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Radiation degradation of MG rubber studied by dynamic mechanical analysis and solid state NMR

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Abstract

Methyl methacrylate grafted natural rubber (NR) prepared by free radical polymerisation of methyl methacrylate in NR latex was irradiated to high energy radiation. Their structure and molecular dynamic changes during exposure to high energy radiation were investigated by dynamic mechanical analysis and solid state nuclear magnetic resonance spectroscopy (NMR). The changes of glass transition temperature and tan δ_{max} with different radiation doses are reported. The effect of the radiation dose on tan δ peak width, tan δ_{max} and area under the tan δ curve are used to understand the miscibility and damping properties of the irradiated rubbers. This data was also used to calculate the radiation chemical yields of crosslinking, *G(X)*, and scission, *G(S)*. Solid state ^{13}C NMR measurements were carried out to determine the several relaxation time parameters; rotating frame and laboratory frame proton and carbon relaxation times. Cross polarisation times and carbon relaxation times were interpreted based on the changes in the molecular motion. Proton relaxation times were interpreted based on the heterogeneity of the matrix. Results confirmed the disappearance of the interfacial region and phase separation during irradiation. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Natural rubber; Grafting; High energy radiation

1. Introduction

Livelihoods of many people and several economies in the developing world depends on the natural rubber (NR). NR is facing a competition from its synthetic counterparts due to development of new materials with improved properties. The properties of NR should be modified to suit different applications if it is to remain competitive in the market. Various chemical modifications have been attempted to modify its properties and extend its use [1]. One such modification is the graft copolymerisation of a second monomer. Even though, grafting could be carried out in solution [2] and in solid rubber [3], latex modification has proved to be the most economical. Several monomers have been copolymerised with NR, but only the product with methyl methacrylate, called MG rubber, have been produced and used commercially. MG rubber is a mixture consisting of the graft copolymer and two homo polymers. They form a partially miscible blend [4] and extent of phase separation depending on the amount of total methyl methacrylate. It is hard and could be used as a reinforcing agent [5]. It gives vulcanizates of high hardness and good retention at elevated temperatures, good mould flow and electrical properties. Owing to their interesting properties, MG rubber could be used in applications where it could be exposed to high-energy radiation.

NR is known to undergo crosslinking during exposure to high energy radiation where as poly methyl methacrylate (PMMA) is a polymer where high energy radiation causes chain scission. It is interesting to study how this ‘partially miscible blend’ of scission and crosslinking polymers will behave under high energy radiation. The glass transition (T_g) is one of the most important properties exhibited by a polymer, determining its physical state and influencing other properties such as rheological characteristics, mechanical stiffness and toughness [6]. However, T_g region of a polymer blend is known [7] to depend on the level of miscibility of the two polymers. Dynamic mechanical analysis (DMA) is a good technique to study the variations in the transition regions during the high-energy radiation treatment of the polymers.

Another technique that is available to obtain motional information on the scale of molecular dimensions [8] and miscibility of blends in domain sizes as low as 20 Å is nuclear magnetic resonance spectroscopy (NMR). Relaxation times which can give motional frequency and

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amplitude information in polymer systems include, ^{13}C spin-lattice relaxation time in the laboratory frame (^{13}CT_1), ^{13}C rotating-frame relaxation time (^{13}C$T_{1}\rho$), and the proton–carbon cross polarisation transfer time measured under spin lock conditions (T_{ch}). In solid polymers, relaxation times are not determined only by dynamic phenomena [9]. The measurement of ^{1}HT_1 and ^{1}H$T_1\rho$ is affected by spin diffusion mechanism. Spin diffusion will be efficient on length scales on the order of 100 and 10 Å during ^{1}HT_1 and ^{1}H$T_1\rho$ determinations, respectively [10]. Thus, the spin diffusion data contain information on the size of the domain in an heterogeneous system.

The present work is aimed at studying the changes in the molecular structure of the MG rubber when exposed to high energy radiation. The changes in the dynamic mechanical properties in the glass transition region and solid state NMR was made for this investigation. The local dynamics were investigated with the measurement of carbon relaxation times and molecular structure was studied with the focus on the level of intermolecular mixing by proton relaxation times.

2. Experimental

2.1. Materials and methods

NR latex was obtained from Malaysia through RLA Polymers, Victoria, Australia. The latex is 60% concentrated, and high ammonia stabilised. MMA was obtained from BASF and was purified by vacuum distillation. The monomer was added dropwise to the latex stabilised with a non-ionic surfactant. MMA and NR latex mixtures were irradiated using a gamma source to a total dose of 5 kGy after passing nitrogen through the mixture for 30 min. At the end of the reaction, the latex was coagulated by adding dropwise into an excess of methanol. The coagulated rubber was recovered and dried in an oven at 30°C. The dried samples were irradiated to required radiation doses at 5 kGy/h dose rate in air.

2.2. Soxlet extractions

Samples were extracted with acetone in a soxlet setup. Acetone is expected to extract the homo polymerised PPMA. The weight deference between the initial sample and extracted sample is a measure of the extent of homo polymer in the product.

2.3. Dynamic mechanical analysis

A Perkin–Elmer DMA7 instrument was used in the parallel plate mode on a sample of approximately 3 mm width and 1.5 mm height. Temperature/time scans were carried out at a frequency of 1 Hz. Dynamic and static stress of 400 and 500 mN were used, respectively. A heating rate of 10 K/min was used for the temperature/time scans. Normally the T_g value is taken as the point of deflection of the tan δ curve from the base line. However, this was difficult in some samples due to the phase separation and appearance of shoulders in the tan δ peak. As such the temperature at the maximum point of the tan δ peak was taken as the measure of T_g.

2.4. Nuclear magnetic resonance

Solution state ^{1}H NMR spectra were carried out using a Varian UNITY 400 machine at 400 MHz for proton. Spectra were obtained in $CDCl_3$, with a spectral width of 6000 Hz, 90° pulse and a pulse delay of 10 s. The peaks at 3.6 and 5.11 ppm due to CH_3O (in PMMA) and olefinic proton (NR), respectively, were used to determine the amount of PMMA in the polymer sample.

High resolution solid state NMR experiments were carried out at 100 MHz for C-13 using Varian Unity 400 Spectrometer. The instrument is equipped with a high-power amplifier for proton decoupling and a Varian VT probe. Spectra were externally referenced to the aromatic peak of hexamethyl benzene (132.2 ppm). Samples were packed in silicon nitride rotors with Torlon end caps and were spun at a speed of 5000 Hz. The sample temperature was maintained at 298 $\pm$ 3 K. The proton decoupling strength was approximately 60 kHz, the delay between successive pulses were 4 s and 90° pulses (5.2 μs), were performed. To enhance the signal to noise (S/N), in some cases the cross polarisation (CP) technique was applied.

Rotating and laboratory frame spin-lattice relaxation times for protons and rotating frame spin lattice relation time for carbon were obtained within the standard cross polarisation schemes. For proton relaxation's a spin lock sequence [11] with varied durations (contact times) for T_{ch} and ^{1}H$T_1\rho$, an inversion recovery sequence [10] for ^{1}HT_1 were used, respectively, followed by cross polarisation and detection through carbons. ^{13}C$T_1\rho$ was determined using methods described in the literature using the decay of the ^{13}C intensities after the cross-polarisation contact was broken [12]. ^{13}CT_1 were obtained using an inversion recovery scheme without cross polarisation and a delay time of 20 s between pulses. In the ^{1}HT_1 and ^{13}C$T_1\rho$ measurements the contact time was generally set to 1 ms and the recycle time was set to 4 s. For each spectrum 1000–2000 scans were accumulated.

3. Results and discussion

3.1. Yield and grafting efficiency

As mentioned in Section 1, MG rubber is a mixture of two homo polymers, namely NR and PMMA and PMMA grafted NR. In the discussion, ungrafted PMMA and NR is referred to as Homo-PMMA and Homo-NR, respectively. Grafted molecules are referred to as PMMA-g-NR. While discussing the morphology of the samples, PMMA refers to

Table 1
Characterisation of MG rubber irradiated to different doses

Sample	Dose (kGy)	Extractables (%)	NR/PMMA ratio of the extracts
MGNR2-2	0	2.3	0.46
MGNR2-2	500	10.5	1.31
MGNR2-2	1500	10.5	0.37
MGNR2-2	3000	11.8	0
MGNR2-3	0	17.2	0
MGNR2-3	500	29.2	0.19
MGNR2-3	1500	29.0	0
MGNR2-3	3000	28.4	0

poly methyl methacrylate as both ungrafted and grafted molecules. Similarly in the case of NR also. TPMMA indicate the total PMMA in the sample as Homo-PMMA and PMMA-g-NR.

The TPMMA (yield) of the initial samples were determined using solution state ^{1}H NMR. The peak at 5.11 ppm due to the olefinic double bond proton of the polyisoprene molecule and the peak at 3.6 ppm due to the methoxy protons of the PMMA was used to determine the PMMA content. Graft PMMA content (grafting efficiency) was determined from the weight loss during soxlet extraction and solution state ^{1}H NMR of the residue of the extraction. The results are summarised in Table 1. The sample MGNR2-2 contains about 17% TPMMA and has a high initial grafting efficiency where the initial sample of MGNR2-3, contains 33% TPMMA and the grafting efficiency is only about 50%.

During the exposure to high energy radiation, more extractable PMMA is formed according to the results given in the Table 1 in both the samples. In MGNR2-2, the limiting amount of extractable material is 11% while in MGNR2-3 it is 29%. Increase in the amount of extractable polymer indicates that there is chain scission of PMMA, which are previously grafted to the NR molecules. The extraction of the MG rubber with acetone has found [4,13] to draw out certain amount of NR in addition to the PMMA. As acetone is a non-solvent to NR, the NR peaks observed in the NMR spectra of the extracts could be arising from PMMA-g-NR with more than one PMMA graft per NR molecule. In the present work the NMR spectra of the acetone extracts show NR peaks in MGNR2-2 (0,500 and 1500 kGy) and MGNR2-3 (500 kGy). The amount of NR in the extract increases with the dose first and then reduces with continuing irradiation. The increase in the NR content in the extract of the sample irradiated to 500 kGy indicate, more formation of NR molecules with more than one graft during this period of irradiation, even though, the total PMMA grafted is low. This is possible as PMMA (ungrafted or grafted) undergoes chain scission, some of the main chain scission radicals produced could undergo grafting to the NR molecules.

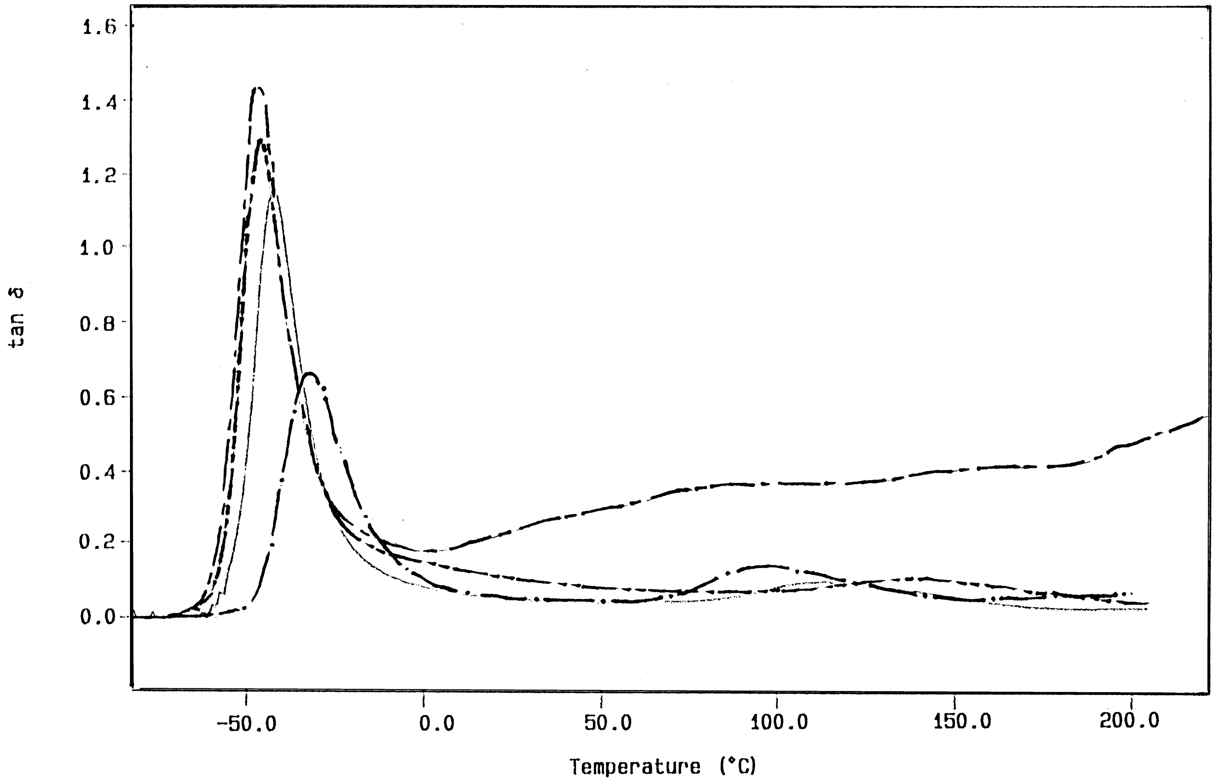

Fig. 1. Tan δ curves of MGNR2-2 irradiated to 0 (– – –), 500 (– - - –), 1500 (——) and 3000 kGy (– · –).

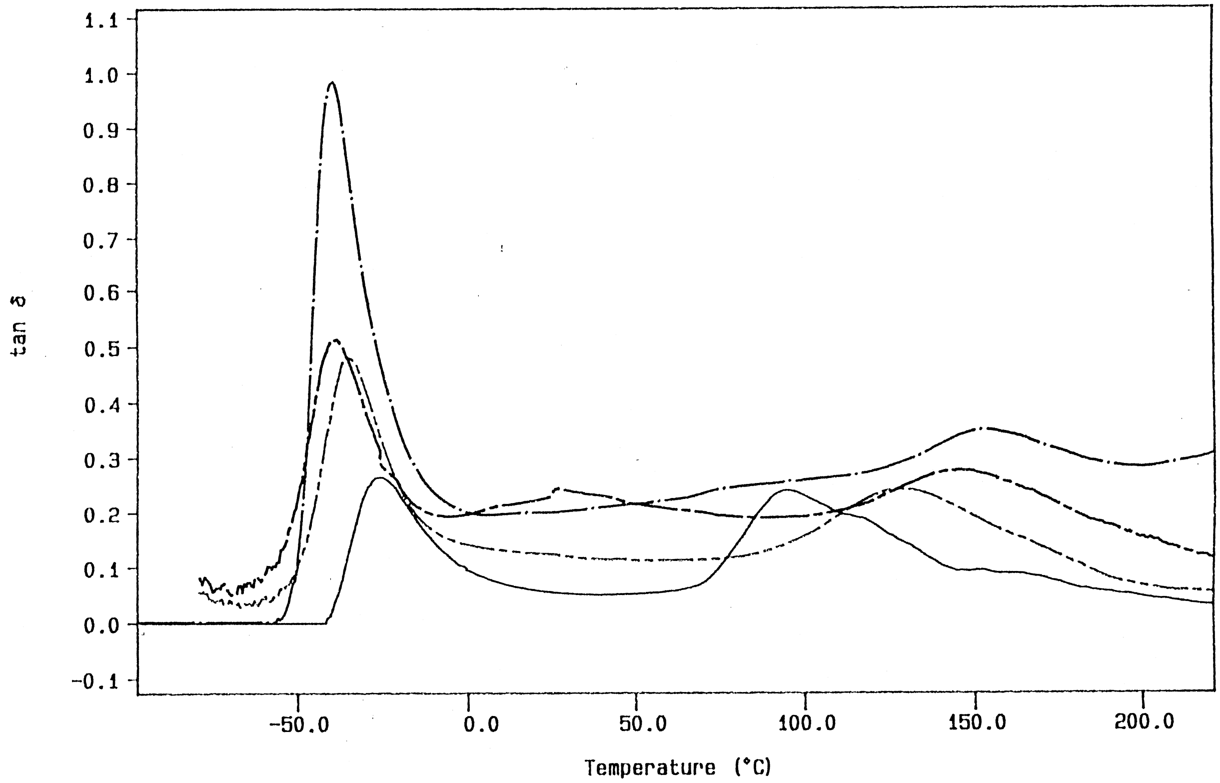

Fig. 2. Tan δ curves of MGNR2-3 irradiated to 0 (– · –), 500 (– – –), 1500 (– - - –) and 3000 kGy (——).

3.2. Dynamic mechanical analysis

The tan δ curve of NR shows [4] a peak at about -48°C due to the α transition arising from the segmental motion. This correspond to the glass transition temperature (T_g) of NR. PMMA shows the T_g at 125°C, as shown by a tan δ peak at 125°C in the curve. NR has higher damping than PMMA because of its rubbery nature. The loss modulus curves also shows the presence of loss maximum for NR and PMMA at -46 and 125°C, respectively. NR has a higher storage modulus than PMMA below the T_g region and the trend is reversed above the T_g.

Dynamic mechanical investigations were used to predict the miscibility of polymer systems by various groups [14]. Generally for an incompatible blend, the tan δ curves show [15] the presence of two damping peaks corresponding to the T_gs of individual polymers. For a highly compatible blend, the curves show [16] only a single peak in between the transition temperatures of the component polymers, whereas broadening of transition occurs in the case of partially compatible systems. In the case of compatible or partially compatible blends the T_gs are shifted to higher or lower temperatures as a function of composition.

The tan δ curves for the MGNR2-2 samples irradiated to 0, 500, 1500 and 3000 kGy are shown in Fig. 1. The unirradiated MGNR2-2 which has 17% TPMMA content shows a peak at -48°C. This peak is due to the NR in the sample. The curve also has a broad peak centred at about 80°C. This broad region indicate some phase mixing which means all PMMA (grafted or ungrafted) in this sample is mixed in some parts of the NR phase. It should be noted that the percentage of Homo-PMMA in this sample is very low. Increase in the dose reduces the tan δ maximum value of NR but shifts the tan δ curve to higher temperatures. For example, the tan δ curve of the sample irradiated to 3000 kGy have shifted to -30°C. The peak width also have increased with dose. All these effects correspond to increase in crosslink density in the NR phase.

The broad peak centred at 80°C observed in the unirradiated MGNR2-2 has disappeared with irradiation. But there is a high temperature tail in the tan δ peak due to the NR phase in the sample irradiated to 500 kGy. This effect corresponds to a drop in the total amount of grafting (grafting efficiency), but an increase in the amount which contain more than one PMMA graft. The reduction in the grafting efficiency makes the amount of PMMA-g-NR, low in the system. As these grafted molecules are known to act as compatibilisers, a reduction in the PMMA-g-NR will make the two polymers to phase separate. This is observed in the appearance of a peak in PMMA region (125–150°C) and a disappearance of the peak centred at 80°C.

The new peak that appear in the PMMA transition region moves to lower temperatures as the radiation dose increases. Further, there is an increase in the tan δ maximum and a

Table 2
Radiation yields of crosslinking and scission in MGNR2-3

Dose (kGy)	*G(X)*	*G(S)*
0–500	1.1	
500–1500	0.9	
1500–3000	1.5	
0–3000		0.9

drop in the peak width. All these effects correspond to a drop in the molecular weight of the PMMA molecules as a result of chain scission during exposure to high-energy radiation.

The tan δ curves for the MGNR2-3 irradiated to 0, 500, 1500 and 3000 Mrad are shown in Fig. 2. The curve for the unirradiated MGNR2-3 sample indicate three T_g regions. This sample has about 33% TPMMA content. The first region with a peak at -48°C is due to the phase separated NR. The second peak with a maximum at 130°C correspond to the phase separated PMMA. The third region is in between and is around 80°C which correspond to the broad peak observed in unirradiated MGNR2-2. This third peak (80°C) indicate some phase mixing where as other two peaks show that some of the NR and PMMA are phase separated.

Similar to MGNR2-2, irradiation causes a drop in the tan δ maximum and an increase in peak width of the NR transition peak and a movement of this peak to higher temperatures. All these show an increase in the crosslink density in the NR phase with irradiation. In MGNR2-2, the tan δ maximum drop is small upto 1500 kGy but drops to about half of the original value at 3000 kGy. In the MGNR2-3 sample, the tan δ maximum drop to about half of the original value at 500 kGy and by 75% at 3000 kGy. This means that the drop in the tan δ maximum is more pronounced in MGNR2-3. It is hard to believe that the *G(X)* in the NR phase will depend on the TPMMA content. Therefore, the increase in the homo-PMMA during irradiation must be the reason for this bigger effect in the MGNR2-3 at 500 kGy.

The peak at 80°C which was due to interface (miscible region) has moved to about 25°C when MGNR2-3 is exposed to 500 kGy. This indicates that there is less PMMA in the interface, which may result from the reduction in graft copolymer. The change in the PMMA transition peak with radiation exposure is even clearer in the MGNR2-3 samples. Increase in the peak area, and peak width is observed with increase in dose. The sample exposed to 3000 kGy shows several shoulders to the tan δ peak of the PMMA transition indicating a heterogeneity in the PMMA. This is likely to result from different molecular weights in different regions.

Crosslinking is known [17] to increase the T_g of a polymer. At low degrees of crosslinking the shift is negligible but at higher degrees the shift is large and is sensitive to small changes in M_c (average chain length between crosslinks). Number of studies [18] have been made relating the degree of crosslinking to the shift in T_g and the average of the results from these studies verify a relationship given in Eq. (1).

$$T_g - T_{g0} = k(1/M_c), \tag{1}$$

where T_{g0} is the glass transition temperature of the uncrosslinked polymer, $k = 3.9 \times 10^4$ and $1/M_c$ is the crosslink density in mol/g. A different equation relating the shift in the glass transition temperature to the degree of crosslinking was derived [19,20] from theory. This equation was simplified using a value of one for the ratio of lattice energies of crosslinked and uncrosslinked polymers (assuming that the density and solubility parameter do not change with crosslinking) and a value of zero for the ratio of segmental mobilities. The simplification results in the relationship given in Eq. (2).

$$(T_g - T_{g0})/T_{g0} = X_c/(1 - X_c), \tag{2}$$

where X_c is the molefraction of monomer units which are crosslinked in the polymer. Both the aforementioned Eqs. (1) and (2) were used to estimate the crosslink density in the samples from the T_g values calculated from the tan δ curves. The temperature at which the tan δ is maximum is taken as the T_g. The crosslink density values were then used to calculate the radiation yield of crosslinking in NR, *G(X)*, using [21] Eq. (3) and the results are presented in the Table 2.

$$\text{Product (mol/kg)} = (1.04 \times 10^{-4})G(X)R, \tag{3}$$

where R (dose) is in kGy. The *G(X)* values given in the table are comparable to the values reported [22] in the literature for pure NR. This indicates that the presence of PMMA do not interfere with the radiation crosslinking in the NR in MG rubber.

It is also known that glass transition temperature is effected by the molecular weight of the polymer below a critical molecular weight. The T_g of PMMA is related [23] to its number average molecular weight by the Eq. (4).

$$T_g = T_{g^\infty} - (2.1 \times 10^5)/M_n, \tag{4}$$

where T_{g^∞} is the glass transition temperature at high molecular weight. The data from the tan δ curves in the PMMA T_g region was used to estimate the M_n of the PMMA segments in the irradiated samples. These M_n values were used to calculate the radiation yield of scission, *G(S)*, using the Eq. (5) and the data are also given in the Table 2.

$$1/M_n = 1/M_{n0} + (1.037 \times 10^{10})G(S)R, \tag{5}$$

where R is the radiation dose in kGy. The *G(S)* values are comparable [24] to those values of pure PMMA.

The intensity of the tan δ peak at the glass transition temperature reflects the extent of mobility of the macromolecular chain segments at that temperature [25]. Any restriction in the main chain mobility in the polymer is expected to decrease the area under the loss modulus curves vs. temperature. This trend will be reflected in the intensity of

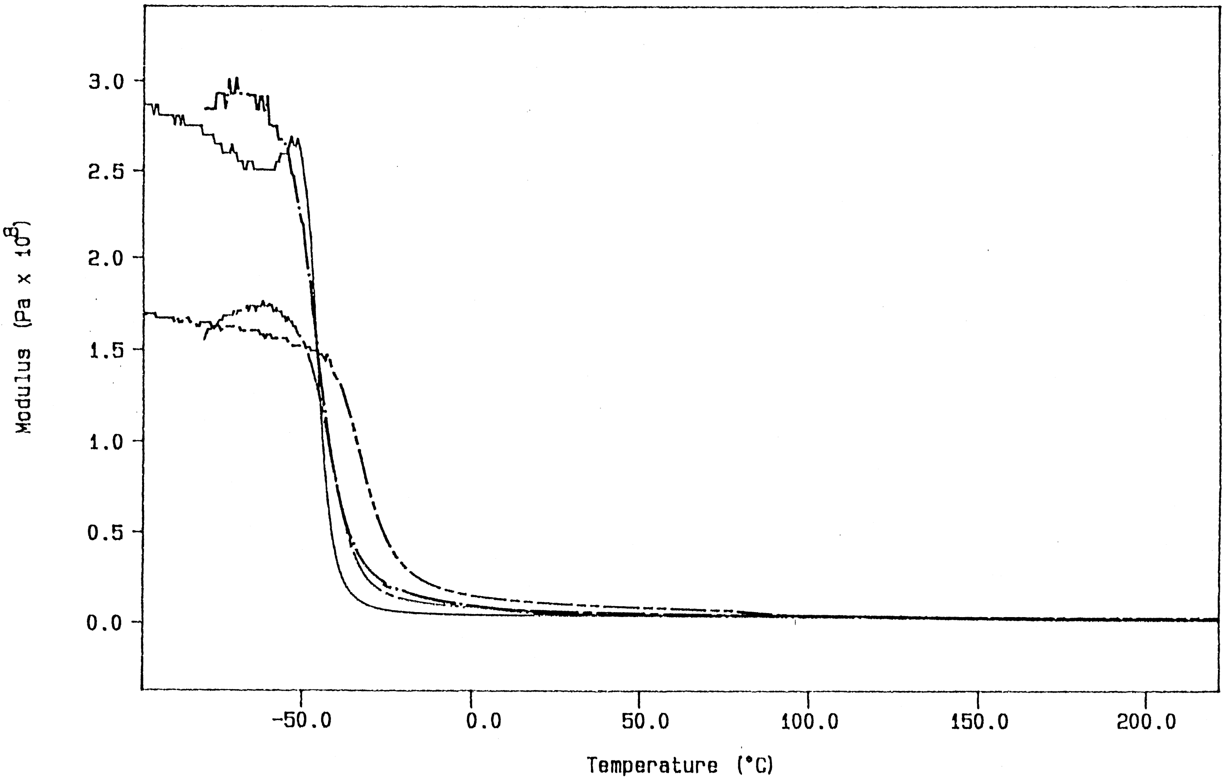

Fig. 3. Storage modulus curves (temperature range from −100 to 225°C) of MGNR2-3 irradiated to 0 (——), 500 (– · –), 1500 (– – –) and 3000 kGy (- - - -).

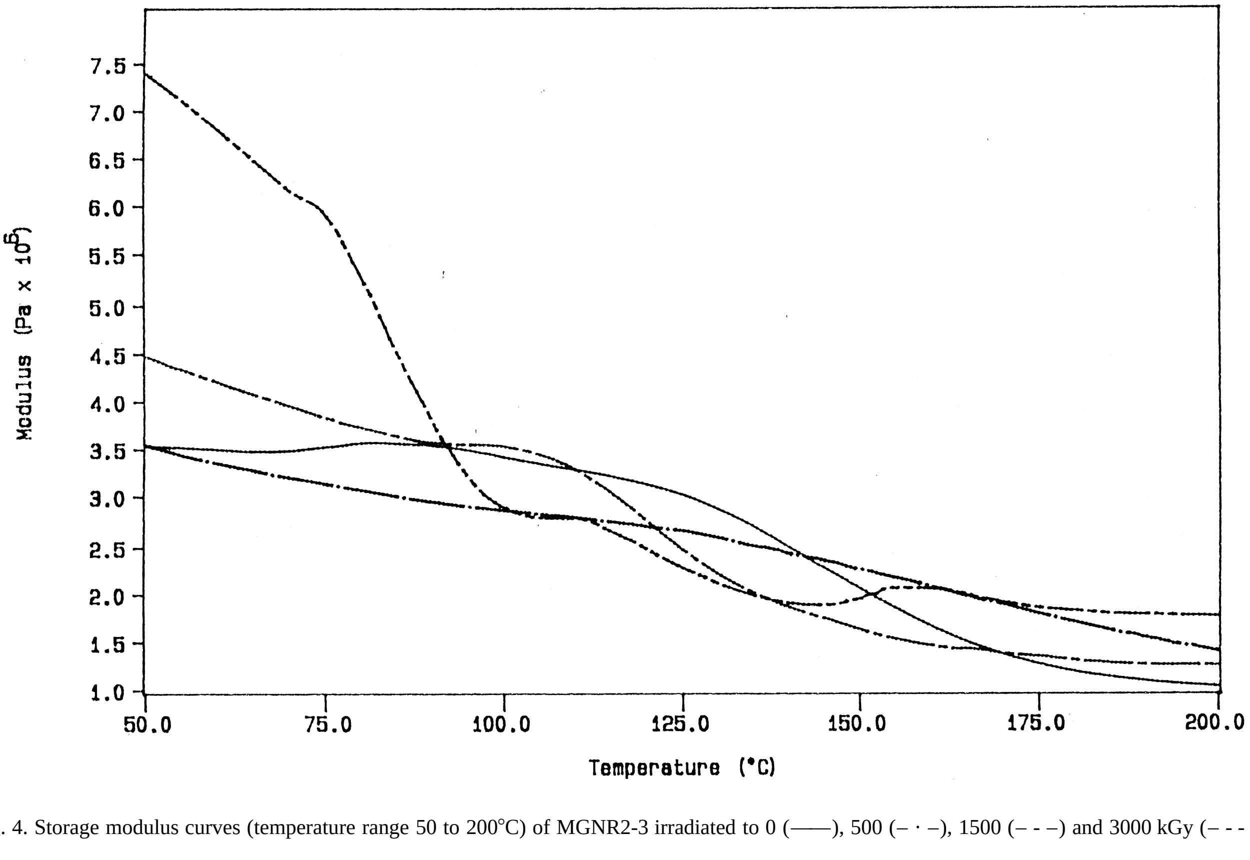

Fig. 4. Storage modulus curves (temperature range 50 to 200°C) of MGNR2-3 irradiated to 0 (——), 500 (– · –), 1500 (– – –) and 3000 kGy (- - - -).

Table 3
Activation energy of transition

Sample	Dose (kGy)	Normalised activation energy of rubber transition	Normalised activation energy of PMMA transition
MGNR2-3	0	1	4.6
MGNR2-3	500	2	1.5
MGNR2-3	1500	2	1.1
MGNR2-3	3000	3.5	1

the tan δ peak. The change in the intensity of the tan δ peak, therefore, indicate that the mobility of the NR molecules are reduced and PMMA molecules are increased by exposure to high energy radiation.

The storage modulus curves for the MGNR2-3 samples are shown in Figs. 3 and 4. A drop in storage modulus below the T_g of NR, is observed with the increase in dose above 500 kGy. Such storage modulus drop below T_g in other polymer systems have been interpreted [15] as due to the change in continuous phase which disturb the continuity in the glassy structure in the polymer. The region between the two glass transition temperatures (~50°C), show a complex storage modulus behaviour. Irradiation upto 500 kGy has little effect on these storage modulus values. This may be due to opposing effects of the removal of interface region (reduce modulus) and introduction of crosslinks in the NR molecules (increase modulus). Further irradiations increase the storage modulus in this region as a result of increase crosslinking. The storage modulus curve of the MGNR2-3 irradiated to 300 Mrad clearly shows the presence of different regions.

From elementary rubber theory

$$G = (d\mathrm{RT})/M_c, \tag{6}$$

where G is the measured dynamic storage modulus obtained from the DMA analysis, d the sample density, R the gas constant, T the absolute temperature and M_c the average molecular weight between crosslinks. While this expression is based on a simple model of rubber elasticity that neglects, for example, entanglement effects, it has been shown [26] to be adequate first approximation in many cases. This equation was also used to estimate the crosslink density of the samples irradiated to 1500 and 3000 kGy.

The area under the tan δ curve has been shown to be related to the activation energy of the backbone motion in magnitude [27]. For example, the average activation energy of transition for materials can be calculated from the dynamic mechanical data as proposed before [28], using the Eq. (7).

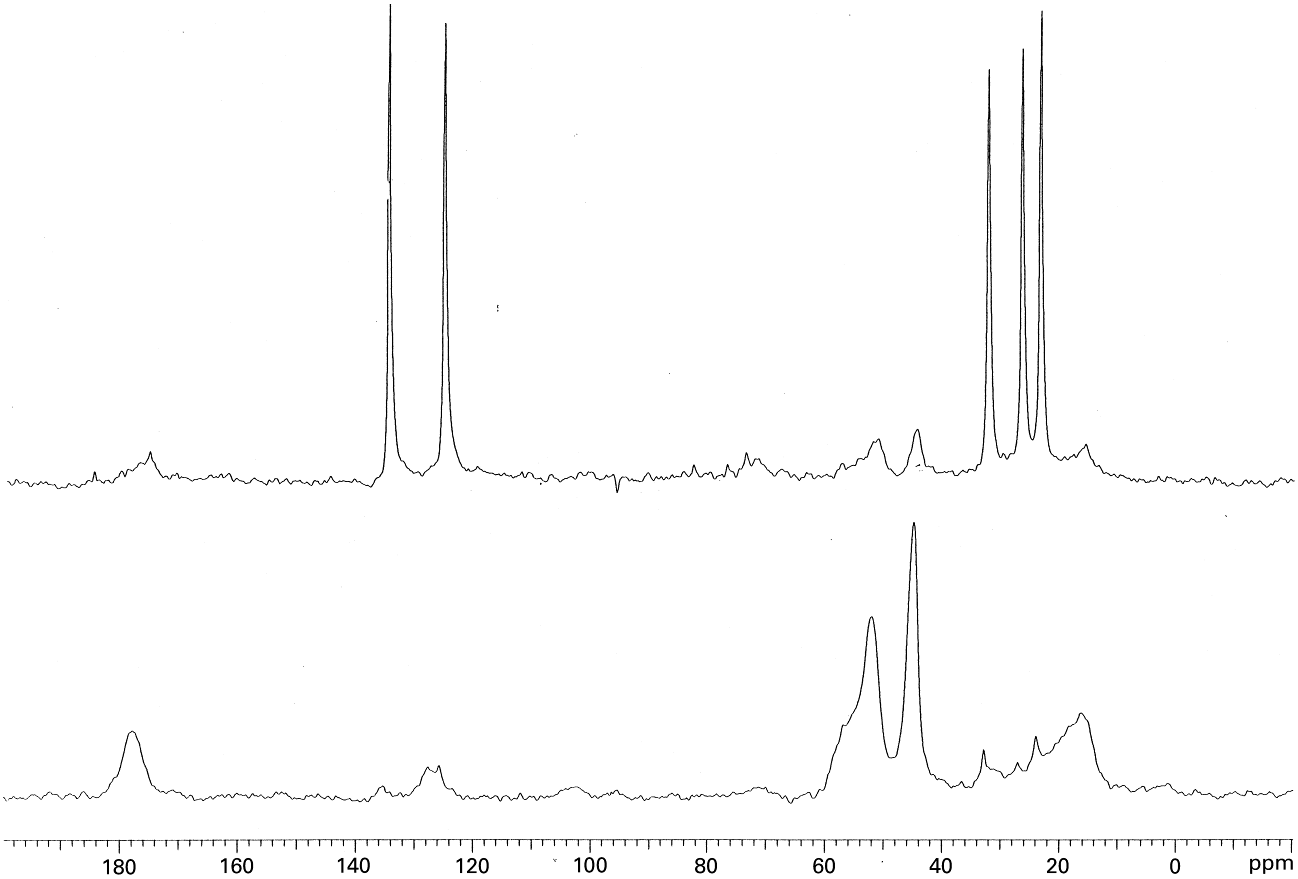

Fig. 5. (a): DD (top); and (b): CP (bottom) solid state ^{13}C NMR of MGNR2-3.

Table 4
Ratio of peak intensities of DD and CP NMR spectra

Sample	Dose	DD/CP NR peaks	CP specrtum PMMA/NR peaks
MGNR2-3	0	102	0.12
MGNR2-3	500	125	0.13
MGNR2-3	1500	92	0.15
MGNR2-3	3000	110	0.19

$$tA = (\ln E_G - \ln E_R)(R/E_A)(\pi/2)(T_g)^2, \tag{7}$$

where tA is the area under the tan δ curve, E_G and E_R are the storage modulus at glassy phase and rubbery phase, respectively, E_A the activation energy. The calculated values of E_A for NR and PMMA transitions are given in the Table 3. The activation energies are the normalised values as the peak areas could not be calculated directly, but had to be calculated by cutting and weighting method. The data given in the table show an increase in activation energy for transition in the NR region with irradiation. Increased amount of crosslinking reduces the backbone motion. There is no change in the activation energy between 500 and 1500 kGy samples. This is likely to be due to the changes in the interfacial region. The activation energy for PMMA transition drops with irradiation confirming the increase in molecular motion with reduction in molecular weight.

3.3. Nuclear magnetic resonance

The ^{13}C CP/MAS NMR spectrum of the MGNR2-3 sample is shown in Fig. 5(a). The peaks at 19, 45, 55, 58 and 180 ppm were assigned to CH_3, backbone quaternary carbon, CH_3–O–, backbone –CH_2– and carbonyl carbon of PMMA, respectively. The peaks at 23, 27, 32, 125 and 135 ppm were assigned to methyl carbon, methylene carbons and olefinic carbons of NR, respectively.

The DD/MAS spectrum of the same sample is shown in Fig. 5(b). A comparison between peak intensities in the DD and CP spectra can be used as a qualitative measure of the local mobilities of particular structural units; higher values of DD/CP intensity ratio indicate higher mobility. The DD/CP peak intensity ratio values calculated for the carbons in PMMA and NR are given in Table 4. All spectra were normalised to the quaternary carbon at 45 ppm. As the sample is irradiated, the NR phase becomes more mobile at 500 kGy. This may be due to the reduction in the amount of graft copolymer content, which reduces the interface. Further irradiations reduce the mobility due to crosslinking.

The DD spectra of the MGNR2-2 unirradiated and irradiated to 3000 kGy are compared in the Fig. 6. Irradiated sample shows two new peaks at 16 and 40 ppm. These peaks may be due to *trans* isoprene unit where *cis–trans* isomerisation is known [29] to occur when *cis* polydienes are exposed to high energy radiation. Another feature that could be observed in this figure is the drop in NR/PMMA peak ratio in the spectrum of the irradiated MGNR samples. This could be caused by either increase in mobility of the PMMA molecules or drop in mobility of the NR molecules. The aliphatic region of the CP spectra of MGNR2-2 irradiated to 3000 kGy obtained with different contact times are given in Fig. 7. At very low contact times, a very broad peak covering the region 10–40 ppm is observed. A similar broad peak was observed in the MGNR2-3 as well. At high contact times this broad peak has disappeared and sharp peaks of NR is observed. The broad peak is due to the crosslinked region of the NR which is rigid. The carbon attached to the crosslink in the polydienes resonate at 45 ppm and this peak has been used [30–33] to estimate the *G(X)* in diene polymers. The calculated values of *G(X)* using the NMR peaks for all polydienes, except for polycloroprene, are much higher than the values calculated from other techniques. This discrepancy was explained by considering crosslink clusters. In the polybutadiene, polyisoprene and nitrile rubber, the NMR spectra show the broad peak at 45 ppm when irradiated to about 1000 kGy.

The cross-polarisation of ^{13}C nuclei by adjacent polarised protons, that is the initial buildup of the carbon magnetisation via polarisation transfer, is assumed to be controlled by a single-time constant T_{ch}. Cross polarisation occurs through a static dipolar coupling of protons and ^{13}C spins which are averaged out by isotropic molecular motions. Low frequency motions have the greatest effect on the T_{ch} where higher the motion, higher are the observed values. Therefore, it is believed [12] that the T_{ch} measurements provide information on near static components in the motion of a particular group.

The T_{ch} values for one of the methylene carbons in NR and backbone quaternary carbon of PMMA for some of the MG rubbers are given in Table 5. Quaternary carbon of PMMA was selected as this carbon gives a peak without any overlapping with other peaks. With increase radiation, the T_{ch} value of NR carbons increase at 500 kGy and then drop. This observation is in line with DD/CP peak ration data. The T_{ch} value of PMMA quaternary carbon remains the same upto 1500 kGy but shows increase mobility at 3000 kGy.

The $^{13}CT_1$ are determined by motional components close to the Larmor frequencies, such as methyl and phenyl rotations or main chain or side chain process of polymers at temperatures well above the glass transition temperature. That is, in the region of few hundred megahertz. As $^{13}CT_1$ could be determined for each carbon, it is useful in distinguishing between polymer side group dynamics and the relaxation of carbons in the main chain. Studies on vulcanisation of butyl rubber [34] and NR [35] to crosslink levels similar to commercial vulcanizates (crosslink density up to 4.5×10^{-5} mol/g) found that $^{13}CT_1$ to be not sensitive to crosslink density at these low crosslink density levels. This indicate that such crosslink levels do not affect relatively rapid segmental motions in rubbers which determine the $^{13}CT_1$ relaxation times. A very small increase in the $^{13}CT_1$ relaxation time values upto 3000 kGy is observed as given in Table 5.

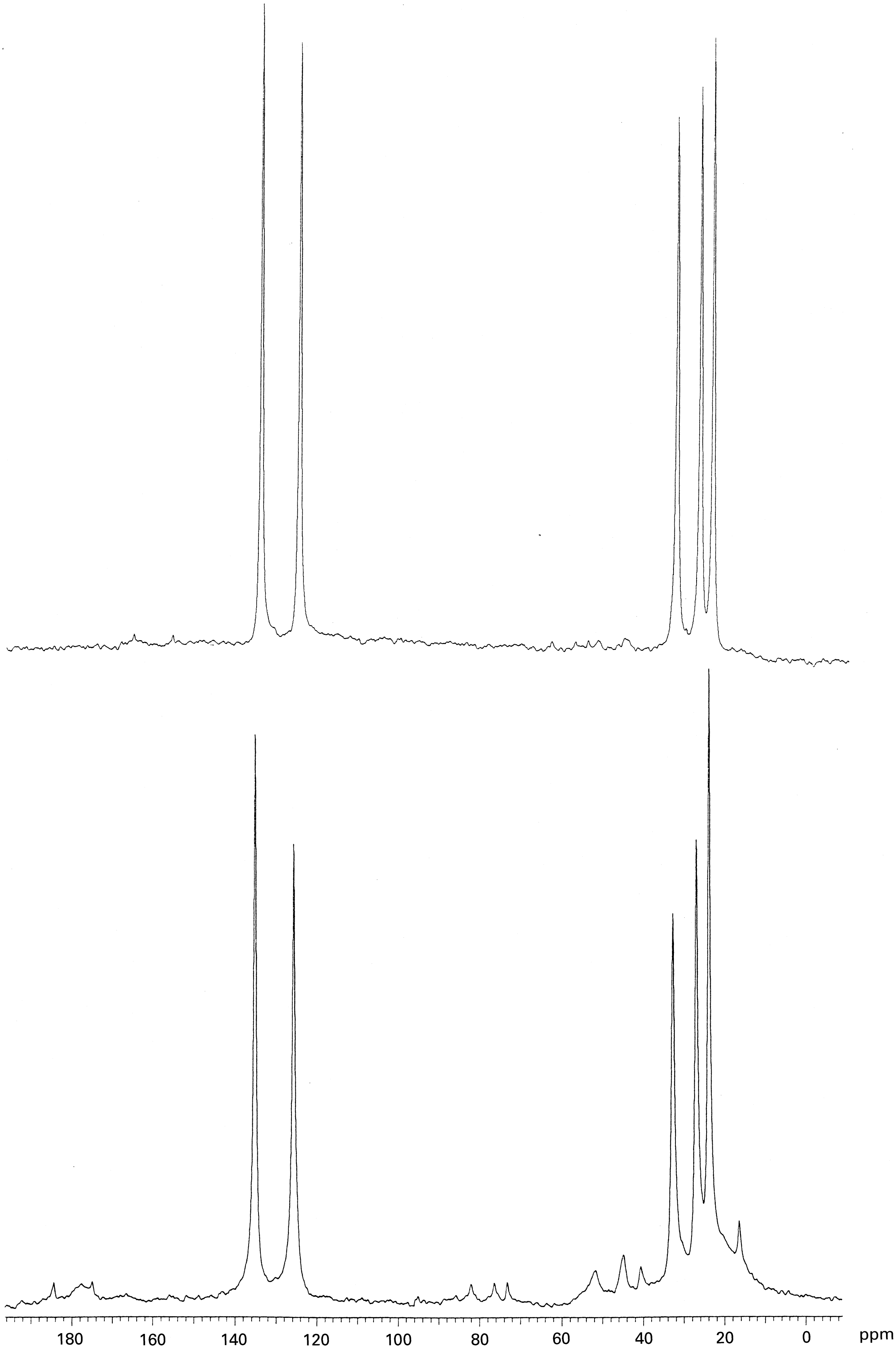

Fig. 6. DD spectra of MGNR2-2 unirradiated (top) and irradiated to 3000 kGy (bottom).

As $^{13}CT_1$ values are expected to be sensitive to the main chain motions, the relaxation times of the main chain quaternary carbon atom of PMMA was measured in the samples exposed to different doses. As the variable temperature experiments [36,37] indicate that for the PMMA and poly-dimethacrylate, molecular motions at room temperature are in the slow motion region relative to T_1 minima, any increase in $^{13}CT_1$ in this system is also expected to indicate a decrease in mobility. The results indicate that the $^{13}CT_1$ values are insensitive to the amounts of TPMMA content in the polymer sample.

This insensitivity of the $^{13}CT_1$ values of the PMMA carbons, to the amount of TPMMA can be understood by considering the molecular motions that are responsible for the relaxations. In PMMA at around room temperature the methyl group reorientations are much decoupled from the extremely segmental motions below T_g. Hence, the protons of the methyl group can move in the glassy state with part of the correlation time distribution even in the megahertz region and relax the neighbouring carbons in the monomer unit despite the r^{-6} proton–carbon distance dependence of relaxation rates. Owing to this methyl dominated relaxation there is little effect of plasticiser on the $^{13}CT_1$ values of the PMMA backbone carbons. Similar findings on the plasticisation of PMMA by dioxane have been reported before [37].

The measurement of $^{13}CT_1\rho$ was performed by an experiment where the spin lock contact was established and then terminated followed by allowing the ^{13}C polarisation to decay in its own rotating field for a determined interval. This was terminated by switching off the carbon field, restoring the proton field and acquiring the data. The decay in the ^{13}C magnetisation in its rotating field was assumed to be controlled by a single relaxation time, $^{13}CT_1\rho$. The $^{13}CT_1\rho$ is sensitive to molecular motions in the 10–100 kHz frequency range, characteristic for relatively long range cooperative motions of a polymer chain below the T_g. The $^{13}CT_1\rho$ values for PMMA quaternary carbon of MGNR2-3 irradiated to different doses are also given in Table 5. There is a slight increase at 500 kGy indicating a reduction in mobility of the PMMA chains. This also complements the explanation that there is a drop in interfacial region during irradiation. However, continued irradiation reduces the $^{13}CT_1\rho$ values confirming molecular breakdown. The $^{13}CT_1\rho$ values of NR carbons increase with dose due to crosslinking.

More detailed information about the miscibility of two polymer components could be obtained from proton relaxation behaviour. The $^{1}HT_1\rho$ values were measured by analysing the decay of the carbon magnetisation for long contact times in a CP experiment. The measurement through the carbon spins has the advantage that the $T_1\rho$ values for protons near carbons with different chemical shifts can be determined separately. By this method it is possible to determine the $^{1}HT_1\rho$ for both components of the matrix. The

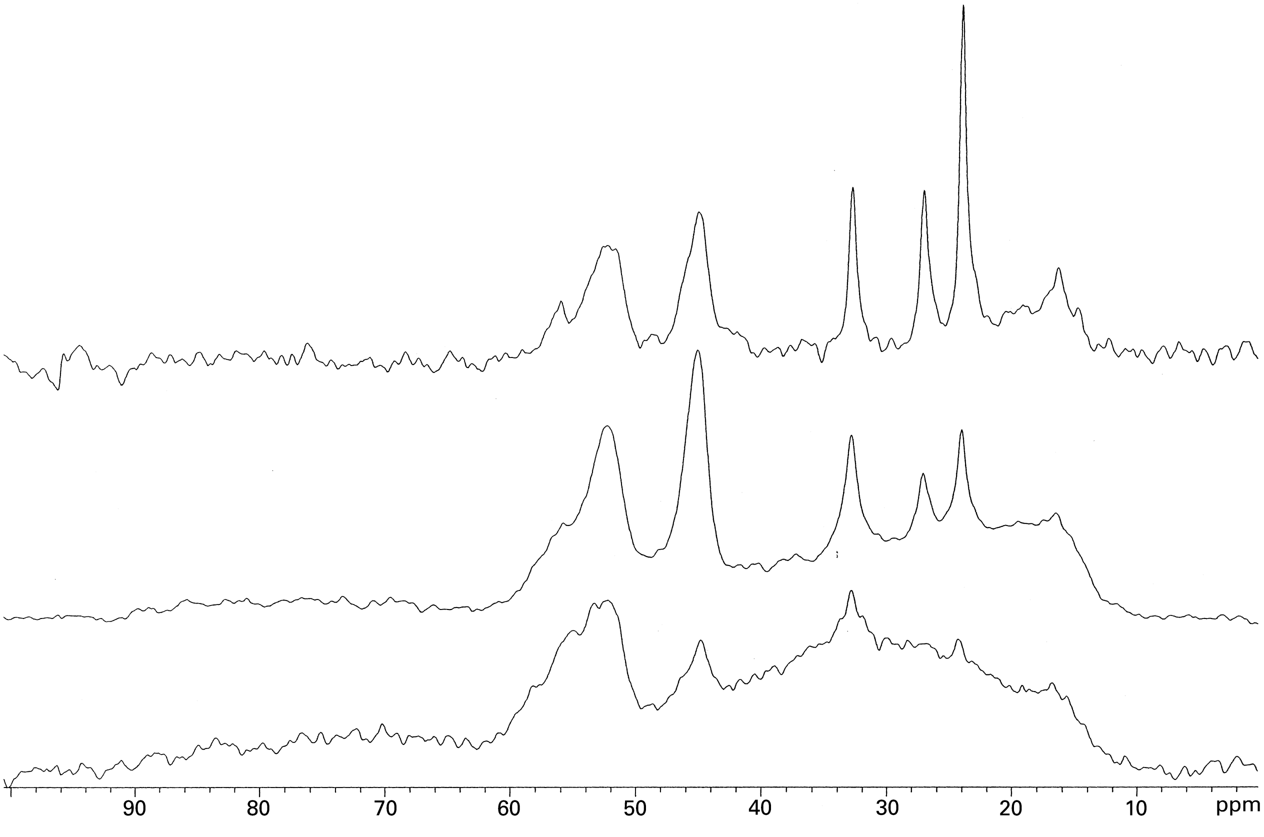

Fig. 7. CP spectra of MGNR2-2 irradiated to 3000 kGy collected with: (a) 50, (b) 1000 and (c) 15 000 μs contact times.

Table 5
Cross polarisation times and C$T_1\rho$

Sample	Dose (KGy)	T_{ch} PMMA (μs)	T_{ch} NR (μs)	^{13}CT_1 NR (s)	^{13}C$T_1\rho$ PMMA (ms)	^{13}C$T_1\rho$ NR (ms)
NR	0		2500			
MGNR2-3	0	256	410	0.19	3.1	0.2
	500	237	1138	0.2	4.6	3.6
	1500	256	627	0.24	3.1	9.6
	3000	479	126	0.28	0.9	13.0
PMMA	0	275			8.4	

protons of the two components of a compatible blend have the same ^{1}H$T_1\rho$ if the molecules are in contact on an intimate molecular distance, L, over which proton can effectively diffuse in a given time, t, related by [38]

$$\langle L^2 \rangle \sim (t/T_2)(l_0^2),$$

where l_0 is the distance between the protons and T_2 the proton spin–spin relaxation or hopping rate. The available time for spin diffusion, t, is equal to spin-lattice relaxation time, ^{1}HT_1 or ^{1}H$T_1\rho$. If the chains are intimately and homogeneously mixed, spin diffusion occurs quickly among the chemically different constituents, and a single value of ^{1}H$T_1\rho$ is determined through analysis of the decay rates for all carbons. If the chains do not interact on the molecular level, different proton $T_1\rho$ values are observed for the carbons corresponding to the different polymers.

The ^{1}H$T_1\rho$ values for the PMMA quartenary carbons in the samples of Homo polymerised PMMA, and MGNR2-3 are given in Table 6. The nuclei from homo polymer PMMA could be characterised by a value of 13. The ^{1}H$T_1\rho$ relaxation behaviour for PMMA carbons in the MGNR2-3 samples irradiated upto 1500 kGy shows a different value to that of homo polymer. This indicate that some phase mixing between the NR and PMMA molecules in these samples even though the DMA graphs show total phase separation in MGNR2-3 irradiated to 1500 kGy. These results are due to the presence of an interface where a certain proportion of NR and PMMA exist in a miscible phase. Even though the PMMA in the interface and phase separated domain should give two different ^{1}H$T_1\rho$ values, such a clear difference is not observed in the magnetisation decay curves. This may be due to the gradual change in blend proportions in the interface from the PMMA domain boundary. As a result it is difficult to observe a two component decay in the magnetisation decay curves of the PMMA carbons. However, the sample irradiated to 3000 kGy show ^{1}H$T_1\rho$ value similar to that observed in homo polymer PMMA confirming total phase separation in this sample. Owing to the very long T_{ch} values for NR carbons, the total decay of the carbons could not be observed with the experimental conditions possible with our instrument (that is the maximum contact time possible).

Table 6
Proton relaxation times

Sample	Dose (kGy)	^{1}H$T_1\rho$ PMMA (ms)
PMMA	0	13
MGNR2-3	0	8.7
MGNR2-3	500	8.0
MGNR2-3	1500	8.3
MGNR2-3	3000	11.5

4. Conclusions

More extractable PMMA was formed during exposure of MG rubber to high energy radiation. This is as a result of chain scission of the PMMA molecules grafted to the NR molecules.

DMA data indicate that the interfacial region observed in the material disappears during irradiation and the PMMA phase separate. This is due to the drop in the grafted molecules which act as compatibilser to the NR and PMMA homo polymers.

Radiation yield of crosslinking and scission in NR and PMMA molecules, respectively, were calculated from the T_g data and are comparable to the values of the homo polymers irradiated separately.

Cis–trans isomerisation of polyisoprene occurs during irradiation and the peaks are observed in the NMR spectra. A broad peak is observed in samples irradiated to 3000 kGy in CP spectra with low contact times, due to crosslinks.

An increase in the mobility of the NR phase is indicated in the samples irradiated to 500 kGy.

A total phase separation indicated by ^{1}H$T_1\rho$ values is observed only in the samples irradiated to 3000 kGy.

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