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CP/MAS ^{13}C n.m.r. analysis of micromorphology in a thermoplastic elastomer prepared from nitrile rubber and poly(vinyl chloride)

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A thermoplastic elastomer (TPE) prepared by mechanical blending of nitrile rubber (NBR) and poly(vinyl chloride) (PVC) was investigated by solid-state ^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy with cross-polarization/magic-angle spinning (CP/MAS). The CP/MAS ^{13}C n.m.r. measurements of $T_1^{\rm H}$ and $T_{1\rho}^{\rm H}$ relaxation times for the TPE were used as a probe to analyse the microphase structures. The double-exponential decay $T_{1\rho}^{\rm H}$ relaxation behaviour confirmed the presence of microphases in the TPE, which were PVC microcrystallites and the unmixed portion of NBR. The sizes of the microphases were about 1.1 nm or smaller. A schematic model of the phase morphology is suggested. The sizes of the PVC microcrystallites were decreased somewhat by mixing with NBR.

(Keywords: thermoplastic elastomer; morphology; n.m.r. spectroscopy)

INTRODUCTION

Thermoplastic elastomers (TPE) are two-phase systems in which the elastomeric performance of a vulcanized rubber (soft phase) is combined with the processing characteristics of a conventional thermoplastic (hard phase)[1,2]. Individual hard and soft phases influence the characteristics of a given TPE and the temperature range of its application; the former serves as physical crosslinks while the latter is deformable under stress. At temperatures above the softening point or melting point of the hard phase, the TPE flows. The TPEs are generally produced by (i) controlling the stereoregularity and crystallinity in an amorphous polymer, (ii) block-copolymerization of hard thermoplastic and soft rubbery segments, or (iii) blending of a rubber and a thermoplastic[1-3].

A TPE prepared by blending nitrile rubber (NBR) and poly(vinyl chloride) (PVC) has been a commercial success because it provides a number of excellent end-use properties by simply changing the ratio of the components[3,4]. Our previous study[5] on melt-mixing showed that first the skins of PVC grains were removed and then hierarchical structures of the PVC particles were broken. The NBR was also broken up and there appeared to be microphases of the pure polymers, even after a considerable mixing time. Other investigators[6,7] have also reported the presence of microseparated structure in blends of the miscible NBR/PVC pair. They employed various analytical techniques such as transmission electron microscopy and ^{1}H-pulsed nuclear magnetic resonance (n.m.r.) spectroscopy. However, microscopy has not provided accurate quantitative information on the microstructures. Neither has the ^{1}H n.m.r. method yielded detailed, precise information about the size and state of the microstructures, because the signals from protons attached to different chemical environments cannot normally be resolved. Recognizing that the size and state of the separated microphase in the TPE determine the physical and mechanical properties at service temperatures, a more quantitatively specific technique is required to analyse the microphase structures of the NBR/PVC TPE. High-resolution, solid-state, pulsed Fourier-transformed (*FT*) ^{13}C n.m.r. spectroscopy capable of magic angle spinning (MAS) and cross polarization (CP) offers a solution; a series of the CP/MAS ^{13}C spectra enables one to measure the spin-relaxation times of individual specific sites in the solid TPE and then analyse the details of the microscopic phase structures in terms of the difference in the molecular mobility[8]. Furthermore, spatial dimensions of the microstructures can be estimated quantitatively through the process known as spin diffusion[9].

Two useful spin-relaxation times obtained from solid-state ^{13}C n.m.r. spectroscopy are the spin-lattice relaxation time in the laboratory frame, $T_1^{\rm H}$, and that in the rotating frame, $T_{1\rho}^{\rm H}$. From the CP technique[10], the transfer of the magnetization from proton (^{1}H) to carbon (^{13}C) spins takes place, generating sensitivity-enhanced carbon signals[11], and from the MAS technique[12] the resonance of chemically different types of carbons can be resolved. It is possible to detect the

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heterogeneous domains and estimate their size because of the existence of a substantial relaxation time difference in the specific carbon between distinguishable regions. Typical values of T_1^H and $T_{1\rho}^H$ for most polymers are in the ranges of hundreds of milliseconds and milliseconds, respectively. These values can be translated into the maximum diffusive path lengths (i.e. spatial dimensions) by a simplified approximate approach[13,14] based on the spin-diffusion phenomenon. Therefore, depending on the relaxation time of either T_1^H or $T_{1\rho}^H$ being used, distinct domains and their characteristic size can be probed at two different scale levels.

The objective of this study is to provide insight into the microstructures and phase morphology of the TPE formed by mechanical blending of NBR and PVC; measurements of both spin-relaxation times, T_1^H and $T_{1\rho}^H$, are employed as a probe and interpretation is assisted by the T_1^H and $T_{1\rho}^H$ of the individual pure components.

EXPERIMENTAL

Materials and TPE preparation

The nitrile rubber was HYCAR VT 380 (Zeon Chemicals), which contains 30% of acrylonitrile and is denoted as NBR-30. It has a single glass transition temperature of −28°C. The PVC resin was Geon 103 EP F-76 (Geon Co.) with number-average molecular weight of 40 000 and weight-average molecular weight of 89 000 (ref. 15).

Fifty parts (by weight) of NBR-30 were first masticated in a non-intermeshing, counter-rotating two-wing rotor internal mixer (1.57 l, Farrel Banbury) for 30 s until it attained 65°C, and then 50 parts of PVC with one part of the thermal stabilizer (Therm-Chek 1872, Ferro Corp.) were charged in the mixer. The mixing continued for 450 s with a rotor speed of 80 rev min^{-1} and fill factor of about 0.7, during which the temperature indicated by the built-in thermometer increased to a maximum of 165°C at 150 s and then decreased slightly by ~10°C to a plateau. Thereafter, the batch was sheeted using a two-roll mill and the sheets were cut into square pieces of about 1 mm × 1 mm for the ^{13}C n.m.r. experiments.

CP/MAS ^{13}C n.m.r. relaxation measurements

The ^{13}C n.m.r. experiments were performed with a Chemagnetic Inc., model CMX-300 spectrometer equipped with an MAS probe at ^{1}H frequency of 299.6 MHz. The sample was packed inside the rotor, being positioned at the centre of the magnet, and then spun at the rate of about 3.5 kHz. A ^{1}H 90° pulse width of 4.25 μs was employed with free induction decay (f.i.d.) signal accumulations.

Proton spin-lattice relaxation times in the laboratory frame, T_1^Hs, were measured by monitoring the series of ^{13}C spectra after a π-τ-$\pi/2$ pulse sequence followed by CP as shown in *Figure 1a*. Proton spin-lattice relaxation times in the rotating frame, $T_{1\rho}^H$s, were measured by observing the carbon-signal intensities obtained with a ^{1}H matched spin-lock–τ pulse sequence prior to CP (*Figure 1b*). A CP Hartmann-Hahn contact time of 1 ms was taken. In all measurements, recycled delays (waiting time) of $5 \times T_1$ were used in order for the net magnetization to be completely relaxed, and the ambient temperature was maintained at 21°C.

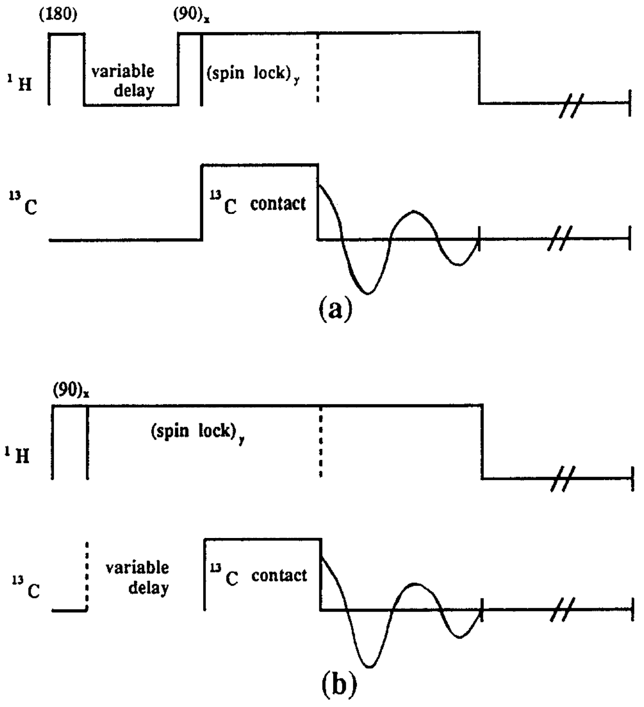

Figure 1 Pulse sequences used to measure (a) T_1^H and (b) $T_{1\rho}^H$ relaxation times

RESULTS

T_1^H Relaxation times

Figure 2 shows the CP/MAS ^{13}C spectra of NBR-30, PVC and the TPE. The two peaks of NBR-30 in the middle spectrum are assigned to specific carbons, i.e. methine/cyanide (CH/CN) carbons and methylene (CH$_2$) carbons, respectively. For PVC, the assignments of the resonance peaks are designated to methine (CH) and methylene (CH$_2$) carbons, respectively. The spectrum of the TPE consists of four peaks arising from a mere superposition of the specific carbons present in the individual spectra of the component polymers. The peak positions designated as 1, 2, 3 and 4 indicate CH/CN carbons of NBR-30 fraction, CH carbons of PVC fraction, CH$_2$ carbons of PVC fraction, and CH$_2$ carbons of NBR-30 fraction in the TPE, respectively. Considering the fact that the miscibility of the NBR/PVC system stems from a polar interaction between polar groups (CN in NBR-30 and Cl in PVC) of the individual polymers[16], the carbon peaks in the TPE with which we are concerned are those for the CH/CN and CH carbons. The height of each peak (i.e. peak intensity) changes when the delay time, τ, in the pulse sequence varies, monitoring of which provides the T_1^H and $T_{1\rho}^H$ determination.

Figure 3 shows a series of ^{13}C spectra (stack spectra) of PVC, which were generated from the pulse sequence of the T_1^H experiment (*Figure 1a*) with variable delay times, τ. *Figure 4* plots the changes in intensity, $I(\tau)$, of the CH and CH$_2$ carbon peaks against the delay times, τ. The individual curves are further analysed by means of a non-linear least-squares computer fitting whereby the T_1^H values of individual carbons are obtained. The mathematical equation of the curve fitting with a single exponential decay function is:

$$I(\tau) = I_\infty[1 - \alpha \exp(-\tau/T_1^H)] \qquad (1)$$

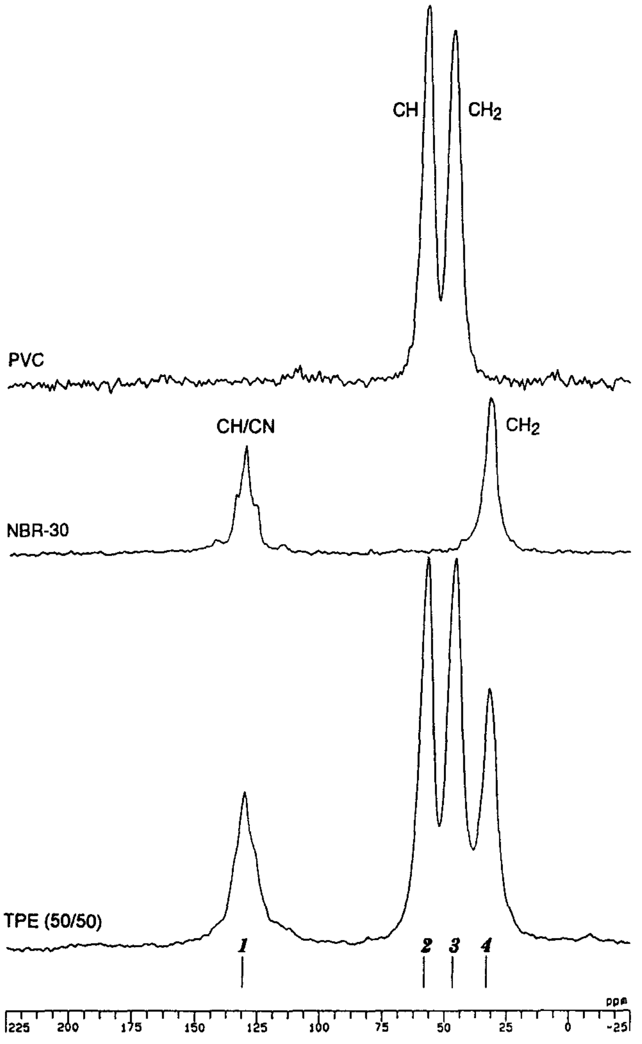

Figure 2 CP/MAS ^{13}C spectra of PVC, NBR-30 and the TPE; peaks 1, 2, 3 and 4 in the TPE spectrum are assigned to CH/CN (NBR-30), CH (PVC), CH_2 (PVC) and CH_2 (NBR-30) carbons, respectively

where T_1^H, I_∞ and α are treated as adjustable parameters. As tabulated in *Table 1*, the T_1^H value of methine carbons is 2.62 s and that of methylene carbons is 2.55 s. Considering that the slight difference in the values may indicate an experimental error, the average (2.59 s) is taken as T_1^H of PVC. It should be noted that this value cannot be directly compared to previously published results because the experimental conditions and the instruments used are not necessarily the same.

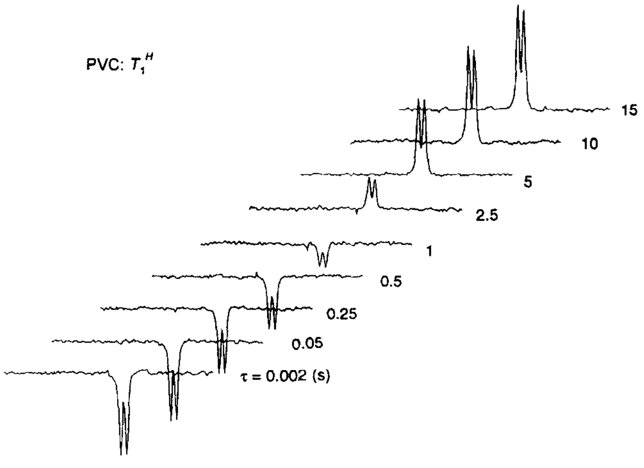

Figure 3 ^{13}C stack spectra of PVC for determination of T_1^H relaxation times

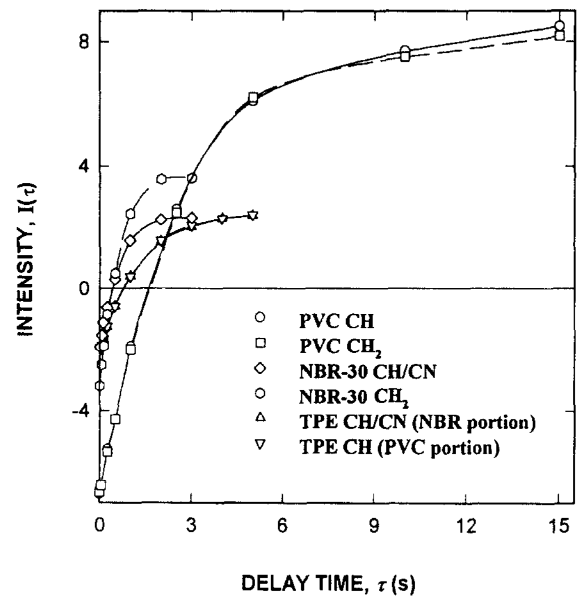

Figure 4 Variation of magnetization intensity of specified carbons in PVC, NBR-30 and the TPE T_1^H stack spectra as a function of delay time, τ (s)

Table 1 T_1^H relaxation times of NBR-30, PVC and TPE

	Carbon	T_1^H (s)[a]
PVC	CH	2.62 ± 0.11
	CH_2	2.55 ± 0.10
NBR-30	CH/CN	0.66 ± 0.04 (0.086)
	CH_2	0.63 ± 0.03 (0.108)
TPE	CH/CN	1.31 ± 0.03 (0.041)
	CH	1.34 ± 0.09 (0.049)

[a] Values in parentheses are standard deviations

T_1^H relaxation data of NBR-30 are also given in *Figure 4*; the intensity variations of the CH/CN and CH_2 carbons in the stack spectra, although not shown, were monitored as a function of delay time, τ. By means of a single-exponential curve fitting (equation (1)), the T_1^H values of the individual carbons were determined to be 0.66 and 0.63, respectively (see *Table 1*); they are very close to each other.

Figure 4 also shows the T_1^H relaxation data of the CH/CN and CH carbons in the NBR-30/PVC TPE; the calculated values of T_1^H are summarized in *Table 1*. Values determined from both NBR-30 and PVC fractions in the TPE are almost identical, within experimental uncertainty.

$T_{1\rho}^H$ *Relaxation times*

Figure 5 shows the stack spectra of NBR-30, which were obtained from monitoring the intensity changes in CH/CN and CH_2 carbon peaks of the spectrum with variable delay times in the pulse sequence of the $T_{1\rho}^H$ experiment shown in *Figure 1b*. The plot of the peak

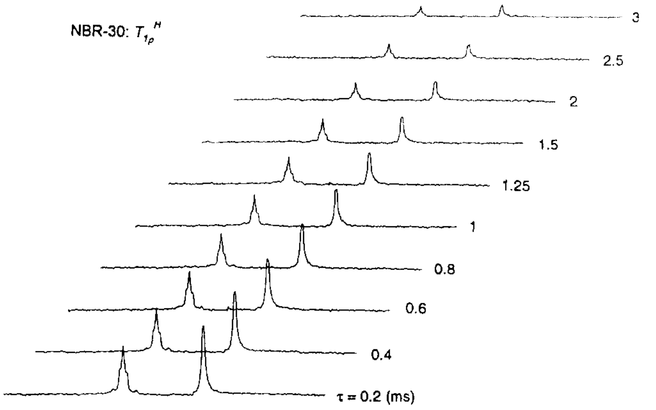

Figure 5 ^{13}C stack spectra of NBR-30 for determination of T_1^H relaxation times

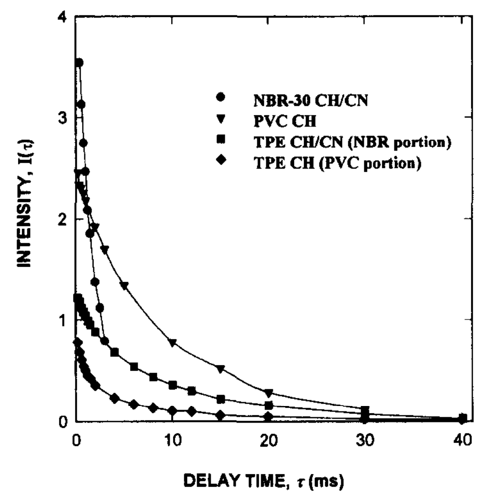

Figure 6 Variation of magnetization intensity of specified carbons in NBR-30, PVC and the TPE $T_{1\rho}^{H}$ stack spectra as a function of delay time, τ (ms)

Table 2 $T_{1\rho}^{H}$ relaxation times of NBR-30, PVC and the TPE

		$T_{1\rho}^{H}$ (ms)	
	Carbon	Single-exponent curve fitting[a]	Double-exponent curve fitting[a]
NBR-30	CH/CN	1.40 ± 0.03 (0.071)	–
PVC	CH	–	4.00 ± 0.20 (0.030) 11.00 ± 0.22 (0.030)
TPE	CH/CN	–	1.53 ± 0.08 (0.006) 9.22 ± 0.70 (0.006)
TPE	CH	–	2.07 ± 0.20 (0.008) 9.34 ± 0.41 (0.008)

[a] Values in parentheses are standard deviations

intensities, $I(\tau)$ *versus* delay times, τ, for the CH/CN carbons is represented in *Figure 6* and its non-linear least-squares curve fitting results in the $T_{1\rho}^{H}$ value (*Table 2*). The curve was well represented with a single-exponential decay function which has the following form:

$$I(\tau) = I_0 \exp(-\tau/T_{1\rho}^{H}) \qquad (2)$$

Figure 6 also shows the $T_{1\rho}^{H}$ relaxation data of PVC observed from the CH carbons. The curve is required to be fitted with double-exponential decay functions rather than the single-exponential decay function:

$$I(\tau) = I_{0,A} \exp(-\tau/T_{1\rho,A}^{H}) + I_{0,B} \exp(-\tau/T_{1\rho,B}^{H}) \qquad (3)$$

and $T_{1\rho}^{H}$ is resolved into two components: 4.0 ms and 11.1 ms (short and long components). The former is due to a more motionally constrained region, which is the crystalline phase (microcrystallites) and the latter indicates a more mobile phase (amorphous chains).

The $T_{1\rho}^{H}$ relaxation data of the NBR-30/PVC TPE are also given in *Figure 6* and the relaxation times were determined with the double-exponential curve fitting, in the same way as for PVC. Referring to *Table 2*, the short-component $T_{1\rho}^{H}$ value of the CH/CN carbons (NBR-30 fraction) in the TPE is somewhat longer than that of the pure NBR-30; the short-component $T_{1\rho}^{H}$ value of the CH carbons (PVC fraction) in the TPE becomes shorter than that of the pure PVC; the long-component $T_{1\rho}^{H}$ values of both carbons in the TPE are practically identical.

DISCUSSION

In the CP/MAS ^{13}C spectrum of the NBR-30/PVC TPE, there were no distinct changes in the lineshape or chemical shift compared to those of the individual polymers. To observe apparent spectral changes, some mixing must occur on a size comparable to a few bonds of polymer chains, where the electron clouds around the interacting carbons are disturbed. In other words, mixing between NBR-30 and PVC did not take place at the atomic level.

However, on the larger size scale the two polymers were mixed. From *Table 1*, observations that (i) T_1^H values of the PVC fraction in TPE are not the same as those of the pure PVC, (ii) T_1^H values of the NBR-30 fraction in TPE are also different from those of unmixed NBR-30, and (iii) T_1^H values of both NBR-30 and PVC in the TPE are identical within experimental error, confirm the occurrence of mixing. Observation (iii) further implies that the spin diffusion across the mixed phase of NBR-30 and PVC occurs efficiently enough to average out the T_1^H values of the individual polymers. The two polymers are homogeneously mixed on the size scale where the spin diffusion proceeds within times T_1^H; the TPE appears as if it had no microphase morphology at this characteristic time-scale.

If the TPE is truly homogeneous on a molecular level (i.e. less than a few nanometres), the $T_{1\rho}^{H}$ relaxation data must follow a single-exponential decay process in a similar manner to the T_1^H relaxation. However, the TPE indicates a two-component relaxation process (*Table 2*), which means that the spin diffusion did not occur so rapidly as to average out the $T_{1\rho}^{H}$ values, and there must be some microseparated domains large enough to obstruct the advance of the spin diffusion. The long-component $T_{1\rho}^{H}$ values of both carbons in the TPE are almost the same and this indicates the presence of the mixed phase. The short-component $T_{1\rho}^{H}$ value of the TPE CH/CN carbons is not much different from that of pure

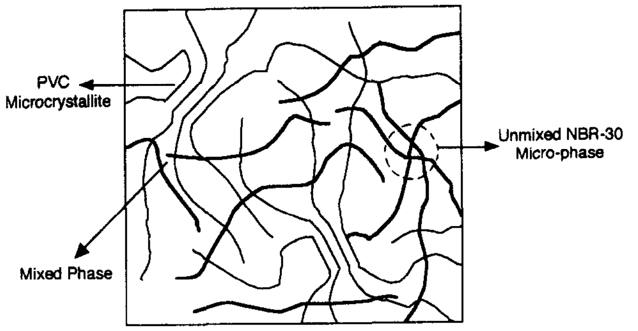

Figure 7 Schematic model of solid-state phase morphology

NBR-30, implying that the unmixed NBR-30 domains are still present in the TPE. The short-component $T_{1\rho}^{H}$ value of the TPE CH carbons is for PVC microcrystallites and shows a shorter relaxation time than pure PVC; evidently the microcrystallites of PVC are affected by the NBR-30 chains on blending. The remaining microcrystallites of PVC provide physical crosslinks (hard phase), preserving the physical strength of the TPE.

The sizes of the microdomains can be estimated from the following approximate expression[13,14]:

$$L \approx (6DT_{1\rho}^{H})^{1/2} \qquad (4)$$

where L is the maximum linear path length (in nm) over which the spin energy diffuses, and D is the spin diffusion coefficient typically taken to be $100\,\mathrm{nm}^2\,\mathrm{s}^{-1}$ (ref. 13). From the $T_{1\rho}^{H}$ value of the short component of the PVC fraction (2.07 ms), the size of the hard microphase is calculated to be 1.1 nm. It must be remembered that the above estimate of size depends on the true value of D in equation (4). Therefore, the absolute value of the microdomain size may be somewhat different. *Table 2* shows that the $T_{1\rho}^{H}$ value of the microcrystallites in the TPE is shorter (2.07 ms) than that of pure PVC (4.00 ms); the estimated sizes from equation (4) are 1.6 nm and 1.1 nm, respectively. The NBR-30 chains penetrate into the PVC microdomains affecting the microcrystallites.

Figure 7 presents a schematic model of the microphase morphology of the TPE, which is composed of (i) mixed phase of NBR-30 and PVC, (ii) unmixed NBR-30 phase, and (iii) PVC microcrystalline phase.

CONCLUSIONS

This paper explores the use of the proton spin-lattice relaxation times in analysing the microscopic structures, determining their domain size, and assessing the phase morphology in the solid-state NBR-30/PVC TPE.

From the single-exponential decay process of the T_1^H relaxation times, the TPE was shown to be homogeneous and seemed to have no microphase separation on the time scale over which the spin energy diffused. However, the double-exponential decay process of $T_{1\rho}^{H}$ relaxation times indicated that microphase separated structures were present. They were PVC microcrystallites and unmixed NBR-30 domains. Their sizes were estimated to be 1.1 nm or smaller. Judging from the size reduction of PVC microcrystallites from the pure state (~1.6 nm) to the blended state (~1.1 nm), the PVC microcrystallites were affected by the NBR-30 upon blending.

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