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Quick Determination of Dry Rubber Content in Natural Rubber Latex by Low-resolution Pulsed NMR Technique†

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Proton Nuclear Magnetic Resonance technique using a spin-echo sequence has been used for quick determination of dry rubber content (DRC) of natural rubber latex. The measurement is based on the fact that the relaxation rates of solid and aqueous phases of the latex are markedly different. The combined signal of the two phases is obtained by sampling the free induction decay (FID) following a 90° pulse (immediately after the dead time of the receiver) in a spin-echo sequence. The echo signal representing the aqueous phase is measured when the solid phase signal has decayed to negligible value. Using these two signal values and correction factor to account for the difference in hydrogen content in the solid and liquid phases, DRC of twenty ammoniated latex samples were determined. The DRC values obtained by this method are in good agreement with those obtained by the standard laboratory method (R^2=0.991, P=0.001). The study shows the feasibility of a quick and precise NMR method of DRC determination without requiring any preparation or weighing of sample or a calibration curve.

The dry rubber content (DRC) of natural rubber latex varies considerably depending on the clone, weather, soil conditions and tapping system. For a quick evaluation of yield of experimental trees and quick payment to latex tappers on the basis of rubber content, there is a need for a rapid and accurate method of determination of DRC in rubber latex. The DRC is measured conventionally by the standard laboratory method (SLM) and its several modifications which generally take several hours[1,2]. Many methods have been developed to determine DRC in rubber latex based on specific heat measurements[3], microwave attenuation[4] and hydrometer[1]. But most of these measurements have the drawback of being either time-consuming or inaccurate or both. Therefore, there is a need to develop a suitable method which is rapid, reliable and easy. This study reports such a method for DRC determination using proton low-resolution NMR.

THEORY

The basic theory of NMR has been described in detail[5–8]. A brief description of the phenomenon of pulsed NMR, necessary to understand its use in this study is given here. When a sample containing nuclei with non-zero spin (I) is placed in a static magnetic field (Ho), the majority of nuclei are aligned and precess around the magnetic field with a characteristic frequency (Wo), which is related to Ho by the well known Larmor equation ($Wo = \gamma Ho$; γ is the gyromagnetic ratio). The interaction between nuclear magnetic moments and Ho results in macroscopic magnetisation $M(t)$ along Ho. The magnetisation $M(t)$ grows exponentially to its maximum value Mo with a time constant T_1 called spin-lattice relaxation time. The radio frequency magnetic field (designated as H_1) applied at resonance frequency and at right angle to Ho flips the magnetisation away from its equilibrium direction (Z-axis).

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The flip angle (α) is given by: $\gamma H_1 tw$; where tw is the time for which rf field is applied. When the rf field is applied for such a duration that $\alpha = 90°$, it is called 90° or $\pi/2$ pulse and if the rf field is applied for a duration that $\alpha = 180°$ (*i.e.* $-Z$ direction), it is called 180° or π pulse.

The application of a 90° pulse flips the magnetisation in a plane perpendicular to the Z-axis resulting in induction of voltage in the detector coil – called NMR signal which is proportional to the number of nuclei (under study *e.g.* ^1H) present in the sample. After the pulse, the signal decays with time and precesses freely without the influence of any field and is called free induction decay (FID). The signal in a perfectly homogeneous magnetic field decays (due to natural spin-spin interactions) exponentially with a time constant T_2 called transverse relaxation time or spin-spin relaxation time. However, in actual practice, decay of the signal becomes faster due to inhomogeneity of the magnetic field and signal decays instead with time constant T_2^* given by: $1/T_2^* = 1/T_2^S + 1/T_2^f = 1/T_2^S + \gamma\Delta Ho/2$ where T_2^S is the T_2 of the sample, T_2^f is that due to field and ΔHo is the inhomogeneity of the magnetic field. T_2^f is <1 ms for the typical low resolution spectrometer used. In fact for most of the liquid samples, T_2^* is primarily governed by field inhomogeneity.

The contrubution of inhomogeneity in Ho to the free induction decay can be eliminated by a well known sequence called spin-echo[5]. The method consists of the application of a 90° pulse followed by a 180° pulse after a time interval τ and observation of a free induction echo formed at time 2τ. The effect of 180° pulse is to re-phase the spins de-phased due to inhomogeneity of the magnetic field. The echo signal decays exponentially with time constant T_2 (neglecting small diffusion effect). A typical spin-echo sequence used for this study is given in *Figure 1*.

The rubber latex consists of a solid phase of which nearly 97% is rubber, and an aqueous phase. The pulsed NMR can distinguish between the proton signals from solid and liquid phases of the sample based on their differences in T_2; T_2 of solid is much smaller than that of liquid[5]. The schematic sequence given in *Figure 1* shows the combined signal '$S+L$' contributed by both solid and liquid phases measured at 24 µs (immediately after the dead time of the receiver) following a 90° pulse in a spin-echo sequence. The echo signal representing the liquid phase is measured at 6 ms when the signal due to the solid component has decayed almost completely. The signal of rubber phase 'S' is obtained by subtracting 'L' from the signal measured at 24 µs. The DRC is determined using the equation:

$$DRC\ (\%) = 100 \times F.S/(F.S+L) \qquad ...1$$

where 'F' is the ratio of hydrogen content of aqueous phase (assumed close to that of water) and of rubber.

MATERIALS AND METHODS

Bruker Minispec pc–20 pulsed NMR spectrometer was used for all the measurements. The rubber latex samples were carefully pipetted in an 18 mm diameter NMR tube to fill the homogeneous region of radio-frequency coil of the spectrometer. The spin-lattice relaxation time (T_1) and spin-spin relaxation time (T_2) for a number of samples were measured at 20 MHz and at ambient temperature using 90°–t–90° and CPMG pulse sequence respectively[5]. The component values of relaxation time of solid and liquid phases were calculated by using semi-log extrapolation method on a personal computer. The ammoniated samples of wide variability in DRC supplied by the Rubber Research Institute of India Kottayam were analysed by setting pulse repetition time of 10 ms and sampling times of 24 µs for the FID and 6 ms for spin-echo signal based on T_1 and T_2 measurements.

The DRC of NMR measured samples were also determined by the standard latoratory *method*[1] *which involves: coagulating* a weighed quantity of latex (about 5 g) by adding acetic acid followed by steam heating to complete the coagulation, the coagulum is pressed into a thin sheet, washed well with water and dried to constant weight at 70°C. *Percentage DRC was calculated from the* weights of dry rubber and latex. The DRC

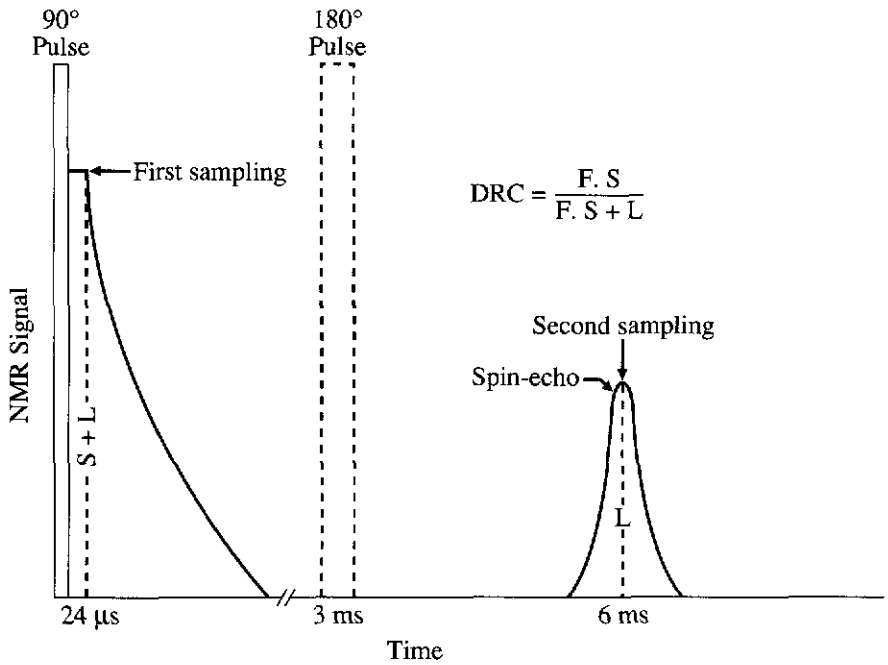

Figure 1. Schematic spin-echo pulse sequence used for dry rubber content determination. 'S' and 'L' indicate the signal contributed by solid and liquid fractions of the latex, respectively.

values obtained by the two methods were subjected to statistical analysis.

RESULTS AND DISCUSSION

The T_1 values ranged from 1000 ms to 2000 ms for the aqueous phase whereas for the solid phase it remained at nearly 30–40 ms for the samples of quite different DRC. Accordingly pulse repetition rate (five times of the highest value of T_1) was kept at 10 s to ensure the growth of full magnetisation of both the phases. The T_2 of samples varied from 1-2 ms for the solid phase and 250–350 ms for the liquid phase. *Figure 2* gives the semi-logarithmic plot of magnetisation $M(t)$ *versus* time t in a CPMG sequence of a typical rubber latex sample. The data in the figure clearly show a non-exponential decay which could be fitted to a sum of two exponentials. The T_2 values suggest that the signal for two phases cannot be resolved by FID following a 90° pulse, since the decay will be governed by T^*_2 which is mainly controlled by magnetic field inhomogeneity. However, solid content in rubber latex using pulsed NMR has been determined[9] by sampling the FID following a 90° pulse at 11 µs and 70 µs. In this method, the samples are thermostatted at 0°C and the calibration curve is prepared by known standard samples. The difference in percentage solid[9] determined by this method and the conventional method are quite large which cannot be attributed to differences in hydrogen atom density in the two phases. The feasibility of measuring the rubber content from the integrated intensities of ^{13}C resonances using high-resolution NMR has also been reported in a sample of rubber latex[10], but this method is of limited practical use not only because of low abundance of ^{13}C nuclei and its longer relaxation times compared to protons but also because of the very high cost of high-resolution NMR spectrometer needed for it.

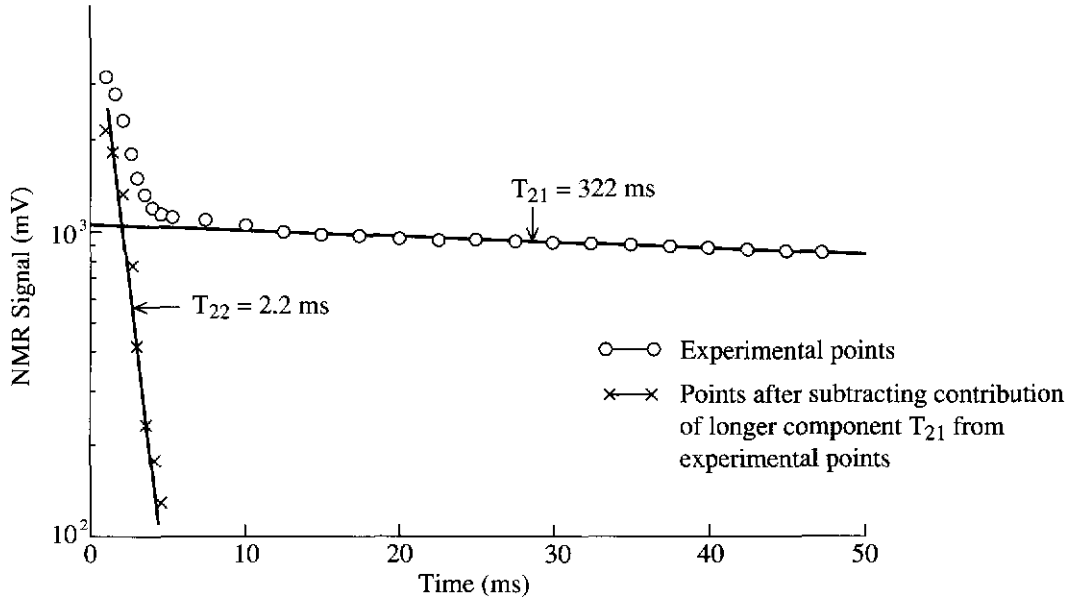

Figure 2. Semi-log plot of transverse magnetisation M(t) versus time for determination of two components of T_2.

In this work, the relaxation times (T_1 and T_2) of samples of varying values of DRC have been measured to choose the appropriate pulse sequence and instrument parameters for accurate measurements. The solid component signal decays slightly at 24 μs which is compensated by near equivalent decay of the liquid component at 6 ms. These sampling times have to be appropriately chosen depending on T_2 values of the latex sample which may vary from one region to another. The correction for difference in hydrogen percentage in the solid and liquid phases is automatically applied through 'CST' key inbuilt in the micro-processor of Minispec pc-20 by feeding the appropriate value. The percentage solid fraction displayed in a few seconds using *Equation 1* has been found to be in very good agreement with those determined by the standard laboratory method (SLM). The method has been extensively tested by measuring the DRC of latex samples covering a wide range of variation and comparing with the values obtained by the chemical method (*Table 1*). The linear regression line of DRC values obtained by the two methods shows a highly significant correlation coefficient ($R^2 = 0.991$; P=0.001) with a slope of 1.013. The DRC values obtained were subjected to student's 't' test and there was no significant difference between the two methods. The large variations in T_2 values (bigger than the range observed under this study) may affect the DRC measurements. The effect of such variations on echo signals can be eliminated by recording the echoes as a function of the pulse interval and extrapolation to zero time or more elegantly by CPMG pulse sequence[5].

The study clearly establishes the feasibility of a very simple, accurate and reliable method of DRC determination in rubber latex in less than 100 s without requiring weighing and any calibration curve or sample conditioning.

TABLE 1. COMPARISON OF PULSED NMR AND CONVENTIONAL METHODS OF DETERMINATION OF DRY RUBBER CONTENT IN RUBBER LATEX

Sample no.	DRC (%) SLM	NMR
1	14 9	15.6
2	26.1	26.6
3	26 1	26.1
4	32.1	32.2
5	32.4	32 9
6	34.8	34.7
7	35.0	35.0
8	35.5	35.6
9	36.1	36.7
10	35.5	36.2
11	36 5	35.6
12	39 5	41.5
13	39.3	39.5
14	39.8	40.5
15	40.4	41.8
16	41.5	42.8
17	42.6	43.7
18	43.7	43.7
19	44.0	45.6
20	46.5	45.9

The DRC values for both SLM and spin-echo methods are the average of three measurements with average standard error of mean of 0 233 and 0.099 respectively.

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