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# Solid-state NMR study of aging of Colorbond polymer coating

F. Separovic[a,*], H.D. Chau[a], M.I. Burgar[b]

[a]School of Chemistry, University of Melbourne, Melbourne, VIC 3010, Australia
[b]CSIRO Materials Science & Technology, Private Bag 3, S. Clayton MDC, Clayton, VIC 3169, Australia

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**Abstract**

The effect of weather and aging on the properties of polymer coatings was studied using solid-state NMR spectroscopy. Colorbond polymer coatings were aged in an accelerated weathering tester and $^{13}$C NMR spectra were obtained. NMR relaxation times ($^{13}$C $T_1$, $^{1}$H $T_1$, $T_{1\rho}$) and line width were measured to study the changes in dynamics and structure of the polymer coating due to the effect of UV light and weathering. No changes in chemical shift were observed between fresh and aged polymer coating. A difference in $^{13}$C $T_1$ and a small change in cross-polarization time between fresh and aged samples were observed. These changes in molecular mobility may be useful in understanding the physical effects of aging and correlating changes in NMR relaxation times to weathering of polymer coatings. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords*: Polymer coating; Solid-state NMR; Molecular mobility

## 1. Introduction

Polymer coatings, including nitrocellulose, polyester, latex and acrylic (a polymer of acrylates, methacrylates and similar monomers), are widely used as paints. The top coat is required for esthetic qualities (color and gloss) and as a protective layer since it interacts with the environment and must provide resistance to the conditions encountered including irradiation, oxidation, hydrolysis and the action of aggressive fluids. Coatings are normally exposed to the environment, leading to changes in density, void space, permeability, elasticity and resistivity [1]. These changes take place with time and are known as aging of coatings.

Chemical aging of coatings involves the process of oxidative degradation. Coating structures should be designed to reduce the absorption of short wavelength solar radiation so as to avoid the generation of radicals and photochemical reactions, which speed up the aging rate of polymer coatings. Physical aging is due to the slow changes that occur in coatings with time. When amorphous polymers are cooled through their $T_g$ (glass transition temperature), they solidify and stiffen to form glasses. In this glassy state, the rate of structural relaxation becomes very slow and the polymer conformations are fixed in a non-equilibrium state. If the temperature is held at some value below $T_g$, the process of relaxation towards an equilibrium configuration continues and as a result many material properties change with time. The process of physical aging is highly temperature dependent, and is fastest at temperatures closest to $T_g$.

Chemical and physical changes due to aging may be detected by nuclear magnetic resonance (NMR) spectroscopy [2–4]. Although solution-state NMR provides the most detailed structural information, solid-state NMR provides important information about internal molecular motions and dynamics and is applicable to insoluble samples such as cured films and paints [5,6]. In the present work, we report changes in NMR parameters of Colorbond polymer coatings with age. Colorbond samples were chosen because of their industrial relevance to current production techniques and their improved product durability. Colorbond is a polyester paint designed to withstand the harsh outdoor Australian climate and is subject to extremes in heat and humidity. Although previous studies have reported on the aging of polymers [7], to date no work has been reported in the open literature on the aging of this class of polymers, which are directly bound to the surface.

The mobility of groups within the polymer can be measured using solid-state $^{13}$C NMR techniques. The polymer basically consists of a carbon backbone surrounded by protons. These protons interact with each other via a dipole–dipole interaction resulting in broad resonance lines for solid samples and, since protons have a small chemical shift range, resonance lines overlap in proton

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* Corresponding author. Tel.: +61-3-9344-6464; fax: +61-3-9347-5180.
*E-mail address:* f.separovic@chemistry.unimelb.edu.au (F. Separovic).

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NMR spectra. $^{13}$C–$^{13}$C interactions, however, are rare since $^{13}$C abundance is only 1.108% and, since $^{13}$C nuclei have a large chemical shift range, better spectral resolution is obtained. $^{13}$C–$^{1}$H interactions are particularly important since a $^{13}$C spectrum can be obtained by transferring magnetization from protons to the less abundant isotope, $^{13}$C. This enhances the $^{13}$C signals and is called cross polarization (CP). CP allows faster signal acquisition since the longitudinal relaxation times, $T_1$, of $^{1}$H are shorter than $^{13}$C [7,8]. Spectral resolution is enhanced by magic angle spinning (MAS), which involves placing a rotor containing the sample at an angle 54.7° to the magnetic field and spinning at several kHz. The line broadening caused by chemical shift anisotropy and dipolar interactions is reduced [9,10].

Molecular motion can be measured using the NMR relaxation times $T_1$, $T_{1\rho}$ and $T_2$. $T_1$ is the spin–lattice relaxation time and relates to fast molecular motion on the $\omega_0$ time scale or Larmor frequency (MHz). Spin–lattice relaxation involves a loss of energy by the excited nucleus to the surrounding environment or lattice [7,8,11]. The rate at which this relaxation process occurs is measured by the spin–lattice relaxation time ($1/T_1 = \text{rate}$). The closer the motional frequencies of the lattice are to the Larmor frequencies of the nuclei, the more efficient is the transfer of the magnetization (i.e. the shorter the $T_1$). $T_1$ measurements are usually limited to molecular motions in the $10^7$ Hz frequency range.

Both proton and carbon $T_1$ measurements are reported in this work. $^{1}$H $T_1$ gives average information about dynamics from all the groups in the molecule since protons are $\approx$100% abundant [12]. The $^{13}$C $T_1$ gives information about the dynamics of individual groups on molecules since the $^{13}$C nuclei are rare and there is little relaxation from other $^{13}$C nuclei [10,13].

$T_{1\rho}$ is the spin–lattice relaxation time in the rotating frame [12]. It is similar to $T_1$ in the static field but due to spin–lattice interactions in the rotating frame. In CP experiments, the magnetization initially builds up to a maximum due to the carbon–proton dipolar interactions in the spin-locking field, $\omega_1$, and decays exponentially to equilibrium with the time constant $T_{1\rho}$. The values of $T_{1\rho}$ are used both to measure the molecular dynamics on the kHz time scale of $\omega_1$ and to report on the length scale of polymer mixing [14,15].

$T_2$ is the spin–spin relaxation time and is the time constant for the decay of the precessing $X$–$Y$ component of the magnetization [7,8,11]. $T_2$ gives information about the distribution of resonant frequencies and about the local fields experienced by the magnetic moments of the nuclei. In liquids, the local magnetic fields fluctuate very rapidly and, therefore, quickly average to $\approx 0$ to yield long $T_2$s and narrow resonance lines. The atoms in solids are in nearly fixed positions, and the internal fields are significant, which results in the rapid loss of coherence and short $T_2$s (microseconds). $T_2$ is related to the inverse of the resonance line width and thus $T_2$ in solids is short and the resonance lines are broad.

Changes in the NMR relaxation times $T_2$, $T_{1\rho}$ and $T_1$ report on changes in molecular motion from slow to fast timescales. Colorbond polymer coatings were exposed for different periods in a weathering test situation and the effect on NMR relaxation times was studied.

## 2. Experimental

### 2.1. Materials and methods

Two samples of polymer coatings, Merino and Off-White Colorbonds, were obtained from BHP Research Laboratory (Melbourne, Australia). Merino and Off-White polymer coatings are polyester paints whose composition includes, diols, diacids, triols, and cross-linkers. The monomer components (diol, diacid and triol) are heated from 60 to 120°C to polymerize. The liquid paint, mixture of polymer, solvent, cross-linkers, catalyst and blocker, are reacted together for a short time at 235°C to produce the coating film. Merino and Off-White Colorbond are made from the same polyester but they differ in color pigmentation.

The colorbond used in the present study was painted onto an aluminum metal surface and cured. The solid coating films were used for NMR studies either as new (fresh) or as aged samples, after being aged for a period of time in an accelerated manner. The fresh coating was smooth and adhered well to the metal surface. The Off-White polymer coating film was cut into three equal sheets ($8 \times 11$ cm$^2$). One was used as the fresh Off-White sample and the other two were aged for 1 and 10 days, respectively.

The aging process of the sample was done in a QUV-accelerated weathering tester at Dulux (Melbourne, Australia). The weathering tester consists of a cabinet with a UV power source and humidity control, which can be set to mimic sunshine and rain and results in the polymer coating being aged much faster than in an outdoor situation. The conditions for aging were a 12-h rotation exposure consisting of: (a) UV cycle (40 W and $280 \leq \lambda \leq 320$ nm) 8 h duration with temperature set to 60°C, and (b) condensation cycle (80% humidity) 4 h duration with temperature at 40°C. Samples aged 1 day underwent two 12-h cycles (24 h) and samples aged 10 days underwent 21 cycles.

Four Colorbond preparations were studied: (i) Merino fresh; (ii) Off-White fresh; (iii) Off-White aged 1 day and (iv) Off-White aged 10 days. The coating film was removed from the substrate for NMR relaxation studies.

### 2.2. NMR

$^{1}$H T$_1$, $^{13}$C T$_1$ and $T_{1\rho}$ relaxation times [10,12–14] were measured for fresh and aged polymer coatings. The polymer coating was carefully removed from the surface of the metal sheet and approximately 0.1 g packed into a MAS rotor. The

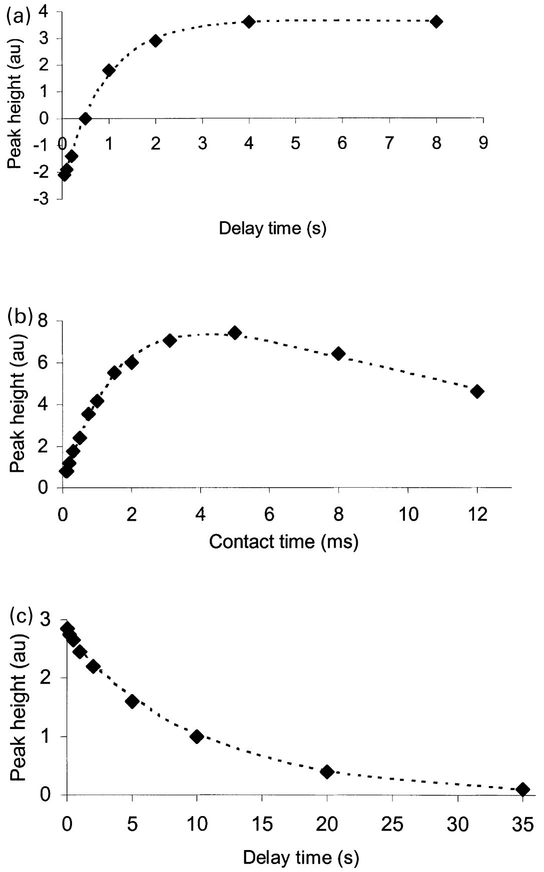

Fig. 1. (a) An example of a $^{1}$H $T_1$ measurement for fresh Merino coating where (◆) represents relative peak height for a particular resonance plotted against delay time ($d_2$) and (- - -) the best fit to the equation: $Y = -A + (H + A)\exp(-d_2/T_1)$; (b) The results of a $T_{1\rho}$ experiment where (◆) represents relative peak height as a function of contact time ($T$) and (- - -) represents the best fit to the equation: $Y = H\exp(-T/T_{1\rho})(1 - \exp(-T/T_{CH}))$; (c) A plot of (◆) relative peak height against delay time $T$ for a $^{13}$C $T_1$ relaxation time experiment. The curve (- - -) represents the best fit to the equation: $Y = H\exp(-T/T_1)$.

Table 1
Assignment of major peaks in $^{13}$C CP MAS spectra of Colorbond polymer coatings

| Peak no. | $^{13}$C chemical shift ($\delta$ in ppm) | Assignment |
|---|---|---|
| Peak 1 | 171.7 | Carboxyl carbons on aliphatic chain |
| Peak 2 | 164.3 | Carboxyl carbons on aromatic rings |
| Peak 3 | 130.3 | Aromatic carbons |
| Peak 4 | 68.2 | Ether carbons |
| Peak 5 | 34.2 | Aliphatic carbons |
| Peak 6 | 21.3 | Methyl carbons |

rotor was a 5-mm thin wall, silicon nitride ($Si_3N_4$) type with Kel-F caps (Doty Scientific Inc., SC).

NMR experiments were carried out using a Varian Inova NMR Spectrometer (Palo Alto, CA) with a fixed magnetic field strength of 7.0461 T and operating at 300 and 75.435 MHz for $^{1}$H and $^{13}$C, respectively. The following experimental conditions were typical: $\pi/2$ pulse = 3.8 $\mu$s, contact time = 2 ms, recycle delay time = 4 or 2 s, sweep width 50 kHz, MAS speed = 8 kHz, number of scans = 2048 and line broadening = 75 Hz.

$^{1}$H $T_1$ was measured using an inversion-recovery pulse sequence with $^{13}$C CPMAS [12]. The graph of relative peak height for each resonance versus delay time was analyzed using both the Varian fitting routine and a curve fitting program with the equation: $Y = -A + (H + A)\exp(-d_2/T_1)$, where $Y$ is the relative peak height, $A$ and $H$ are constants, and $d_2$ is the delay time, typically from 0.1 to 8 s. An example of a $^{1}$H $T_1$ measurement for fresh Merino is in Fig. 1a. $^{1}$H $T_1$ measurements were repeated at least three times for each sample to obtain an average value and standard deviation.

$T_{1\rho}$ was determined by varying the proton–carbon contact

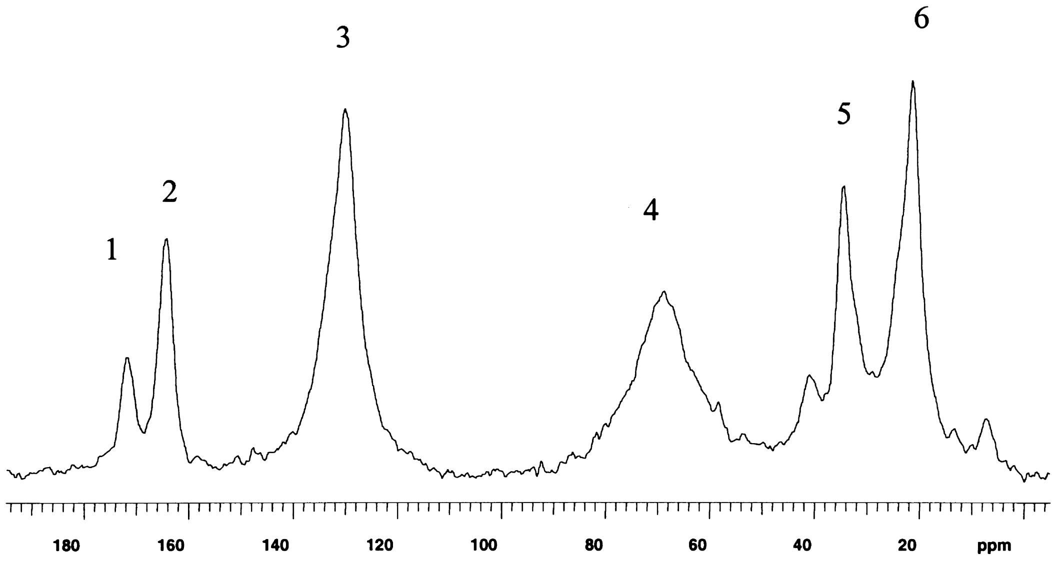

Fig. 2. A $^{13}$C CPMAS spectrum of a Colorbond polymer sample, fresh Merino spinning at 10 kHz. The main carbon chemical groups were assigned as listed in Table 1 and conditions used were 2 ms contact time, 2 s repetition delay and 25 Hz line-broadening.

Table 2
$^{13}$C $T_1$ relaxation times of fresh and aged Colorbond polymer coatings

| Sample | $^{13}$C $T_1$ (s) | | | | | |
|---|---|---|---|---|---|---|
| | Peak 1 | Peak 2 | Peak 3 | Peak 4 | Peak 5 | Peak 6 |
| Merino fresh | 8.4 ± 1.4 | 33.2 ± 4.1 | 12.1 ± 1.1 | 2.4 ± 0.7 | 5.1 ± 0.4 | 0.6 ± 0.1 |
| Off-White fresh | 8.5 ± 0.6 | 33.1 ± 3.3 | 12.1 ± 1.1 | 2.3 ± 0.5 | 4.8 ± 0.4 | 0.6 ± 0.1 |
| Off-White aged 1 day | 7.6 ± 0.6 | 18.3 ± 1.7 | 10.3 ± 0.5 | 2.2 ± 0.3 | 5.2 ± 0.6 | 0.6 ± 0.1 |
| Off-White aged 10 days | 7.5 ± 0.5 | 21.9 ± 1.9 | 10.8 ± 0.5 | 2.1 ± 0.3 | 4.6 ± 0.6 | 0.6 ± 0.1 |

time for CPMAS experiments and then plotting relative peak intensity against the contact time [12]. The growth of the curve represents the build-up of magnetization and gives the $T_{CH}$, and the decay yields $T_{1\rho}$. The results of a $T_{1\rho}$ experiment are shown in Fig. 1b. The curve represents the best fit using the equation: $Y = H\exp(-T/T_{1\rho})(1 - \exp(-T/T_{CH}))$, where $Y$ is the peak height, $H$ a constant, and $T$ the contact time, typically between 0.1 and 12 ms.

The measurement of the $^{13}$C spin–lattice relaxation time was obtained using the NMR pulse sequence of Torchia [13], which is a CP method for measuring $T_1$ of $^{13}$C nuclei with several advantages compared to the usual inversion-recovery methods [13]. The $^{13}$C $T_1$ relaxation time value was obtained by plotting peak height against delay time and fitting the equation: $Y = H\exp(-T/T_1)$, where $Y$ is the peak height, $H$ a constant, and $T$ the delay time, typically between 0.05 and 35 s (see Fig. 1c).

## 3. Results and discussion

### 3.1. NMR chemical shift assignments

An example of a $^{13}$C CPMAS spectrum of a polymer sample, spinning at 8 kHz is shown in Fig. 2. The $^{13}$C NMR spectra of both Merino and Off White polymer coatings were similar with six main carbon chemical groups that were assigned as listed in Table 1.

### 3.2. Line width and $T_2$

Since the value of $T_2$ is related approximately to the inverse of line width, the line widths of individual groups from the $^{13}$C NMR spectrum were measured for fresh and aged Off-White coating. $T_2$ estimated from the line width for all groups other than the ether carbons where spectral overlap was a difficulty, was approximately 0.2 ms for fresh and aged Colorbond coating. Little difference was seen indicating that this $T_2$ does not change during the aging process of the polymer. In addition, no chemical shift change was detected, indicating little change in the chemical nature of the coating.

### 3.3. $^{13}$C $T_1$ relaxation times

A summary of $^{13}$C $T_1$ relaxation times for fresh Merino, fresh Off-White and aged Off-White coating is shown in Table 2. The $^{13}$C $T_1$ for fresh Merino and fresh Off-White were very similar. This is not unexpected since both samples

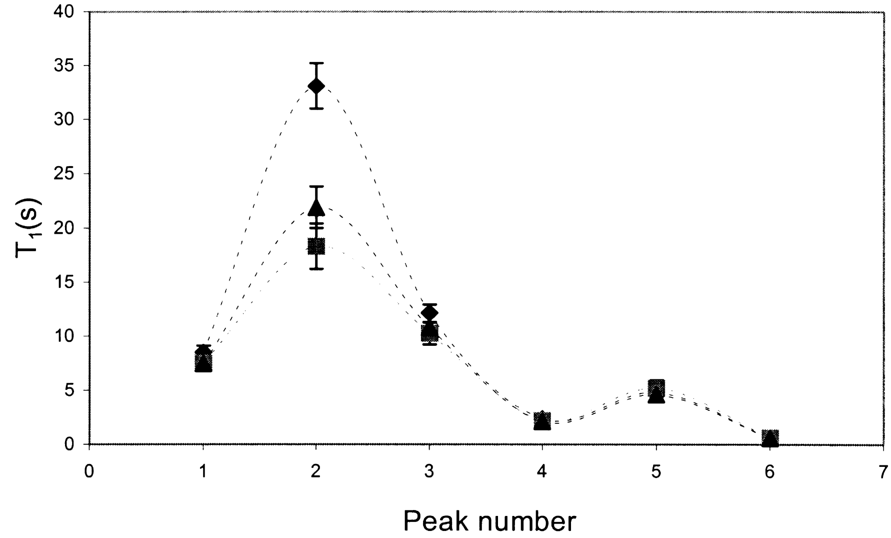

Fig. 3. Graph of $^{13}$C $T_1$ relaxation times for major resonances of fresh and aged Off-White Colorbond coating: ◆ fresh coating; ■ accelerated aging for 1 day; and ▲ accelerated aging for 10 days.

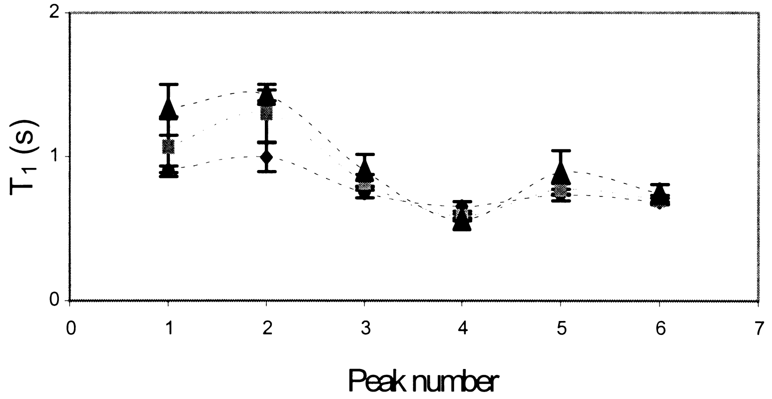

Fig. 4. A graph $^1$H $T_1$ relaxation times for fresh Off-White and aged Off-White Colorbond polymer coatings: ◆ fresh coatings; ■ accelerated aging for 1 day; and ▲ accelerated aging for 10 days.

have similar physical and chemical properties and are only slightly different in color.

A graph of $^{13}$C $T_1$ relaxation times for resonances of fresh and aged Off-White Colorbond is shown in Fig. 3. It was observed that the $^{13}$C $T_1$ value for the carboxyl group with the aromatic group attached (peak 2 at 164.3 ppm) decreased as the polymer coating was aged. This difference between the fresh and aged polymer may be due to the compacting of the sample (density increases with aging). This could shorten the $^{13}$C $T_1$ value as the aromatic group was restricted and hence was able to relax faster. The restriction of the rings increased the intensity of motion on the $\omega_0$ timescale, and relaxed the carboxyl carbons to which the aromatic groups were attached. However, since the aromatic groups are relatively isolated from one another, and there is little change in the mobility of the polymer backbone, the $T_1$ relaxation of the rings showed little change.

The small difference observed between the aged 1 day and aged 10 days Off-White coating could be that, as a result of aging, the polymer compacts to a certain point beyond which the molecular groups cannot get closer.

### 3.4. $^1$H $T_1$ relaxation times

It was observed that the value of $^1$H $T_1$ for fresh and aged polymer coating was very similar with an average value of around 1 s. A graph of $^1$H $T_1$ for fresh Off-White and aged Off-White Colorbond is shown in Fig. 4. The $^1$H $T_1$ results were shorter and showed less variation between groups than $^{13}$C $T_1$ values in fresh and aged polymer coating due to the abundance of protons in the carbon backbone of the polymer. These protons interact with each other, causing the proton magnetization to relax quickly. Since the $^1$H $T_1$ reports on the average relaxation rate of protons of the whole sample, specific changes in molecular motion as seen by $^{13}$C $T_1$ for the carboxyl carbons are not easily detected by $^1$H $T_1$.

### 3.5. $T_{1\rho}$ and $T_{CH}$

The $T_{1\rho}$ relaxation time of fresh and aged polymers did not show much change and had an average value around 12 ms for each group. However, it was observed that the $T_{CH}$ (the build-up of magnetization) for different molecular

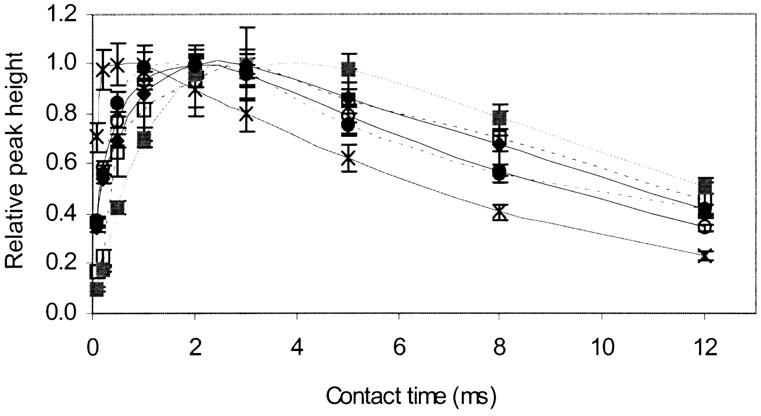

Fig. 5. A graph of relative peak height versus contact time for fresh Off-White Colorbond for each of the major $^{13}$C resonance; □ peak 1; ■ peak 2; ◆ peak 3; × peak 4; ● peak 5; and ○ peak 6.

groups of the polymer varied with the carboxyl carbons having longer $T_{CH}$ values than the aliphatic carbons [16]. A graph of relative peak height versus contact time for fresh Off-White Colorbond is shown in Fig. 5. The parallel decay curves indicate that all peaks had similar $T_{1\rho}$ values.

A small change in the build up of magnetization between fresh and aged polymer coating (i.e. a change in the proton–carbon cross polarization time, $T_{CH}$) was detected for peak 2 (164.3 ppm, carboxyl adjacent to aromatic groups). Smaller changes were seen for peak 1 (171.7 ppm, carboxyl next to aliphatic carbons) and peak 5 (34.2 ppm, $R{-}CH_2{-}R$).

The signal intensity depends on the CP or contact time and it is a result of the net magnetization transfer from proton to carbon nuclei. The efficiency of this process is dependent on the C–H dipole interaction, which may alter as the polymer ages. Changes in C–H distance, molecular motion and viscoelastic properties [17] can result in a change in the rate of magnetization transfer. Although a small change was observed for the carboxyl peaks, $T_{CH}$ for the other resonances was observed to be similar for fresh and aged polymer coating.

The $T_{CH}$ values for peak 2 was ~1 ms for fresh polymer and ~2 ms for aged polymers. Parker et al. [18] have shown that the Young's modulus is proportional to $(1/T_{CH})^2$. This would suggest, therefore, that Young's modulus of the aged polymers was four times smaller than that of unaged polymer, opposite to that reported for rubber [17]. An increase in the Young's modulus and in $T_{CH}$ are both normally associated with an increase in motion. However, the timescale of the motions that affect $T_{CH}$, dominated by dipole–dipole interactions, are slower than those that affect $T_1$. The restriction of the aromatic groups has led to a decrease in faster motions (i.e. the $T_1$ timescale, ns–μs), and led to an increase in intensity in slower motions (μs–ms timescale of $T_{CH}$); leading to changes that affect both the $T_1$ and $T_{CH}$ of the carboxyl carbons to which the rings are attached. AFM and FTIR studies of Colorbond also showed an increase in molecular packing with age (unpublished results). With age, the polymer coatings normally became less permeable and more motionally restricted, which was reflected in the changes seen in the NMR relaxation times.

## 4. Conclusions

In summary, there are only minor changes in $^1H$ $T_1$ and $T_{1\rho}$ between the fresh and aged Colorbond polymer coating. Similarly, no changes in line widths between fresh and aged coatings were seen. On the other hand, a change in $^{13}C$ $T_1$ values was observed between fresh and aged Colorbond polymers for carboxyl carbons adjacent to aromatic rings ($\delta = 164.3$ ppm). The carbon network was more sensitive to changes in intermolecular distances as a result of 'shrinkage' of the coating induced by weathering. Although protons are more sensitive to intermolecular interactions, they are not affected as much as the backbone carbons by changes in polymer structure. The $^{13}C$ $T_1$ relaxation of the carboxyl carbons decreased as the polymer aged indicating that the distance and/or orientation to the CP protons was changed as the structure condensed. Since we saw an increase in $T_{CH}$ values, this suggests a restricted magnetization transfer in aged Colorbond samples.

The NMR parameters $^{13}C$ $T_1$ and $T_{CH}$ changed with aging of Colorbond samples and hence, provide a measure of changes in molecular motion of polymers during the aging process. These changes in molecular mobility are also related to changes in bulk properties of the polymer coating.

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## References

[1] Marrion A. Chemistry and physics of coatings. London: Royal Society of Chemistry, 1961 (chap. 3, p. 21–7; chap. 6, p. 78–88).
[2] Perera MCS. Polymer 1999;40:1667.
[3] Perera MCS, Rowen CC. Polymer 2000;41:323.
[4] Laviolette M, Auger M, Desilets S. Macromolecules 1999;32:1602.
[5] Garbow JR, Goetz J, Asrar J. Macromolecules 1998;31:3925.
[6] Heatley F, Humadi M, Law RV, D'Emanuele A. Macromolecules 1998;31:3832.
[7] Koenig JL. Spectroscopy of polymers. Washington, DC: American Chemical Society, 1992 (chap. 8, p. 211–6; chap. 10, p. 257–83).
[8] Homans SW. A dictionary of concepts in NMR. Oxford: Claredon Press, 1992 (p. 74–5, 189, 260–3).
[9] Linberg JJ, Hortling B. Advances in polymer science. Heidelberg: Springer, 1985 (p. 3).
[10] Whalley LR, Tarr CE. J Magn Reson 1997;26:237.
[11] Bovey FA, Mirau PA. NMR of polymers. San Diego, CA: Academic Press, 1996 (p. 65–88; p. 353–5).
[12] Braun S, Kalinowski H-O, Berger S. 100 and More basic NMR experiments. New York: VCH Publishers, 1996 (p. 125–31).
[13] Torchia DA. J Magn Reson 1978;30:613.
[14] Separovic F, Lam Y-H, Ke H, Chan HK. Pharmaceut Res 1998;15:1816.
[15] Cheung MK, Zheng SU, Mi YL, Guo QP. Polymer 1998;39:6289.
[16] Fyfe CA. Solid state NMR for chemists. Guelph, Canada: CFC, 1983 (p. 140, 515).
[17] Assink RA, Gillen KT. NMR Newslett 1997;467:23.
[18] Parker AA, Marcinko JJ, Rinaldi PL, Hedrick DP, Ritchley WM. J Appl Polym Sci 1993;48:677.