핵자기공명 현미영상법을 이용한 생체고분자의 팽윤현상에 대한 비파괴연구

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Noninvasive study of the swelling effect for biopolymers using NMR Microimaging

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Abstract

Polymers have been developed and applied in many biomedical areas as well as engineering and industrial fields. The first essential to achieve successful development and applications is that properties of such polymer materials would be investigated. In many cases, such investigations are accomplished by observing polymeric behavior arising from the environmental changes such as pH, temperature, and ionic concentration. It has long been known that NMR is extremely sensitive to many biochemical and physical changes occurring in the polymer samples.

In the present study we focus our study on NMR Microimaging, which is one of the important NMR applications, to characterize the swelling effect by observing the time dependent spatial variations of polymer specimens. For the samples three kinds of polyvinyl alcohol (PVA) specimens are prepared with different degrees of cross linking density. ^{1}H NMR microimages are acquired as a function of time to visualize the swelling behavior as well as volumetric changes occurring in the specimens. From the acquired time dependent images, the swelling process is exploited.

Introduction

Polymers have been used in many biomedical materials which would be applicable to the human body. For human applications of such biopolymers, noninvasive characterization is one of the important requirements to obtain valuable information. Among others, degree of swelling is one of the important measurements needed for the characterization of many biopolymers. However, the swelling effect of polymers is one of the most poorly understood areas in polymer science.[1] The conventional method of measuring the degree of swelling of a polymer specimen uses the gravimetric method which is to measure the weight change due to the solvent absorption in the specimen.[2,3] Unfortunately, this method is time consuming and generates inconsistency as a result of frequent removals of the specimen out of the solvent. NMR has been recognized for many years as a noninvasive technique for investigating such a material, since it is sensitive to many biochemical and physical changes occurring in a specimen. In addition, NMR techniques possess many useful intrinsic properties such as the relaxation and diffusion effects.[4] Among the NMR techniques, NMR Microimaging has become an increasingly important tool in investigating a variety materials such as polymers, petrochemicals, and many biomaterials.[5] This is due to the reason that NMR Microimaging has the capability of producing high resolutions on top of the properties that the conventional Magnetic Resonance Imaging (MRI) possesses.

In the current study PVA specimens are employed as the samples to image. PVA has been widely used for many biomedical applications such as contact lenses, artificial vein, *etc.*

Materials and Methods

PVA specimens are prepared with three different degrees of cross linking density. 20% of polyvinyl alcohol is dissolved in deionized water, in which H_2SO_4 is added. Different amounts of formaldehyde are deposited in the mixed liquid, depending on the degree of cross linking density. The mixture of the liquid is placed in a mold at 60~80^{o}C for 5~48 hours until the solidification is completed. The prepared specimens are dried in the mixture of methanol and distilled water. The proportion of water in the mixture is gradually reduced for 6 days until pure methanol remains. Each dry specimen, which has the form of a solid cylinder, is positioned in a 17mm inner diameter vial filled with distilled water at 290K.

Figure 1 shows the experimental setup which includes a sample vial placed in the solenoid type probe, located in the magnet. NMR microimaging is then performed on a 2.0T whole body MRI scanner as shown in Figure 1. The RF probe is a capacitively coupled solenoid type coil (2cm diameter) placed in a 6cm diameter gradient coil which is capable of producing the gradient strengths up to 100G/cm. The conventional spin echo sequence images (TR/TE=300/30ms, field of view of 20mm, and slice thickness of 1mm) are acquired at every 10~15 minutes for a period of about 5 hours. Figure 2 displays the timing diagram of the spin echo imaging sequence. The sequence can be used to obtain 2 dimensional images with an appropriate slice thickness depending on the amplitude of the slice selection gradient. Using the imaging sequence, the time dependent images are acquired along two different directions (on Figure 1, an image along the z-axis: an xy plane image or an axial image; an image along the y-axis: an xz plane image or a coronal image) to analyze and the image profiles are then extracted.

Results

Figures 3 and 4 display two sets of images of one PVA specimen which has the highest degree of cross linking density. The numbers, separated by a colon, next to each image represents the elapsed time in hours and minutes, respectively, since the specimen is loaded in water. Horizontal profiles (cut views) along the horizontal line drawn on the top image, which display signal intensities along the horizontal line drawn on each first image, are shown for the coronal images (see Figure 3), while both horizontal (x) and perpendicular (y) profiles are obtained for the axial images (see Figure 4). Selected cut views, which present signal intensities arising exclusively from a polymer sample, are displayed in Figure 5. Namely, water signal intensities are excluded to expose signals arising from the polymer specimen.

Profiles of the acquired images are obtained to show the ingress process of water as well as the expansion behavior of the specimens due to the swelling effect. The swelling process of each sample due to the ingress of water is clearly observed in the time dependent images. The profile of each image delineates the ingress of water as well as the rate of growth of each specimen. For the profiles acquired, linear water ingress behavior is shown in Figure 6a. Furthermore, the expansion process of the coronal plane is displayed in Figure 5b and the expansion rate as a function of time is approximately 0.04mm^2/min. Volumetric expansion rate can be anticipated using the plane rates along the two perpendicular directions since the similar geometrical variations may yield the comparable diffusion behavior along the two directions.[6]

Figure 7 displays the selected images for each PVA specimen after the comparable time elapsed (about 2~2.5 hours) since each specimen is immersed in water. It is observed that water diffusion is faster with the decrease of the degree of cross linking density, and that the expansion rate of the specimen is increased with the lowest degree of cross linking density.

Discussion and Conclusions

In the present study time dependent NMR microimages are acquired to show evidence of the geometrical changes along with the ingress of water into PVA specimens. In conclusion, we find that NMR microimaging is an important analytic tool for the study of polymers noninvasively.

Acknowledgment

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Figures

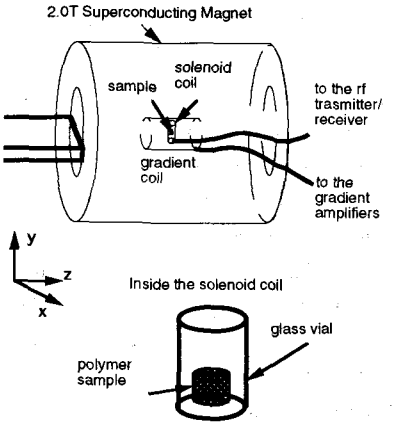


Figure 1. NMR Microimaging setup for the 2.0T superconducting whole body MRI scanner.

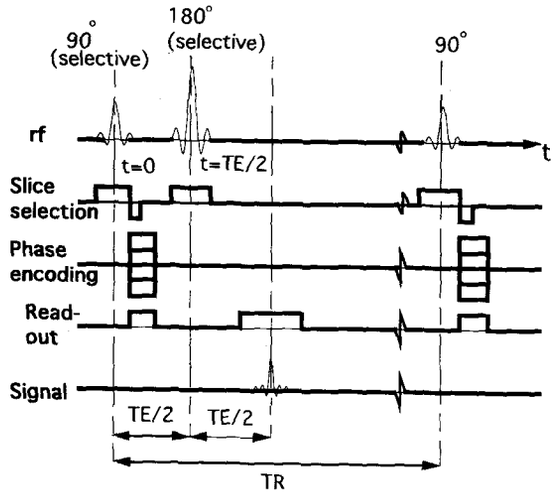


Figure 2. Timing diagram of spin echo imaging sequence

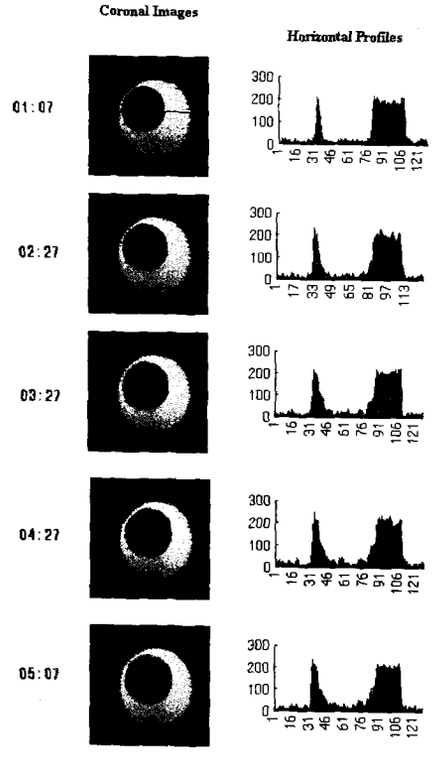


Figure 3. Time dependent coronal images of a PVA specimen with the highest degree of cross linking density and their corresponding profiles.

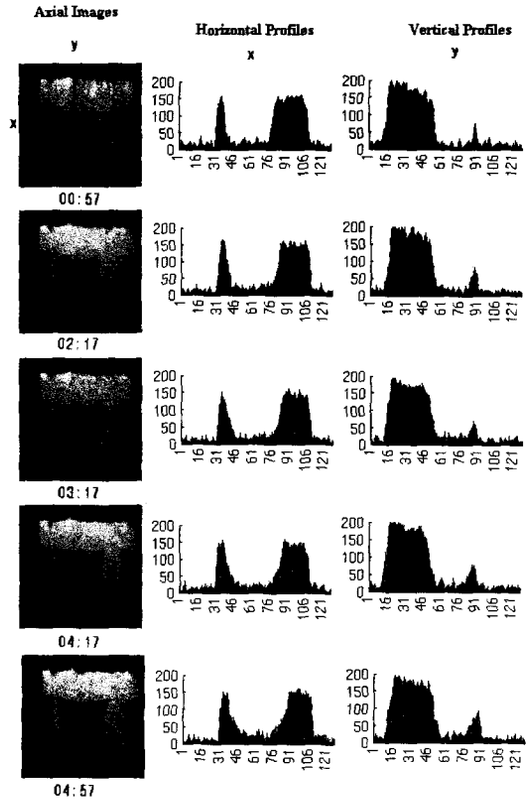


Figure 4. Time dependent axial images of the same PVA specimen as for Figure 3 and their related profiles along both horizontal (specified as 'x') and .perpendicular (denoted as 'y') directions.

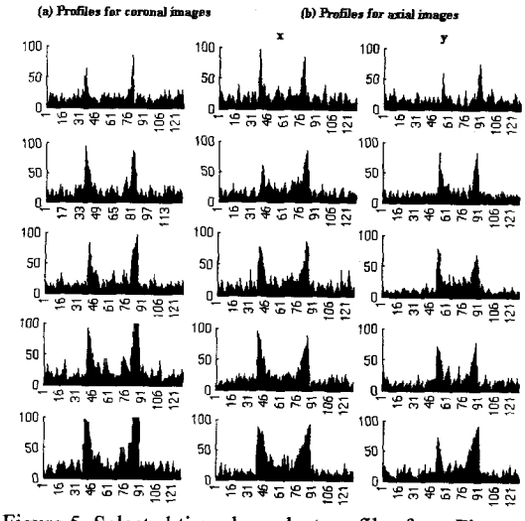
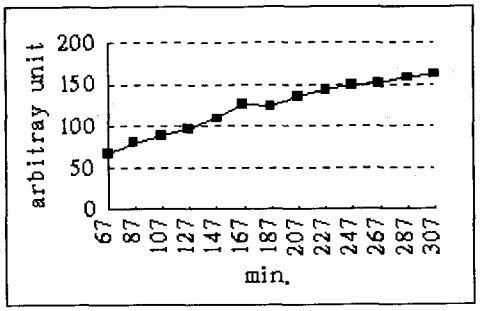
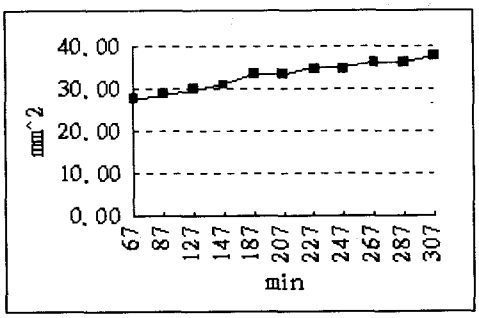


Figure 5. Selected time dependent profiles from Figures 3 and 4, which show signal intensities arising particularly from a polymer sample with water signal intensities excluded. (a) horizontal profiles for coronal images; (b) both horizontal (x) and vertical (y) profiles for axial images.



(a)



(b)

Figure 6. (a) Linear water ingress process as a function of time in mintues (vertical axis represents the amount of water diffused through the sample in an arbitrary scale); (b) coronal plane expansion behavior as a function of time in minutes

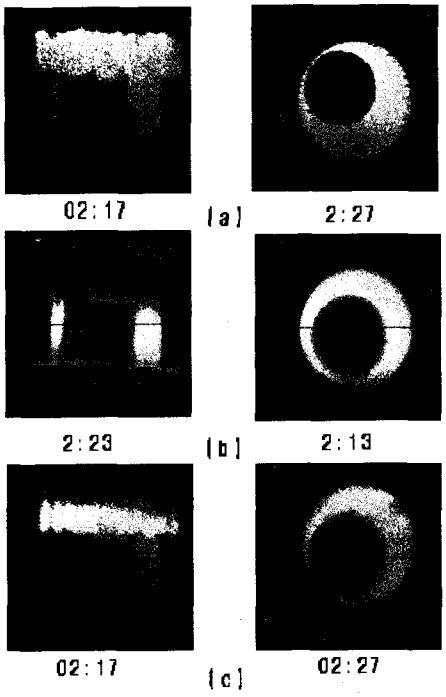


Figure 7. Selected sets of both axial and coronal images for the three PVA specimens at a particular time elapsed since the samples are immersed in water: from (a) through (c) display the images of the three PVA samples from the highest through the lowest degree of cross linking densities.