

Assessment of Degradability of Polymeric Packaging Materials Using Nuclear Magnetic Resonance (NMR)-based Techniques

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Abstract

Degradation of a polymer is governed by the chemical composition and structure and the morphology of the polymer, and the biological and environmental conditions surrounding the polymer. Some properties such as crystallinity, hydrophobicity or hydrophilicity, diffusion, porosity, and viscosity of a polymer are of great importance to the chemical and biological degradation of the polymer. Nuclear magnetic resonance (NMR)-based techniques and analysis of the relationships between the NMR relaxation properties and the degradation kinetics, and magnetic resonance imaging (MRI) technique which is an extension of NMR, could be fast, non-destructive and non-invasive tools to determine the mobility characteristics of the packaging materials in relation to degradation and to monitor the spatial information on the physicochemical properties of the materials.

Key words: degradation, polymer, NMR, MRI

Introduction

Crystal structure and morphology were associated with biodegradability of polymers (Gan *et al.*, 2004; Gan *et al.*, 2005). Chain mobility has been linked to degradation rate in some studies. It was found that an increase in polymer chain mobility was the main factor in increasing degradation rates with increasing temperature and this polymer-related effect affected the biological activities leading to degradation (Marten, 2003; Gan *et al.*, 2005). Marten *et al.* (2005) proposed that the concept of chain mobility may be a universal way to describe and predict the biodegradation rate of synthetic polyesters independent on their composition or microstructure.

Many instrumental methods have been used to study the mobility of polymers. Glass transition temperature has been traditionally used to measure the physicochemical state of polymers and is thought to relate to

chemical reaction kinetics and phase transition characteristics. The mobility characteristics of a polymer chain (its backbone and branches) are thought to determine the state or phase transition process. Alves *et al.* (2005) provided a comprehensive review of thermally simulated recovery (TSR) method for study of molecular mobility in polymers. Kuwabara *et al.* (2004a and 2004b) used solid state ^{13}C NMR to measure spin-lattice relaxation times (T_1) of biodegradable poly [(R)-3-hydroxybutyric acid-co-(R)-3-hydroxyhexanoic acid] and poly(butylenes adipate), and poly(ethylene succinate) and poly (butylenes succinate). They assigned two relaxation times to two different crystalline regions: the longer T_1 was assignable to the internal region of crystalline lamellae and the shorter T_1 to the interfacial crystalline region near the amorphous phase. Shi *et al.* (2005) used the similar solid state NMR technique to analyze the molecular mobility of a biodegradable polymer. The authors were able to demonstrate three different T_1 values for three distinct units of the polymer.

Theoretical Background for NMR Methodology

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Many nuclei spin about an axis, and the spinning generates magnetic field known as magnetic moment. Like a normal magnet bar, this magnetic moment has a north and a south pole, which is called nuclear magnetic dipole. When the nuclei are placed in a static magnetic field, most nuclei align themselves in the same direction as the static magnetic field, and represent a low energy state while the rest in the opposite direction as the static fields are in a high-energy state. The net magnetization at equilibrium is proportional to the difference in population between the two energy states. When a second magnetic field, normally in the form of radio frequency (RF) pulse, is applied to this equilibrium system, the nuclei will be excited. After excitation, the nuclei tend to return to their equilibrium states or equilibrium population distribution. The majority upward transition population, that is, the originally lower energy level population, returns to its equilibrium state by losing energy in the form of an RF wave via various radiationless transition processes termed "relaxation processes. The RF wave signal is characterized by the Larmor frequency of the nuclei, and can be received and recorded by NMR instrument (RF receiving antenna).

There are two kinds of relaxation processes: spin-lattice (or longitudinal) relaxation and spin-spin (or transverse) relaxation. The time constants describe these exponential relaxation processes are known as relaxation times. The spin-lattice relaxation time is denoted by T_1 and the spin-spin relaxation time by T_2 . As illustrated in Fig. 1, the longitudinal relaxation process follows a recovery or growth curve and the transverse relaxation process follows a decay curve. Both relaxation processes reach their equilibrium state after at least 5 times of their relaxation time constants.

Relaxation time is a function of the spin species and the chemical and physical environments surrounding the spins. In other words, the relaxation time constants are a fundamental property of the chemical and physical environment. A long T_1 or T_2 indicates a slow relaxation; a short T_1 or T_2 value indicates a rapid relaxation. The relaxation rate is related to the physical states of polymers. Therefore, analysis of T_1 and T_2 of a sample will permit the study of chemical and physical

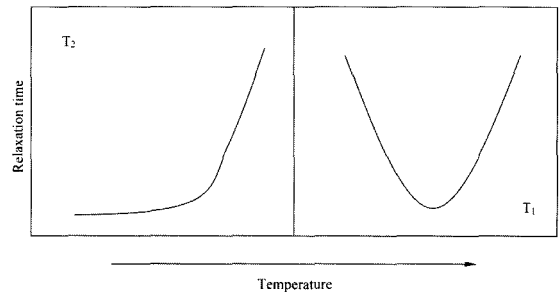


Fig. 1. Relaxation times of solids as a function of temperature.

properties of the sample. A long T_1 or T_2 indicates a slow relaxation; a short T_1 or T_2 value indicates a rapid relaxation. Relaxation time constant should not be confused with relaxation rate. The relationship between relaxation rate R and time constant is simple and takes the form of

$$R_l = \frac{1}{T_l} \quad (1)$$

where l takes the value of 1 and 2, for spin-lattice relaxation and spin-spin relaxation respectively.

Measurement of T_1 and T_2

NMR signals are produced by a series of RF pulses and/or magnetic field gradients (pulse sequence). A common pulse sequence for T_1 measurement is the inverse-recovery pulse sequence. The relationship between the T_1 and time can be established through the following equation

$$M_z(\tau) = M_0 \left(1 - 2e^{-\frac{\tau}{T_1}} \right) \quad (2)$$

T_2 describes the decay of transverse signals, and is readily detectable. A 90° RF pulse sets the magnetization signal to its maximum value which begins to decay immediately after the 90° pulse. The decay curve is normally termed free induction decay or FID, and can be described by the following equation:

$$M_{xy} = M_0 e^{-\frac{\tau}{T_2}} \quad (3)$$

Other common pulse sequences for T_2^* measurement are "spin-echo" and the Carr-Purcell-Meiboom-Gill or CPMG pulse sequences. These pulse sequences produce

more accurate T_2 values than the simple 90° pulse in an inhomogeneous magnetic field.

Multi-component Model

Multi-component model has been suggested for heterogeneous systems,

$$A = \sum A_i e^{-\frac{t}{T_{2i}}} \quad (4)$$

where $i = 1, 2, 3 \dots$, is the number of components in the system, which is dependent on the physical and chemical conditions of the system. In food systems, two-, three-, and four-component models have been used. This model can result in isolated amplitudes and relaxation time constants. The classical approach is to predefine a discrete number of T_2 for a particular system, and obtain the T_2 's by using mathematical models to fit the NMR experiment data. The most common approach to the analysis of multi-exponential relaxation behavior is to fit the relaxation curves with the smallest number of discrete exponential terms that provide a satisfactory representation of the experimental data.

Relaxation Times as a Function of Temperature

Usually, relaxations times of liquids increase linearly with temperature. However, at very low temperatures or with solid materials, relaxation times behave drastically different. For solids, with rising temperature, T_2 changes little at low temperatures and increase rapidly above certain temperatures, characterized by a mirrored-L shape while T_1 decreases rapidly to certain point and goes up again rapidly, characterized by a minimum (Fig. 1).

MRI methodology

A micro-image probe equipped with an 18 mm ID sample bore will be employed for imaging. The maximum gradient strength is 116, 121 and 199 G/cm for the X, Y and Z directions, respectively. Images will be acquired using the SPRITE pulse sequences. Image processing and NMR data processing will be conducted using the RI Advanced Image Display software (Resonance Instruments Ltd., Oxon, UK). Intensity and

relaxation time images will be produced from the raw data acquired.

Previous works

Use of low resolution NMR in the study of mobility of food ingredients and products has been widely reported. Ruan and his co-workers (Chung *et al.*, 2000; Chung *et al.*, 2001; Chung *et al.*, 2003; Ruan *et al.*, 1998; Ruan and Chen, 1998) have developed numerous NMR techniques to measure the molecular mobility and relate it to sensory attributes and shelf stability of foods and biological materials. Their NMR relaxometry technique is able to assign multiple components of spin-spin relaxation time (T_2) and spin-lattice relaxation time (T_1) to regions of different molecular mobility in foods and biological materials. They also use T_2 spectra (continuous distribution of T_2) to characterize a sample in terms of molecular mobility. These relaxometry techniques are fast and non-destructive and require little sample preparations. They are perfect candidate for analysis of molecular mobility, crystallinity and moisture characteristics in synthetic polymers in connection to degradation.

Recently, they proposed a new concept, "NMR State Diagram," which could be used to analyze the reaction kinetics of food ingredients and products in relation to molecular mobility. An NMR state diagram is a plot of temperature vs. spin-spin relaxation time (T_2). Our research has demonstrated that the shapes of temperature- T_2 curves may show different shapes (Fig. 2). There are three significant features of these curves. The first important feature is the transition point with a corresponding transition temperature of T_{Tran} . The second and third important features of these curves are the slopes of the near-linear portions before and after the transition point, respectively. The occurrence and position of the transition point and levels of the slopes are found to highly correlate to the physicochemical states of the samples. Therefore the temperature- T_2 curves can be treated as a state diagram.

An example of application of the NMR state diagram concept is the study of caking characteristics of dry soup mixes (Chung *et al.*, 2000). They found that the shapes of temperature- T_2 curves (Fig. 3) fell into the four

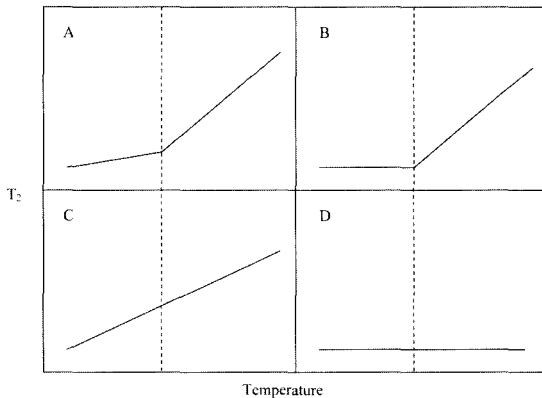


Fig. 2. Schematic demonstration of four different temperature- T_2 curve patterns (patterns A, B, C and D are illustrated in Table 1).

patterns illustrated in Fig. 2. Patterns A and B show a transition temperature while Patterns C and D do not. Ruan *et al.* (1998) reported that such a transition temperature is related to the glass transition temperature. Patterns A and C show that T_2 increases with increasing temperature from the beginning while Patterns B and D do not. In Fig. 2, the portion on the left side of the dotted line corresponds to before-transition changes in T_2 and the one on the right side of the dotted line corresponds to post-transition changes in T_2 as a function of temperature. We denoted the slope for the before-transition portion as k_{BT} and the slope for the post-transition portion as k_{PT} . Table I shows whether the curve has a transition temperature, and whether k_{BT} and k_{PT} are approximately equal to or greater than zero.

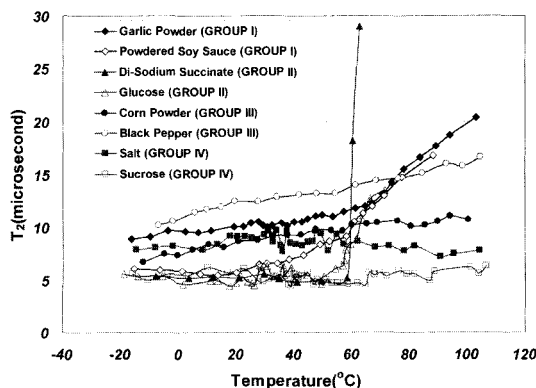


Fig. 3. NMR state diagrams for dry soup mixes (reprinted from Chung *et al.* (2000)).

Table 1. Significant features of temperature- T_2 curves for dry soup mixes.

Pattern	T_{tran}	k_{BT}	k_{PT}
A	Yes	> 0	> 0
B	Yes	≈ 0	> 0
C	No	> 0	> 0
D	No	≈ 0	≈ 0

*See text for explanation.

A non-zero k_{BT} or k_{PT} indicates that the sample experiences molecular or segmental movements at certain temperatures, which caused measured T_2 to change. We hypothesize that these movements are associated with the onset and/or progress of caking processes. We observed during the NMR measurements two types of changes in relation to caking of the samples that were subjected to temperature changes (temperatures ranging from -20 to 120°C): (1) Type I: slow and gradual agglomeration and water vaporization, and (2) Type II: abrupt caking. We found that a transition on the Temperature- T_2 curve coincides with the occurrence of Type II change (Patterns A and B), and a greater-than-zero k_{BT} coincides with the occurrence of Type I change (Patterns A and C). No Type I and II changes occurred to the samples with a straight line parallel to the x-axis (Pattern D).

Ruan and his co-workers are recently conducting preliminary study on moisture absorption and degradation kinetics of poly lactic acid (PLA), a biodegradable polymer. The main challenge was to acquire reasonable signals from extremely low moisture content samples like PLA. They have developed both the NMR and MRI (magnetic resonance imaging) for the study of PLA and other low moisture materials. Fig. 4 shows an NMR state diagram of PLA. They believe the NMR state diagram technique is an excellent tool for studying the degradation kinetics of the polymeric packaging materials.

Biodegradation is a gradual process and also depends on moisture absorption. The MRI technique would be a suitable tool for monitoring the degradation in progress in spatial perspective, for example moisture distribution, crystallinity distribution vs degradation patterns, etc. Magnetic Resonance Imaging (MRI) techniques can

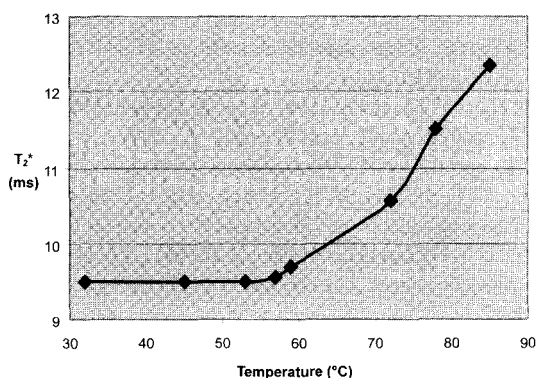


Fig. 4. NMR state diagram of PLA.

provide spatial-distribution information on the chemical composition, state and mobility of water, and temperature in many materials. Acquisition of images of materials containing low moisture and/or low proton content presents a challenge. These materials often have very short spin-spin relaxation times (T_2), and may not be imaged using the commonly used spin-echo MRI techniques. Recently, it was reported the single-point ramped imaging with T_2^* enhancement (SPRITE) technique could be applied to samples of extremely low moisture content such as spaghetti, corn kernel and dry wood (Qi *et al.*, 2005). Compared with conventional spin-3D pulse sequence, the SPRITE sequence could capture the very weak signals. Fig. 5a and 5b show images of a corn kernel obtained with the two pulse sequences. With the Spin-3D sequence, only the germ with high protons (from lipids) is visible and the signals from endosperm (dry and low fat) were lost. On the other hand, with the SPRITE sequence, the entire corn is visible.

Conclusion

Nuclear magnetic resonance or NMR-based techniques are expected to be a new advanced tool for the characterization of physicochemical properties of the polymeric packaging materials in relation to their degradability. NMR techniques are usually fast, non-destructive and non-invasive. Magnetic resonance imaging (MRI), an extension of NMR, will also be used to monitor the spatial information on the physicochemical properties of the materials. If proven valid,

these techniques can become a powerful tool for rapid characterization of polymeric materials as well as providing basic understanding of polymer degradation process.

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