular weight decrease for the remaining materials after degradation.<sup>33</sup> Small particles were observed on the surface of the matrix material at higher magnification [Fig. 3(d)]. They may represent the degraded products that were formed after acid exposure. At present, there is no evidence whether only amorphous regions within the starch granule were degraded or both crystalline and amorphous regions were degraded by the acid medium.

To assist with further identification of the domains in the blend system and to get a better explanation to the results obtained by AFM, S : PE blend was exposed to HCl vapor and chemical changes were studied by ATR-FTIR. Figure 4 showed the ATR-FTIR spectra obtained from the S : PE film before and after exposure to HCl vapor. In unexposed blend film, peak at 1738  $\text{cm}^{-1}$  that correspond to the ester group in vernonia oil, that is, the additive added to improve the

mixing of starch and PE,<sup>34</sup> and the peaks around 993  $\text{cm}^{-1}$  were attributed to C—O stretching vibrations in starch. The peak at 1462  $\text{cm}^{-1}$  was mainly due to CH<sub>2</sub> scissoring and asymmetric bending in PE,<sup>23</sup> with small contribution from starch.<sup>35,36</sup> Additionally, from the inset plot that ranged from 855 to 1500  $\text{cm}^{-1}$ , the splitted peaks at 1471 and 1462  $\text{cm}^{-1}$  were observed. These splitted peaks because of the crystal field splitting are one of the characteristic features of semicrystalline PE.<sup>37</sup> When the film was exposed to acid vapor for 7 days, the broad band at 993  $\text{cm}^{-1}$  shifted to a more diffused peak at 1031  $\text{cm}^{-1}$ , and a new peak at 1708  $\text{cm}^{-1}$  appeared. Because the ATR-FTIR intensity is dependent on the contact area between the sample and the ATR crystal, which is substantially influenced by the sample surface roughness and vary within different samples, we used the relative intensity of the C—O absorbance around 993  $\text{cm}^{-1}$ , with respect to the intensity of CH<sub>2</sub> vibration at 1462  $\text{cm}^{-1}$  to quantitatively evaluate the relative amount change of starch in the blend during exposure. The spectra shown in Figure 4 were normalized by the intensity of the peak at 1462  $\text{cm}^{-1}$ . The normalized spectra, in particular the inset plot, clearly show the decrease in relative intensity of C—O absorbance after exposure. The aforementioned results indicated that the starch was preferentially degraded, and the degraded products and the partially hydrolyzed starch were formed. The appearance of new peak at 1708  $\text{cm}^{-1}$  suggested that



**Figure 4** ATR-FTIR spectra of S : PE film before (solid line) and after (dotted line) exposure to 2M HCl vapor for 7 days. Inset is the spread out of the region between  $1500\text{ cm}^{-1}$  and  $855\text{ cm}^{-1}$ . The dotted line is normalized by the peak at  $1462\text{ cm}^{-1}$ .

glycosidic bonds (C—O—C) in starch underwent hydrolysis and new carbonyl functionalized products are formed. The ATR-FTIR results are consistent with the pit formation in the domain regions of the blend as observed by AFM (Fig. 3). However, it is difficult to ascertain whether the morphological changes in the matrix region of the degraded blend film [Figs. 3(b) and 3(d)] was a result of the degraded product moving from starch occupying sites to the surface of the film or the surface rearrangement that has been previously postulated in several polar/nonpolar systems.<sup>38,39</sup> A separate study on PE by ATR-FTIR did not show the chemical change after the same exposure. From the above ATR-FTIR and AFM results, it can be suggested that in S : PE film, the domains, where the pits formed after degradation, were acid hydrolyzable starch-rich granules and the matrix is the nondegradable PE-rich region. This conclusion is indeed confirmed by our mass loss results, showing negligible mass loss and little visible change on PE film after acid hydrolysis, while a considerable mass loss with discoloration of the film for the S/PE specimen after the same exposure. However, the reason for the morphological change in the matrix after exposure needs further exploration.

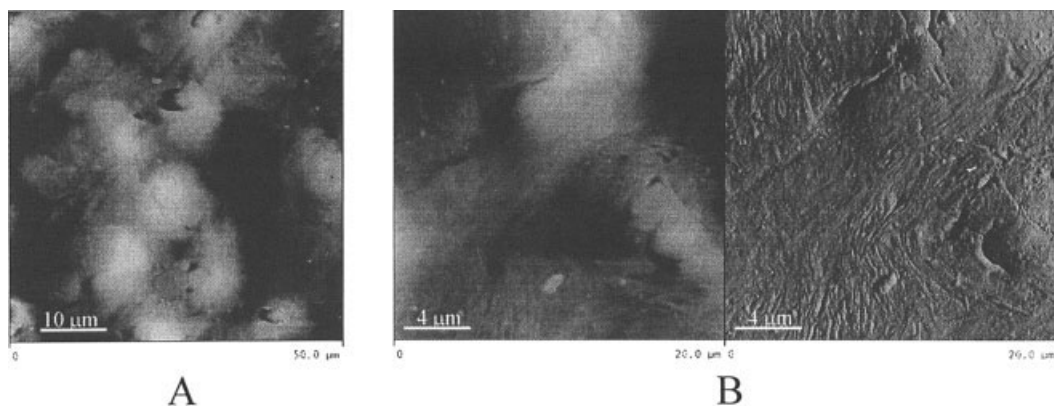
#### Characterization of S : PHBV blend

Here, we extend the AFM/chemical modification approach of acid hydrolysis in combination with AFM to

characterize phase-separated regions of completely renewable polymer blend, where the individual degradable materials have different time scales of hydrolysis in a particular acid environment. Figure 5 presented AFM images of the S:PHBV blend film before exposure to acid environment. In the topographic image of Figure 5(a), we observe disc-like domains dispersed in S : PHBV blend. At higher magnification in Figure 5(b), the amplitude image displays the crystalline structures around the domain particles. As previously mentioned in S : PE blend, the disc-like domains could be starch granules. On the other hand, the matrix with crystalline structures may be PHBV-rich region. It must be noted that pure PHBV is a semicrystalline polymer, and the degree of the crystallinity of PHBV decreases with the increase in the amount of valerate content.<sup>40</sup> However, additional characterization of S:PHBV blend is needed to confirm the AFM observation.

2D height images of the S : PHBV blend films before and after exposure to HCl vapor were shown as Figures 6(a) and 6(b), respectively. Substantial topographic changes were observed for the same location after exposure. The center region that was originally occupied by disc-like domains became considerably rough; the regions neighboring to the domain were elevated while the other regions were depressed. It is believed that the hydrolysis of the domain regions is partially attributed to the topographical changes. The swelling of the degraded materials and the residual





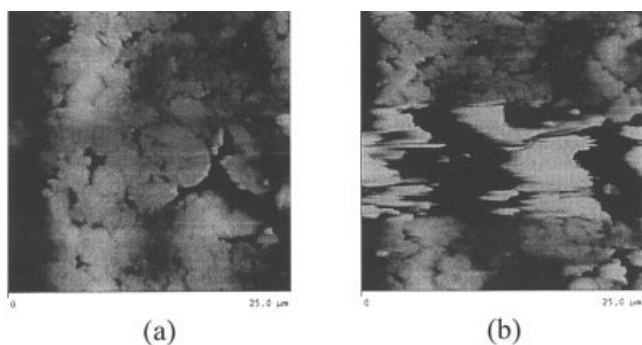
**Figure 5** AFM images of unexposed S : PHBV (60 : 40 w/w): (a) topographic image and (b) topographic (left) and amplitude image (right). Color contrast from black to white represents a total range of 800 nm in the height image and 2 V in the amplitude image.

materials because of moisture absorption could be another factor in observed topographical changes. The abrupt height change in this region made AFM scanning of degraded S/PHBV blends difficult with time.

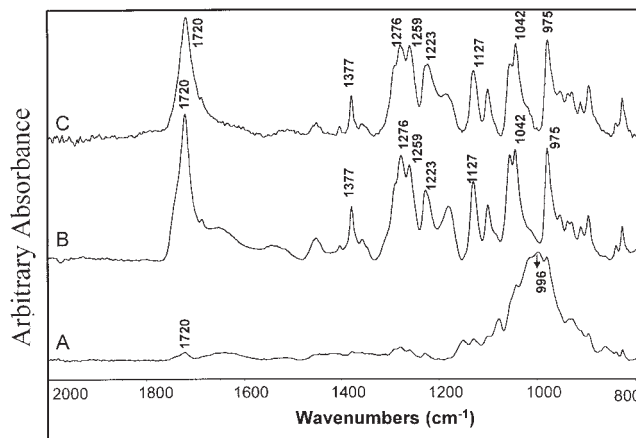
To assist with the identification of the hydrolyzed component in the S:PHBV blend, the film was exposed to HCl vapor for predetermined time intervals and the chemical changes were studied by ATR-FTIR. Figure 7 presented the ATR-FTIR spectra of unexposed S : PHBV (a), exposed S : PHBV (b), and pure PHBV (c) in the range between  $2000\text{ cm}^{-1}$  and  $800\text{ cm}^{-1}$ . As expected, upon acid exposure of the blend film for 5.5 days, the broad band attributed to C—O stretching vibration around  $996\text{ cm}^{-1}$  became narrow and the peak shifted to  $975\text{ cm}^{-1}$ . The relative intensity of C—O bands decreased with respect to C=O band of PHBV at  $1720\text{ cm}^{-1}$ . Furthermore, the spectrum of the exposed S : PHBV had considerable resemblance to the spectrum of pure PHBV both in the peak positions and the relative intensities. The results indicated that the sample surface became more occupied by PHBV and the starch was predominantly hydrolyzed after

exposure. Although PHBV is acid hydrolyzable, the aforementioned results suggested that starch is more hydrolyzable than PHBV in the present acid environment during the initial time scales. Because little amount of starch was observed on the exposed sample surface from ATR-FTIR, the highly elevated, irregular regions observed in AFM of degraded film could be primarily PHBV. During initial starch degradation, it is possible that PHBV swelled with exposure to moisture. Based on the AFM and FTIR data, it can be concluded that in S : PHBV film the hydrolyzed domains were mostly starch granules, and the matrix was the PHBV-rich region.

Thus, we have demonstrated the use of chemical-based method in combination with tapping mode AFM to map the degradable regions in PEA : PS, S : PE, and S : PHBV blend films and to study the early stage of the degradation of these systems under exposure to acid vapor. The results have indicated that the



**Figure 6** Two dimensional topographic image of (a) unexposed and (b) 5.5 days acid exposed S : PHBV (60 : 40 w/w). Color contrast from black to white represents a total range of 500 nm.



**Figure 7** ATR-FTIR spectra in the region of  $2000\text{ cm}^{-1}$  to  $750\text{ cm}^{-1}$  of (A) S : PHBV film before exposure to acid vapor, (B) S : PHBV film after exposure to acid vapor for 3 days, and (C) pure PHBV film.

degradation of all the three blend films is localized, for example, pit/hole formation. The degradation first takes place in the regions that are more hydrophilic or hydrolyzable (such as PEA, starch). During degradation, the hydrolyzed regions would produce the degradation products of low molecular mass, which could promote the degradation hydrophilic regions. This effect is probably one of the reasons for the localized pits/holes formation. The structural rearrangement of nondegradable regions or less degradable regions could also happen during degradation due to long-range attractive forces between the hydrophilic/hydrolyzable regions and the moisture in the acid environment or the hydrolyzed regions. This rearrangement can make pathways, allowing the degradation to develop in vertical direction by exposing the underlying hydrolyzable regions to the acid. The above hypothesis can further explain the deepening and enlarging of the pits in systems, where the hydrolyzable regions may not be spatially continuous in the blend films.

### CONCLUSIONS

We have demonstrated the use of chemical hydrolysis in combination with tapping mode AFM to map the phase-segregated regions in synthetic, partially renewable, and completely renewable blend films. ATR-FTIR was used along with tapping mode AFM results to assist in the identification of degradable regions in the blend. During the course of hydrolysis of degradable regions, pits were formed and nonuniform degradation took place. The more susceptible component in the blend was predominantly hydrolyzed during the early stage of degradation. It has been shown that a combination of AFM and chemical hydrolysis can be used to successfully characterize the chemically heterogeneous regions and study the early stages of degradation in multiphase polymer blends when exposed to aggressive environments.

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