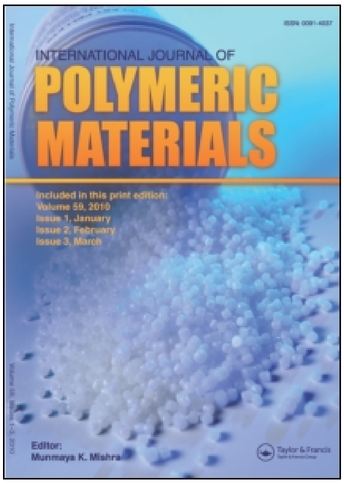

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M. M. El-awady[a]; A. M. Ghoneim[b]
[a] Polymers and Pigments Dept., [b] Microwave Physics Dept., National Research Centre, Giza, Egypt

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Controlled Release Formulations from SBR/NBR Rubber Blend. 1. Dielectric and Thermal Studies

M. M. EL-AWADY[a,*] and A. M. GHONEIM[b]

[a]Polymers and Pigments Dept., ; [b]Microwave Physics Dept., National Research Centre, 12622-Giza, Egypt

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Styrene butadiene Rubber (SBR) and acrylonitrile butadiene rubber (NBR) blends were prepared with different concentration ratios, namely, 0:100, 20:80, 40:60, 60:40, 80:20 and 100:0. The blends were mixed with multifunctional monomer (triethylene glycol dimethacrylate) and copper sulphate monohydrate. The blends obtained were vulcanized with γ-radiation at a dose of rate 7.51 rad/sec. The thermal properties of the blends obtained were characterized using differential thermal analysis (DTA). The dielectric permittivity (ε') and dielectric loss (ε'') were also measured. The experimental results were analyzed and discussed to show that the dielectric properties of the blends are greatly affected by γ-irradiation and decreased by grafting and cross-linking processes. The results obtained also show that the irradiated rubber blends in the absence of multifunctional monomer are incompatible over the entire range of irradiation dose as proven by the DTA. On the other hand, in the presence of the monomer, they are partially compatible but under certain conditions of blend concentration ratio and irradiation dose.

Keywords: SBR/NBR blends; γ-radiation; Multifunctional crosslinker; Copper sulphate; Compatibility; Incompatibility

INTRODUCTION

There is a growing realization that conventional application of pesticidal, mulluscidal, or herbicidal chemicals is often wasteful, and can cause toxicity problems to non-target species. Delivery from

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[*] Corresponding author. Fax: (202) 3370931.

controlled-release formulations is a promising concept, and many advances have been made in recent years [1]. Synthetic and naturally occurring polymers are the cornerstones of this technology. Different formulations can be prepared with several polymers such as cellulose acetate, poly-acrylamide, polyester, polyurethane, urea formaldehyde and polyvinly chloride [2–4]. The active ingredient is dissolved, dispersed, or encapsulated in the polymeric matrix, and under field conditions it is released owing to diffusion through the polymer to the surrounding environment. For agricultural applications the polymers used for controlled release formulations should be biodegradable to avoid environmental pollution. For this purpose several derivatives from natural polymers such as cellulose, starch, and wood sawdust have been developed for control release formulations. Alginate gels (polysaccharides) were also used as matrices for controlled release in certain agricultural applications because of the biodegradability of the gels [5].

Elastomers are used as binding matrices for controlled release of molluscides, herbicides and pesticides and also in some agricultural applications [6–8]. They are formulated and processed by well-known techniques using conventional equipment. These formulations are composed basically of four ingredients: the elastomer binding matrix, additives necessary for curing, additives essential to regulate the bio-active agent loss rate, and the bio-active agent (mollusicidal, herbicidal, or pesticidal materials). The cured formulations can take the form of discs, granules, or any shapes suitable to rubber. To control the leaching of bio-active material, hydrophillic additives such as carboxy methyl cellulose (CMC) [9], or blowing agent such as profor [10] can be added to the formulations to the desired amount of release by changing the content of additive used.

Since 1973, inorganic copper salts have been successfully formulated in slow-release matrices and evaluated as molluscides [11]. The techniques for formulation of controlled release molluscides, which are based on elastomers (or plastics), are now well developed. In the present work the use of elastomeric blend as binding matrix instead of the use of single elastomer phase was fulfilled for the first time. Thus, the aim of the present work is to evaluate an elastomeric blend consists of polar (NBR) and non-polar (SBR) elastomer at different concentration ratios as a new binding matrix for the active agent

$CuSO_4 \cdot H_2O$, releasing it in minute amount over long periods of time to evaluate them as a controlled release molluscide. The incompatibility property of such blend affected copper leaching is the cornerstone of this study.

This work is subdivided into two parts. The present one dealt with the dielectric and thermal studies of the blends. The second part concerning the leaching of Cu ions from such incompatible system will be discussed in another article.

MATERIALS AND EXPERIMENTAL TECHNIQUES

Materials

Binding Matrix: Styrene butadiene rubber (SBR), 1502, Shell Chemicals Co., USA. Acrylonitrile butadiene rubber (NBR) with acrylonitrile content 35%. They were blended in the following (SBR : NBR) ratios: 0 : 100; 20 : 80; 40 : 60; 60 : 40; 80 : 20 and 100 : 0.

Bio-active Material: $CuSO_4 \cdot H_2O$: It was prepared from $CuSO_4 \cdot 5H_2O$ by heating at 110°C in an oven until constant weight. The obtained $CuSO_4 \cdot H_2O$ was ground and sieved to particle size of 125 micron.

High Abrasion Furnace (*HAF*) of particle diameter 290 Å and surface area $8\,m^2/g$ was used.

Multifunctional Monomer (*Crosslinking Agent*), triethylene glycol dimethacrylate (TEGDMA) was kindly supplied by Shin-Nakamure Chemicals Co., Ltd, Japan.

Ammonium Sulphate: Analytical grade reagent from Prolabo. This salt was used for pH control at water–elastomer blends interface. This apparently prevents the buildup of an insoluble copper carbonate film on the disc surface.

Mixing and Blending Process

The formulation contains: 100 phr (parts per hundred parts rubber) mixed elastomer, 100 phr $CuSO_4 \cdot H_2O$, 50 phr HAF, 2 phr ammonium sulphate and 10 phr multifunctional monomer. The compounding and mixing was carried out on a laboratory two-roll mill [diameter 470 mm, width 300 mm, speed of slow roll 24 rev/min and gear ratio 1:1.41]. The compounded rubber blends were made into sheets with constant thickness of 3 mm and left over night. Samples mixed with or without multifunctional monomer were cut into discs of diameter 20 mm.

Vulcanization of the Blends

The vulcanization of the blends was carried out using high energy γ-radiation at a dose rate of 7.51 rad/sec. A cobalt 60 source was used for irradiating samples under investigation. The specimens were subjected to different irradiation doses from 2 to 24 Mrad.

Dielectric Measurements

The dielectric permittivity ε' and dielectric loss ε'' were measured in the frequency range 10^2-10^5 Hz, using LRC meter type AG-4311B, Ando Electric Ltd, Japan. The methods of measurement were described elsewhere [12]. A guard-ring capacitor type N7M 5/T from Wissenschäftlich-Technische-Werkstättten (WTW) was used. The cell temperature can be controlled using an ultra-thermostat. The dielectric measurements were carried out at 30°C. ε' and ε'' were measured to an accuracy of 1% and 3%, respectively. Discs of 20 mm diameter and 3 mm thickness were used for the electrical measurements.

Thermal Analysis

The differential thermal analysis (DTA) was carried out under nitrogen atmosphere at heating rate of 10°C/min using a Shimadzu-DTA50 Thermal Analyzer. Thermograms were recorded at room temperature up to 800°C. Differential scanning calorimetry (DSC) was also carried out under the same conditions of atmosphere and heating rate using a Shimadzu-DSC-50 Thermal Analyzer.

Shore A Hardness

Measurement of Shore A hardness was carried out using Härleprüfer according to the ASTM D-2240, DIN 53505. Testing was performed at ambient conditions (25 ± 3°C). Specimens of diameter 20 mm and thickness 3 mm were used for the measurements. Values reported are averages of at least five readings.

RESULTS AND DISCUSSION

Dielectric Properties of Vulcanized Blends

In this study two synthetic rubbers were chosen, styrene butadiene rubber as non-polar type and acrylonitrile butadiene rubber as a polar one, to be mixed with triethylene glycol dimethacrylate (TEGDMA) monomer. Figure (1) shows the dielectric properties [permittivity ε' and loss ε''] in the frequency range 0.1 – 100 KHz for unvulcanized pure rubber blends with different concentration ratios. This figure indicates that ε' and ε'' increase systematically by increasing the polar partner NBR content. Figure (2) shows the permittivity (ε') in the frequency range 0.1 – 100 kHz for vulcanized rubber blends at different concentration ratios. The decrease in ε' with frequency is due to the dielectric dispersion resulting from the lag of molecular polarization behind the alternations of the applied electric field [12]. The frequency dependence of the dielectric loss ε'' is displayed in Figure (3). The effect of vulcanization by γ-radiation can be significantly noticed by comparing Figures 1 – 3. Figure (4) exhibits the fluctuation in ε' and ε'' values in the absence of TEGDMA at three different frequencies (100 Hz , 1 kHz and 20 kHz) *versus* blend composition. Also, it is evident from these curves (Fig. 4) that the values of ε' and ε'' for various blends deviate appreciably from the straight lines that can be obtained by joining the values for the two individual rubbers (SBR and NBR). In other words, the curves show non linear relation with the blend ratios and the departure from linearity gives an evidence that these blends are still incompatible despite the long term exposure to high energy irradiation. These results are in agreements with previous studies concerning the compatibility of SBR/NBR blend [13].

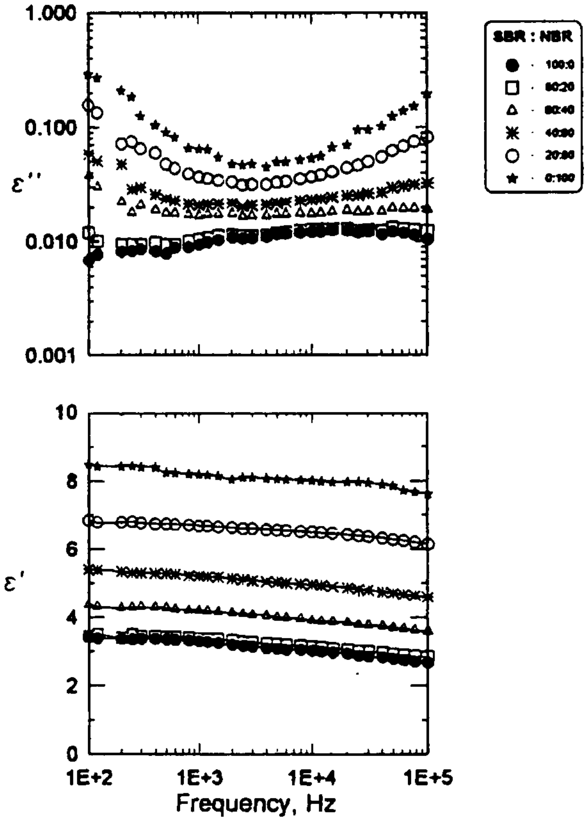

FIGURE 1 The frequency dependence of the dielectric properties (permittivity ε′ and dielectric loss ε″) for un-irradiated pure SBR/NBR blends.

Figure (5) shows the dependence of ε′ and ε″ on the irradiation closes for the different blends at the frequency 20 kHz in the presence and absence of TEGDMA. In general, the blends have higher ε′ and ε″ values than those for SBR and NBR samples. From this figure it can be seen that, with the exception of 100% SBR samples, ε′ and ε″ have their maximum values at 8 Mrad, which are independent either of the blend ratios or the crosslinking agent (TEGDMA). This behavior suggests that such dose is considered to be the optimum dose for such system and the onset of the reaction by ionizing γ-radiation actually starts at 8 Mard. At such dose, there are one or more of the following factors that may play a significant role in increasing the ε′ and ε″ of the

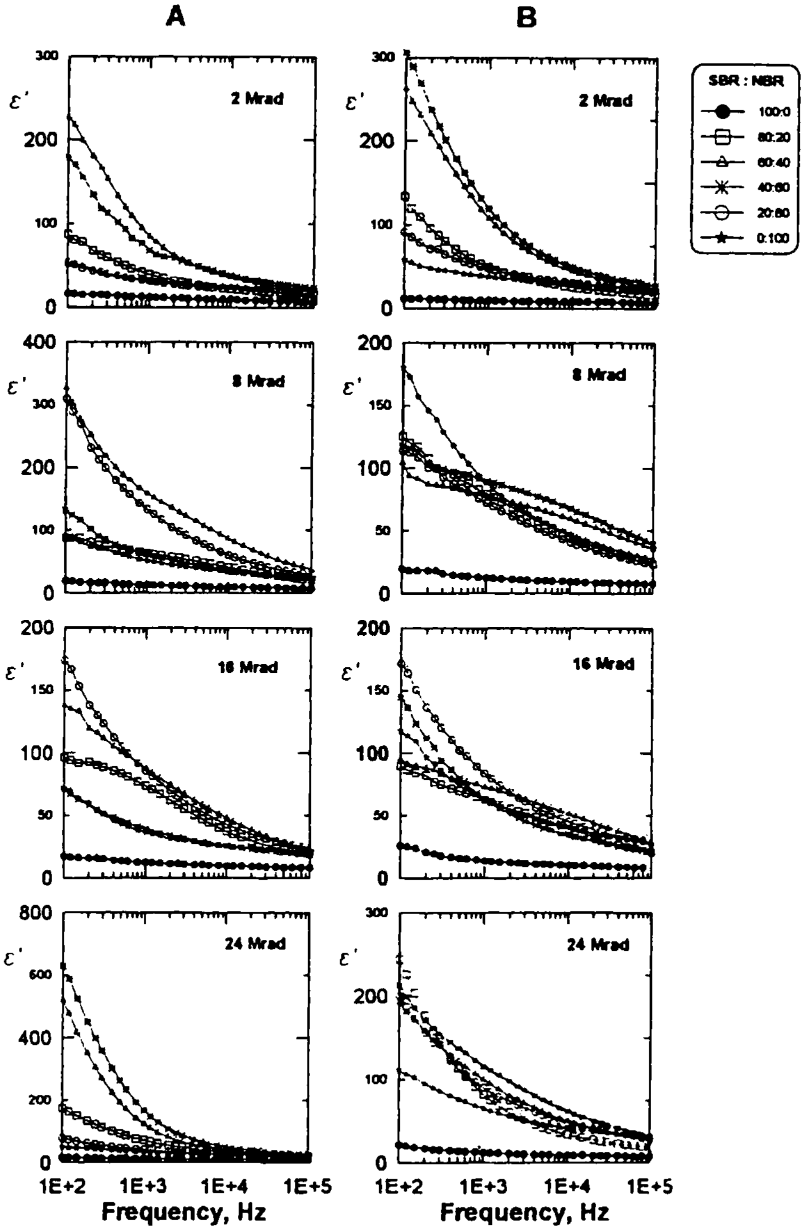

FIGURE 2 The frequency dependence of the permittivity ε' for SBR/NBR blends irradiated at different doses of γ-radiation. A) without TEGDMA; B) with TEGDMA.

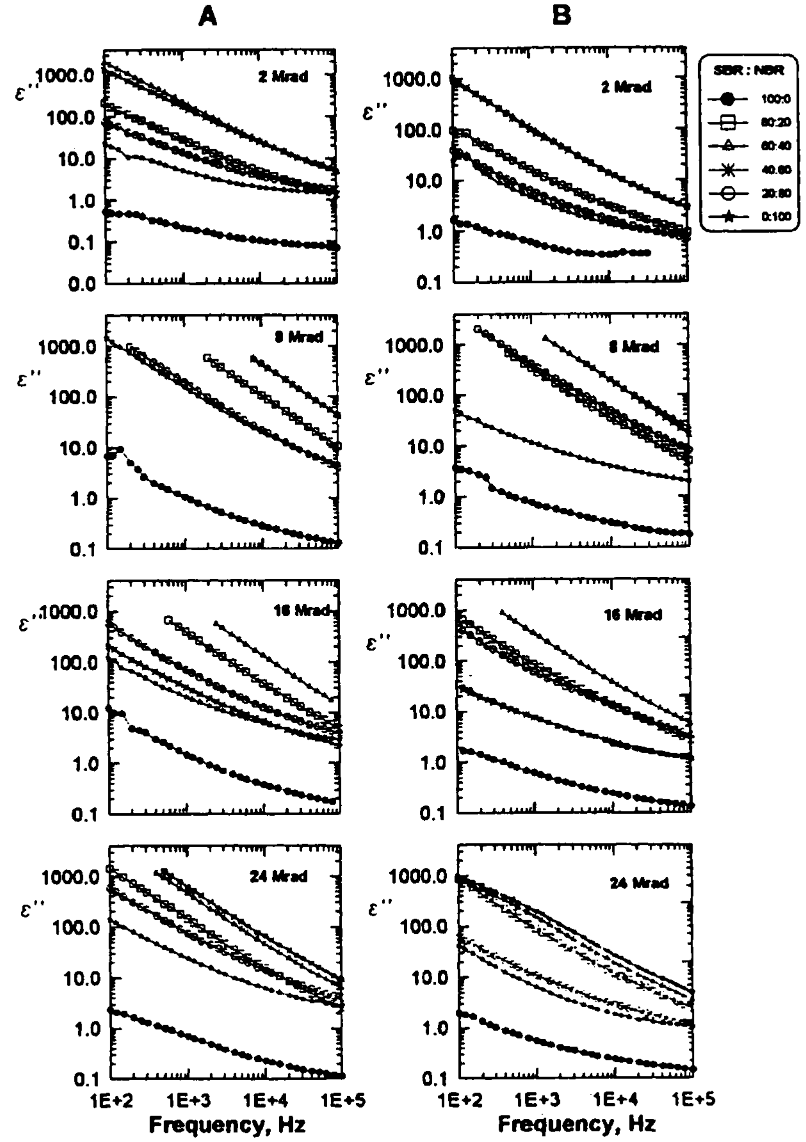

FIGURE 3 The frequency dependence of the dielectric loss ε'' for SBR/NBR blends irradiated at different doses of γ-radiation. A) without TEGDMA; B) with TEGDMA.

blends. First, the fact that the NBR segments contain the strong cyano dipoles (4.18 Debye) compared with the weak dipoles of styrene (0.21 Debye) in the SBR [13]. Second, the rate of radical production

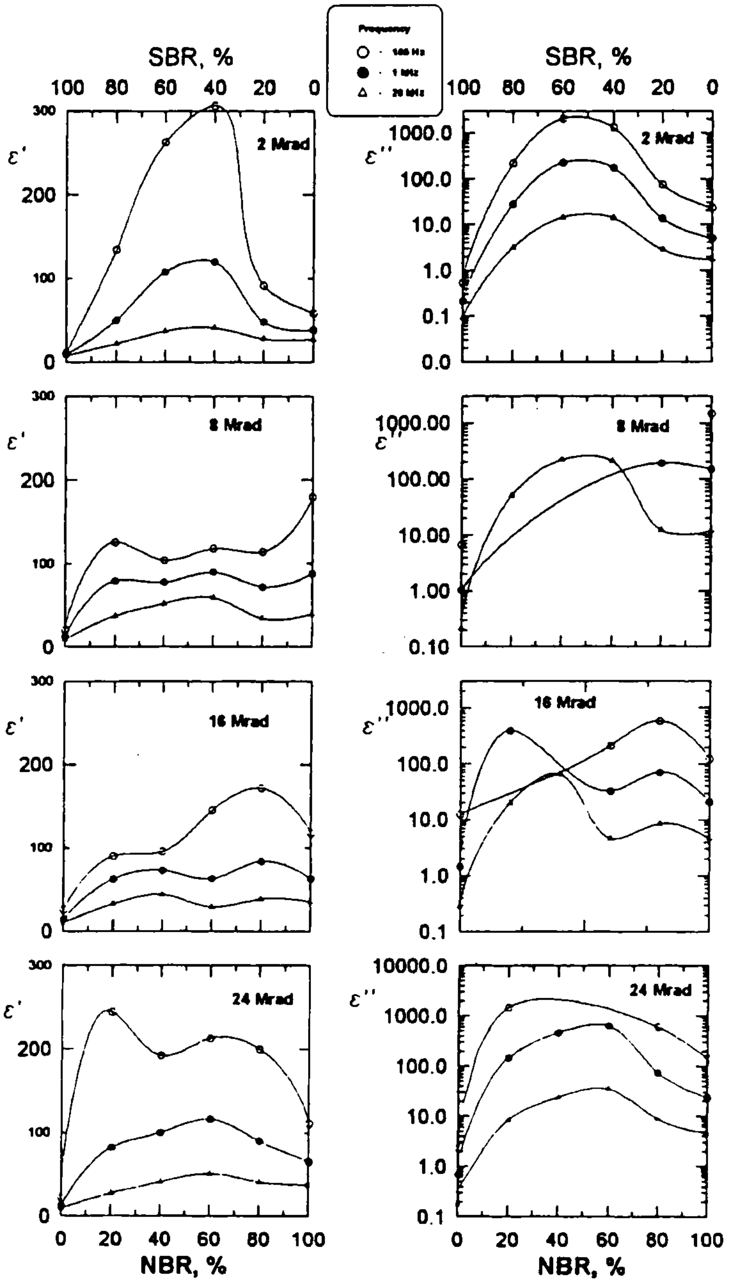

FIGURE 4 Dielectric properties ε′ and ε″ of SBR/NBR blends in the absence of TEGDMA at the frequencies 100 Hz, 1 kHz and 20 kHz.

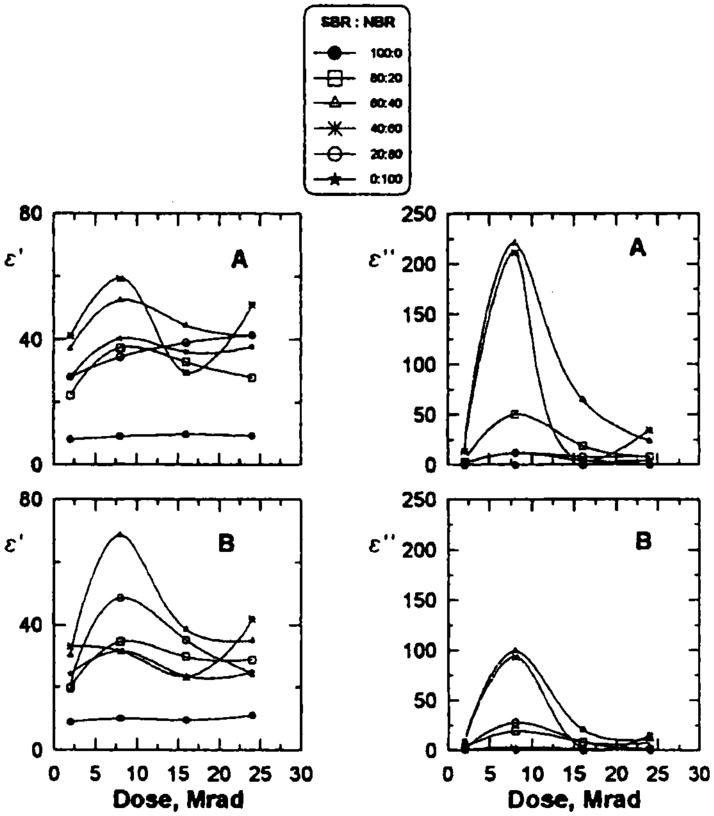

FIGURE 5 Effect of γ-radiation on the dielectric properties ε′ and ε″ for SBR/NBR blends A) without TEGDMA B) with TEGDMA.

can be excessively increased at such dose, thus enhances irradiation ionization reactions. Third, in such heterogeneous system an individual Maxwell–Wagner–Sillars (MWS) polarization [14] should develop not only as a result of the interfacial polarization at the inclusions, but also mainly at the phase separation of the rubber components. However, for irradiation doses lower than 8 Mard (2 Mard), where the dose was insufficient to induce reasonable degree of initiation [15, 16] for rubber blends, the ε′ and ε″ are found to be relatively lower in their levels than that of the specimens at 8 Mrad. While for doses above 8 Mard (16–24 Mrad), the dielectric loss ε′ starts to decrease considerably as the curing process proceeds. This decrease may be attributed to the lack of further reaction due to the exhaustion of the reactive groups and decay of the free radicals. In all cases, the pure SBR mixed with or without TEGDMA shows the lowest ε' and ε'' levels compared with the corresponding levels of pure NBR specimens or their blends. This may be due to the presence of benzene ring on SBR backbone, which acts as a radical trap, the effect which extends to the neighbouring molecules such as TEGDMA, a presumably by some form of energy transfer mechanism [15].

When the rubber blends are irradiated in the presence of TEGDMA, the reaction is believed to proceed faster the way of curing and crosslinking, Figure (6). This figure indicates that all the values of ε' and ε'' are lowered on adding TEGDMA. This behavior may be attributed to the lateral reactions between the different components in the blend as well as the formation of TEGDMA homopolymer. However, when this crosslinking agent (TEGDMA) is added to the blend 80/20 (SBR/NBR), a slight change in ε' and ε'' is recorded. A possible interpretation of the observed behavior is that, this blend can be considered as a dispersion [17] of isolated domains of polar ingredients (NBR & TEGDMA) in a continuous matrix of non-polar SBR rubber and that the dielectric properties [14] are determined predominantly by the matrix behavior against γ-radiation as well as by its protection effect [15] towards the other minor ingredients in the blend. Thus, it is possible at 2 and 8 Mrad that part of the TEGDMA is polymerized separately and NBR is partially vulcanized in the matrix, while at high doses (16–24 Mrad), the complete curing and crosslinking reactions between both components and the matrix may be occurred *via* the unreacted uncrosslinked chains present in the blend. Correspondingly, ε' and ε'' values do not change as a function of curing and crosslink density as well as due to the hindering effect by the non-polar matrix.

When the blends at all concentration ratios are immersed in water for the purposes of sustained release of Cu and then subjected to complete dryness [18], the dielectric parameters in this case show fairly high values especially at irradiation doses 2–8 Mrad, (Fig. 7). Inspection of ε' and ε'' values indicates that the mixed blends with TEGDMA are found to be higher than those of non mixed ones. In comparison to the case observed in Figure (6), this opposite case gives another evidence that the homopolymerization of TEGDMA is

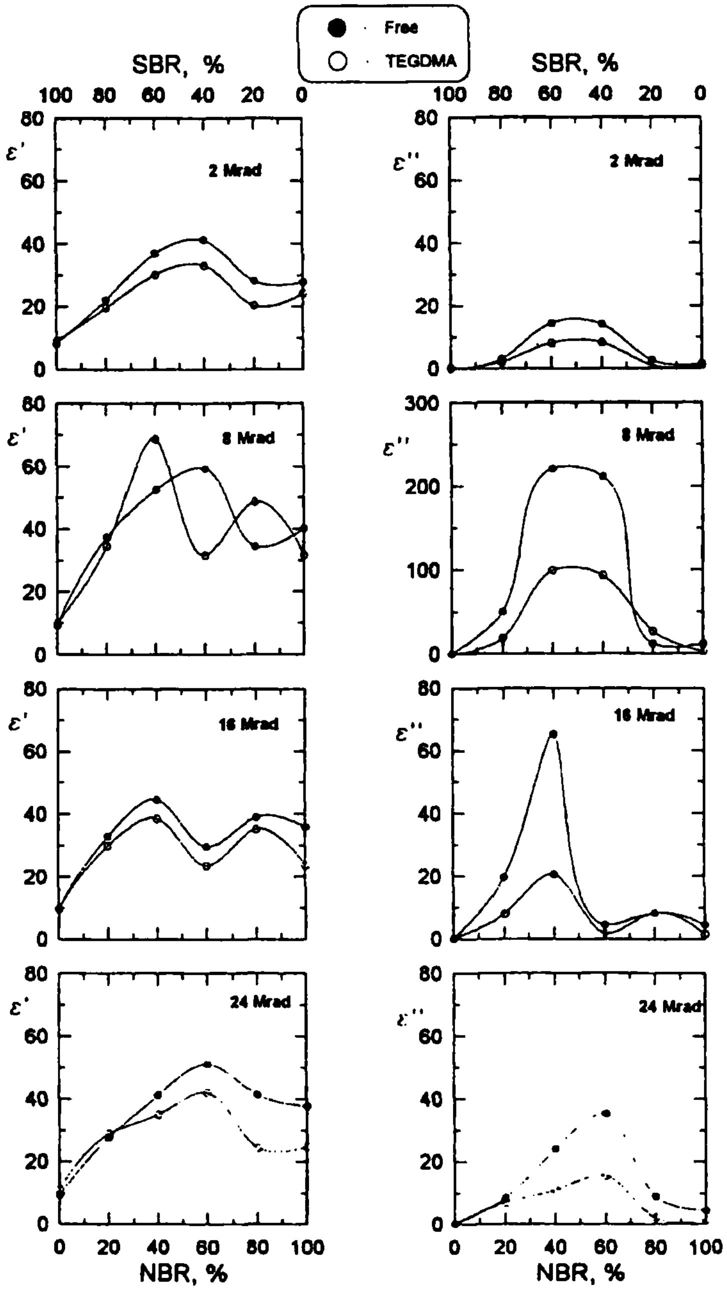

FIGURE 6 Effect of crosslinking agent TEGDMA on the dielectric properties ε' and ε'' at 20 kHz for SBR/NBR blends.

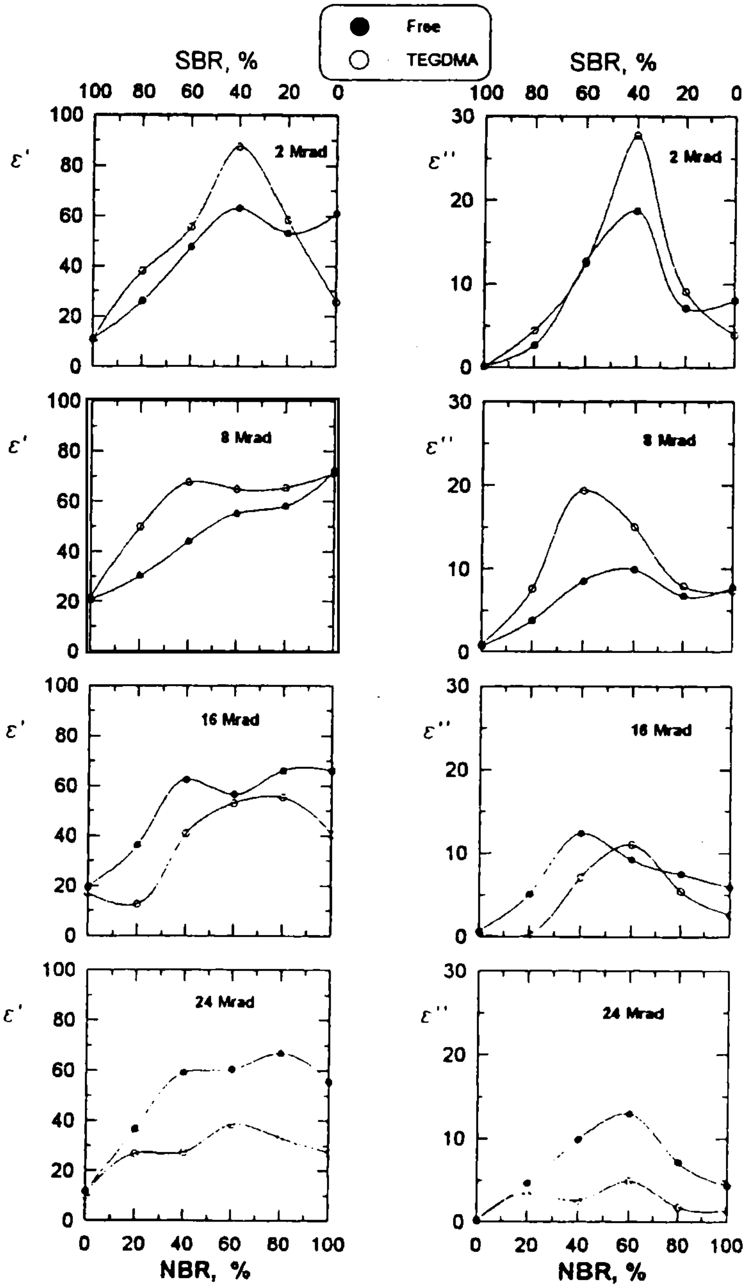

FIGURE 7 Effect of water immersion on the dielectric properties ε' and ε'' for the different SBR/NBR blends.

considered to be the main reaction observed at such doses and the vulcanization process of rubber blends is usually proceeded along crosslinking at higher doses. So, in all cases of reaction the polar groups of OH in TEGDMA and CN in NBR are found to be responsible for the high hydrophilicity [18] of the samples at such doses and in turn the high values of ε' and ε''. These items will be discussed later in connection with thermal analysis of vulcanized blends.

Thermal Analysis of Vulcanized Blends

After extracting the vulcanized rubber specimens with the suitable solvents in a soxhlet extractor for 48 hours [18]; the samples were dried at 100°C to a constant weight, and the DTA of the dried samples was measured.

In this part we shall discuss the radiation-induced changes in NBR, SBR and their blend at concentration ratio of (40/60) by DTA for the samples subjected to 24 Mrad. In the absence of TEGDMA, the thermal behavior of the above rubber samples are represented in curves A, B and C, respectively, Figure 8(A). It is clear from the curves that, the first decomposition stages occur at endothermic reaction peakings at 96°C, 101°C and 118°C, respectively. These peaks are due to the adsorbed moisture or water contaminations in the blend. The second endothermic peaks occur at 241°C, 245°C and 242°C on curves A, B and C, respectively. These peaks are attributed to the dehydration of $CuSO_4 \cdot H_2O$ according to the following equation [19]:

$$CuSO_4 \cdot H_2O \xrightarrow{200-275^{\circ}C} CuSO_4 + H_2O$$

Curve A (NBR) shows the endothermic reaction peakings at about 336°C and 454°C. The first peak is associated with the volatilization of 7–8% of NBR content and this is due to the loss of plasticizers and other ingredients [20], while the second peak is associated with melting point of NBR. Thermogram B, shows the endothermic peak at 461°C for SBR rubber. When SBR and NBR are blended thoroughly, the DTA of the blend (curve C) is found to be characterized by two endothermic peaks occurred separately at 441°C for NBR and 481°C for SBR rubber components. The endothermic peak at 306°C shows

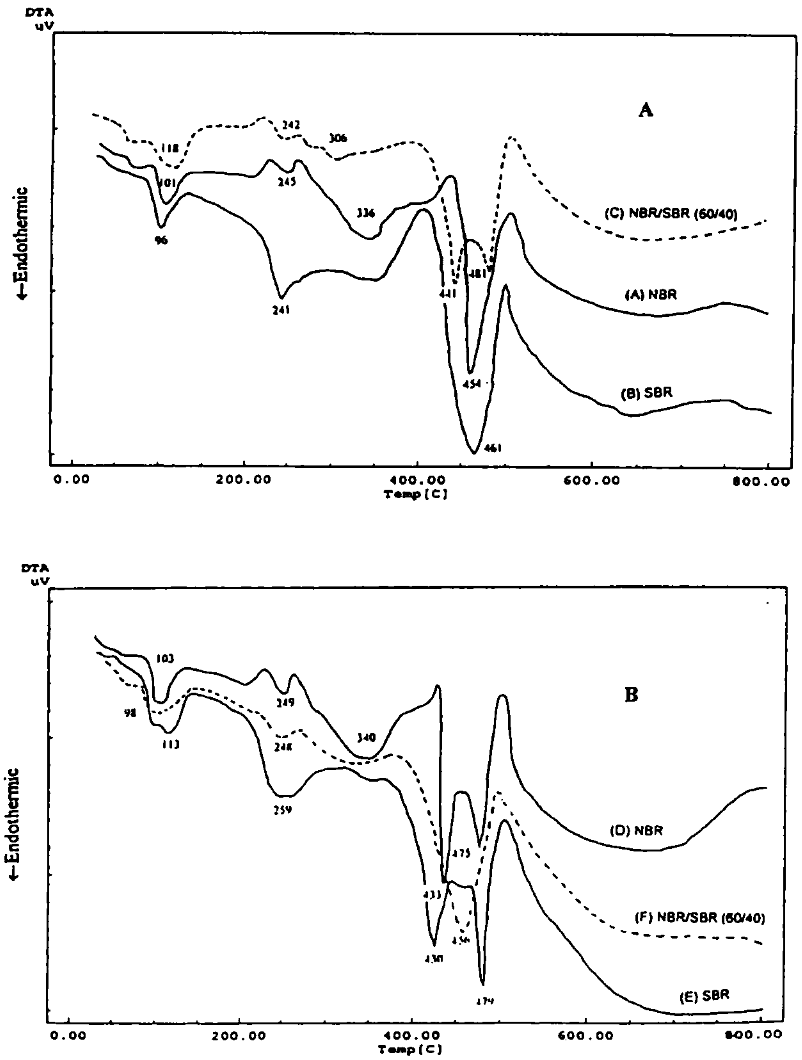

FIGURE 8 Differential thermal analysis (DTA) of SBR/NBR blend (40/60) exposed to 24 Mrad dose of γ-radiation.

the same variation as was observed with thermogram A, but in this case it is characterized with a smaller area and lower temperature. In addition, the blend ignites 20°C higher for SBR and 13°C lower for NBR than that of the corresponding components pre-blending. This behaviour gives an indication that both components are partially reacted with each other but at the expense of the volatile and plasticizer fraction of the NBR. Consequently, this contributes to a remarkable reduction in the endothermic peak area with a decreasing in the associated temperature of about 30°C than the temperature recorded in curve A (336°C). In any case, such separation in the resultant peak gives, in general, an evidence that this blend is still incompatible, despite the high doses used in the vulcanization process. This conclusion is in agreement with that reported by other investigators [21].

The thermal behavior of SBR/NBR and their blend at concentration ratio (40/60) in the presence of TEGDMA monomer are shown in curves D, E and F, respectively (Fig. 8B). It is evident from curves D and E that each mixed component exhibits two endothermic peaks. The first is due to the partial interaction between rubber chain and TEGDMA monomer, while the other peak resulting from homopolymerization of the monomer which is usually formed at lower irradiation doses [22]. Moreover, each product was found to ignites 21°C for NBR and 18°C for SBR higher than the corresponding temperatures 454°C and 461°C of non mixed rubber specimens, respectively. This reaction most probably results in increasing more the polarity of NBR and changing the non polarity of SBR to a partially polar phase. When both rubber components are blended, then mixed with the monomer and subjected to γ-radiation dose of 24 Mrad, the DTA of the mixed blend is found to be characterized by only an endothermic peak occurred at 456°C. This behavior is unexpected because the blends investigated at 2, 8 and 16 Mrad are found to be characterized by two distinct endothermic peaks. Verification of this behavior was further investigated by DSC thermal analysis and the thermograms obtained are represented in Figure 9. It is evident from this figure that the thermogram of the mixed blend with TEGDMA shows the occurrence of two endothermic peaks, one is characterized by a very large peak area at 411°C and the other with a very small area at 439°C. Such behavior gives an evidence that a limited interaction (crosslinking) was taken place between the two rubber components in the presence of the monomer. It is possible at 24 Mrad that the unreacted uncrosslinked chains of the polymer (TEGDMA) would react further with rubber or with its grafted chains

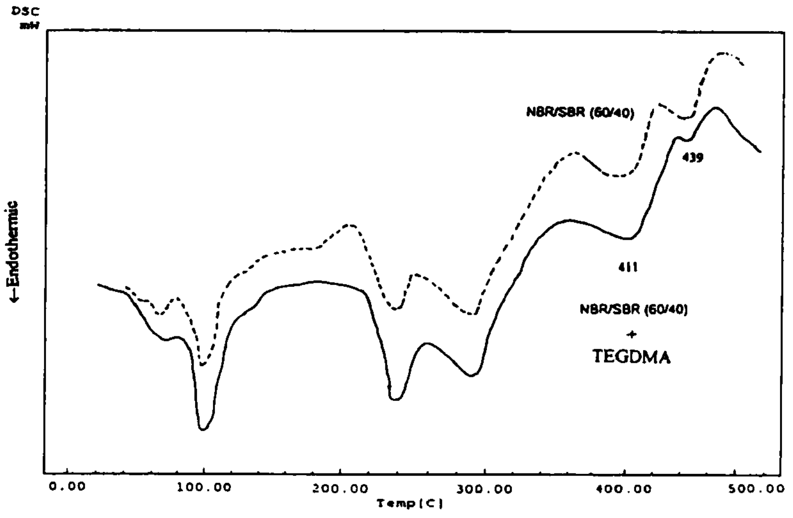

FIGURE 9 Differential scanning calorimetry (DSC) of SBR/NBR blend (40/60) exposed to 24 Mrad dose of γ-radiation.

to form a partial crosslinked net work structure. The same conclusion can be also noticed for the other blend specimens exposed to 24 Mrad.

Shore A Hardness of Vulcanized Rubber Blends

The Shore A hardness of the investigated SBR/NBR rubber blends exposed to 8 and 24 Mrad at different concentration ratios are illustrated in Figure 10. It is clearly seen that, in the absence of TEGDMA, the Shore A hardness of all blends has relatively lower values than those of the parent rubbers. This is due to the poor bond strength which is referred to the high polarity in NBR and the non-polarity of SBR. While in the presence of TEGDMA, the hardness is found to be higher at 24 Mrad and lower at 8 Mrad. In other words, the hardness of the blends at 24 Mrad can be improved by addition of 10 phr TEGDMA, where at 8 Mrad an opposite phenomenon is observed. This behavior is not unexpected since the inclusion of uncrosslinked TEGDMA polymer as a separate polar phase in the blend composite may reduce the interfacial tension and partially enhances the adhesion between the SBR and NBR phases. Thus, the Shore A hardness under these condition is probably dependent on the

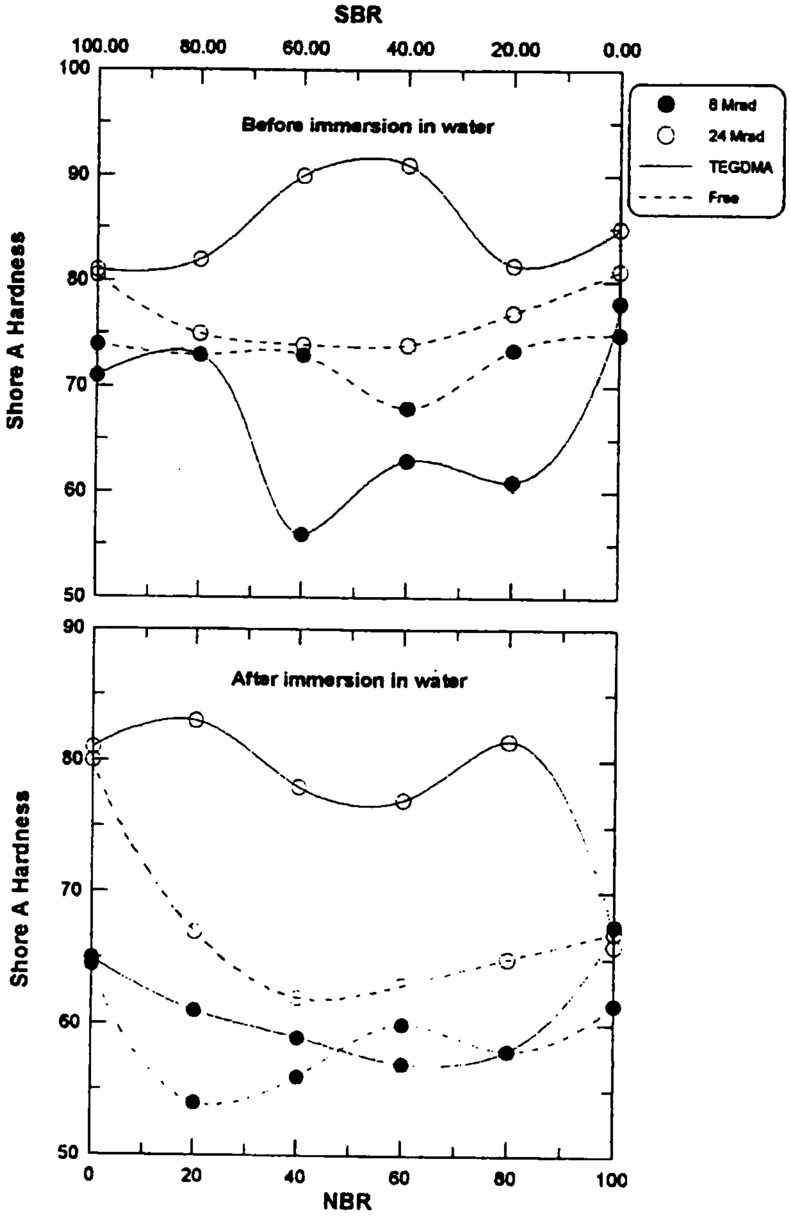

FIGURE 10 Shore A hardness for the different SBR/NBR blends exposed to 8 and 24 Mrad.

hydrogen bonds formed between TEGDMA and the rubber blends. Furthermore, the molecular structure in the blend composite contains a considerable concentrations of polar groups (*e.g.*, OH in TEGDMA and CN in NBR) and this may result in strong intermolecular (Van der Waals) forces [23]. These bonds, as a result of their great sensitivity to water, are seriously affected when they are immersed in water for the purposes of controlled release of copper. In this case, the dried blends exhibit a remarkable decreases in Shore A hardness except for 100% SBR samples. The possible explanation for this behavior was already discussed in the preceding parts of this article.

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