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Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Swelling characteristics and application of gamma-radiation on irradiated SBR-carboxymethylcellulose (CMC) blends

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Received 23 July 2010; accepted 29 August 2010
Available online 7 September 2010

KEYWORDS

Styrene butadiene rubber;
Carboxymethylcellulose;
Mechanical, physical and
thermal properties

Abstract Blends of styrene butadiene rubber (SBR) with varying loading degree from 60 wt% to 100 wt% of carboxymethylcellulose (CMC) have been prepared. Gamma radiation vulcanization of prepared blends was carried out with doses varying between 50 kGy and 250 kGy. Mechanical properties, namely, tensile strength (Ts), elongation at break (Eb) and hardness were followed up as a function of loading degree of CMC and gamma irradiation dose. Moreover, physical properties, specifically swelling number (SN) and gel fraction % (GF%) were undertaken. Results obtained showed an improvement in mechanical as well as in physical properties with increasing either CMC content or dose of irradiation. Thermal properties namely thermo gravimetric analysis (TGA) was carried out.

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1. Introduction

One of the most widely used synthetic rubbers is styrene butadiene rubber (SBR), as it is practically used in all automotive tires due to its good crack resistance, wet grip as well as weather and abrasion resistance (Henderson, 1987). Moreover, it is

used in a wide range of industries (George et al., 1999; Ray and Ray, 2006; Wang and Wen, 2005) such as that of cables and wires, etc. due to its availability in a wide range of grades. As a diene-based synthetic rubber, SBR would be expected to undergo crosslinking by high energetic radiations such as gamma rays. However, the presence of phenyl rings with its protective effect against irradiation, the degree of crosslinking for straight radiation vulcanization of SBR would be expected to be a limited one.

Carboxymethylcellulose is a cellulose derivative with carboxymethyl groups bound to the hydroxyl groups of the glucose unit, and it is an industrially important cellulose derivative, primarily due to its high viscosity, non-toxicity and non-allergic character (Guo et al., 1998). On the other hand, and as a derivative of cellulose, which is known to be the most degraded polymer under irradiation with its G (degradation) of about (7) Ershov et al., 1986 CMC is categorized also as a degraded polymer under gamma irradiation.

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However, under suitable conditions it may undergo partial crosslinking (Fei et al., 2000; Liu et al., 2002; Wach et al., 2001; Wach et al., 2003).

With respect to water, SBR as an elastomer is known to be impermeable to water whereas CMC is known to undergo appreciable swelling (Pukanszky, 1990). SBR-based blend containing CMC as the main component of not less than 50 wt%, would be expected to behave like a rubber which may swell to a noticeable extent. Such blends, whether uncured or cured may be used industrially in several applications such as a binder for negative electrodes in lithium-ion batteries (Buga et al., 2006).

The aim of the present investigation is the application of γ -irradiation for the preparation of SBR/CMC blends and following their different properties such as mechanical, physical, and thermal properties as a function of irradiation dose and content of CMC.

2. Materials and methods

2.1. Materials

Commercial grade styrene-butadiene rubber of grade 1502 with 23.6 wt% of styrene content was used as the matrix polymer. Sodium carboxymethylcellulose with low viscosity was supplied by pure lab. Chemicals City Land. The recipe of this study also contained other additives, namely: ZnO, and stearic acid; these two additives from El-Nasr phosphate comp. (Egypt) act as accelerators as well as activators and their content is 5 wt% and 1 wt%, respectively.

2.2. Sample preparation

SBR, stearic acid, (CMC), ZnO, and HAF carbon black were mixed in a two roll rubber mill (300 × 470 mm) with a gear ratio of 1.14:1. The weighed additives were quantitatively incorporated for mastication in air on the rubber mill. The masticated sheets were prepared to 1 mm thick sheet using a hot press at 150 °C for 10 min and under 16 MPa pressure.

Gamma cell type 4000 A from Bhabha Atomic Center, Bombay, India giving a dose rate of 5.4 kGy/h. was used for gamma irradiation vulcanization under atmospheric pressure and at a temperature of ~40 °C.

3. Measurements

3.1. Mechanical properties

Mechanical properties measurements were carried out on dumbbell-shaped specimens of 4 mm width and 20 mm length. Tensile strength, (TS) elongation at break percentage $E_b\%$ and hardness have been measured using a universal testing machine. The given results are the mean value of three separate specimens. The error in these measurements is $\pm 5\%$.

3.2. Physical properties

The physical properties that have been followed up are the swelling number (SN) and the gel fraction %.

3.3. Swelling number

Degree of equilibrium swelling in distilled water for 24 h at room temperature was calculated using the following equation:

$$\text{Swelling number} = W_2 - W_1/W_1$$

where W_1 is the initial weight of samples; W_2 is final weight of samples (after swelling).

Moreover, SN has been determined for samples which have been subjected to boiling water for 24 h. The above equation was also used whereby W_1 , refers to weight of samples after extraction in distilled boiling water and W_2 is its weight after swelling in distilled water for 24 h at room temperature.

3.4. Gel fraction % (GF%)

Gel fraction expressed as the fraction of insoluble weight, was obtained by extracting the soluble part in boiling distilled water using soxhlet for 24 h, and drying the insoluble part completely in a vacuum oven at 50 °C. It is given by:

$$\text{Gel fraction \% (GF\%)} = W_1/W_0$$

where W_0 is the initial weight (soluble weight + insoluble weight of samples); W_1 is final weight (weight of insoluble part of samples after extraction).

3.5. Thermal analysis

Thermal analysis was carried out using a thermal gravimetric analysis (TGA) apparatus; samples of 0.98–1.5 mg were encapsulated in aluminum pans and heated from 50 up to 500 °C at heating rate 10 °C/min under N_2 atmosphere.

4. Results and discussion

The kind of SBR used in the present investigation, namely SBR-1502 is non-pigmented rubber obtained by cold polymerization process and is characterized by its easy processibility and uniform properties. On the other hand, CMC is used as its sodium salt, i.e. sodium carboxymethyl cellulose. The prepared blends were characterized through measurements of their mechanical, physical or thermal properties.

4.1. Mechanical properties

Tensile strength, elongation at break % and hardness were measured for blends loaded with 60 wt% to 100 wt% CMC and gamma rays irradiated with doses ranging between 50 kGy and 250 kGy.

4.1.1. Tensile strength

Fig. 1 shows the variation of tensile strength of gum SBR as well as its blends with CMC as a function of irradiation dose. Also, data for the same unirradiated samples are given whereby it may be observed that their TS values are always less than those of the vulcanized ones. Moreover, gum SBR has attained TS values less than that of its blends with CMC over the whole range of irradiation. For one and the same irradiation dose, the TS values increase with the content of loading with CMC. It can be seen also that the TS values for all the samples increase with increasing irradiation dose up to 150 kGy and then decrease for doses higher than that.

The relatively limited increase of gum SBR on irradiation may be attributed to the fact that during mastication the high molecular weight SBR rubber breaks down, under atmospheric conditions, to fragments of comparatively lower

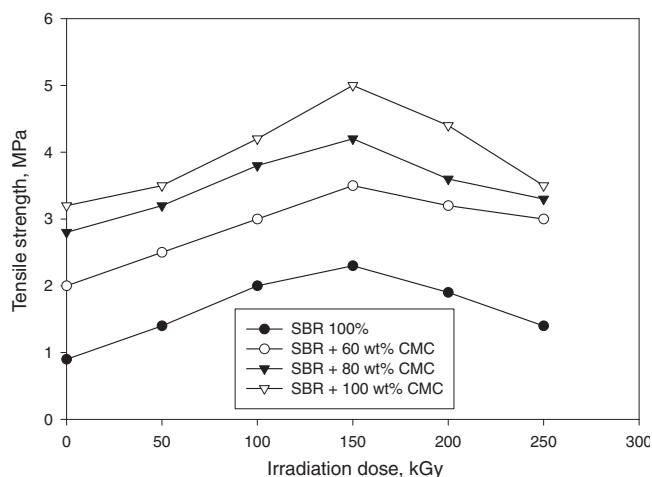


Figure 1 The relation between the tensile strength of gum SBR rubber and loaded with different concentration of (CMC) and irradiation dose.

molecular weight. Moreover, and as mentioned before, the presence of the phenyl ring of the styrene units perform protection against irradiation that contributes to the poor TS attained at its highest value, namely 2 MPa at 150 kGy. The decrease in TS values with the increase of irradiation higher than 150 kGy may be correlated with increased rate of degradation with respect to crosslinking.

The higher TS values attained for the SBR/CMC blends with respect to gum SBR may be attributed to the assumption that CMC has encountered partial intra-crosslinking as well as inter inter-crosslinking with SBR and its magnitude is a function of the degree of loading of CMC as well as the irradiation dose. The CMC-limited reinforcing character obtained, however, may be attributed to its faster rate of radiation degradation with respect to its rate of radiation crosslinking. This behavior is affiliated with the character of CMC itself as it has been reported that its radiation degradation density is always higher than its radiation crosslinking density (Pengfi et al., 2002). Apparently, the H abstraction by the limited OH radicals would lead to crosslinking whereas the occurrence of radicals on the several tetrasubstituted carbon atoms of CMC and its propagation hindrance would be affiliated with the degradation (Woods and Pikaev, 1994).

4.1.2. Elongation at break %

The relation between elongation at break % of gum SBR rubber and loaded with different concentration of CMC and irradiation dose is shown in Fig. 2. Also, the values of E_b of unirradiated samples are given in the same figure whereby it may be observed that the unvulcanized SBR has attained relatively very high E_b values with respect to that of uncured blends. Apparently, CMC still attains a high degree of the crystalline nature of cellulose which restricts the high flexibility of SBR and hence the apparent decrease in E_b values of its uncured blends.

On irradiation, the E_b value of gum rubber encounters a marked decrease which is affiliated with the radiation-induced crosslinking and hence results in a noticeable decrease in the flexibility of its chains. On the other hand, the E_b values of cured blends decrease relatively slowly with the increase of irradiation with respect to the values of uncured blends which accounts for a limited but noticeable extent of crosslinking.

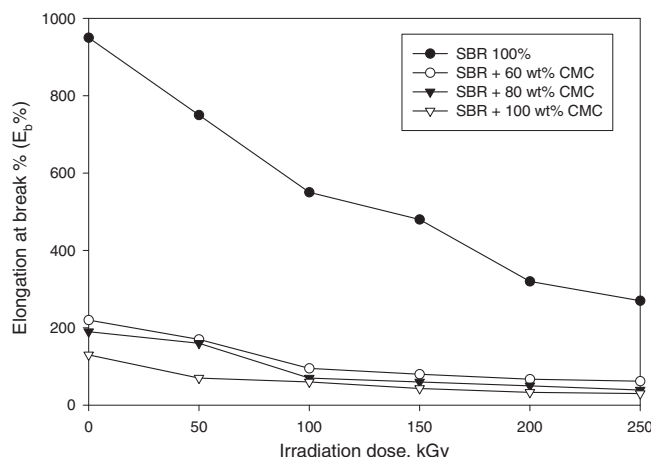


Figure 2 The relation between elongation at break % of gum SBR rubber and loaded with different concentration of (CMC) and irradiation dose.

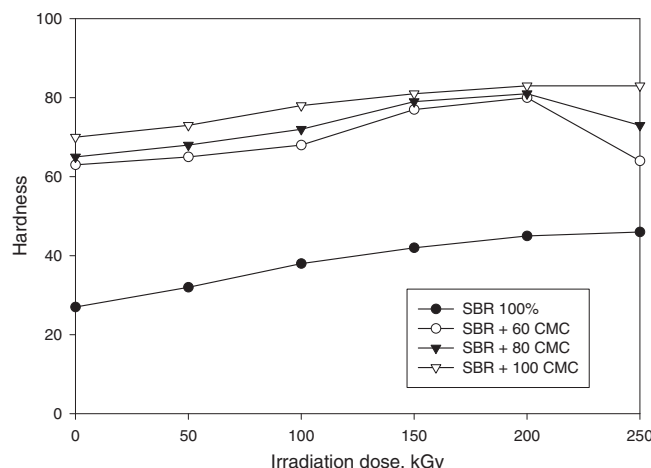


Figure 3 The relation between hardness of gum SBR rubber and loaded with different concentrations of (CMC) and irradiation dose.

4.1.3. Hardness

The results given in Fig. 3 illustrate the relation between the hardness of gum SBR rubber and loaded with different concentration of CMC and irradiation dose. The values of hardness attained by gum SBR as well as its vulcanized samples are relatively small with respect to the corresponding ones of the blends. Moreover, the increase encountered with the irradiation dose for the hardness values of SBR alone or its blends with CMC is a limited one which accounts for a limited contribution of crosslinking to hardness values. The relatively high values of hardness of the blends are mainly due to the hard nature of CMC, as mentioned before, which also accounts for the increase of hardness with the increase of the degree of loading with CMC.

4.2. Physical properties

4.2.1. Swelling number

It has been reported that γ -radiation-crosslinked CMC alone goes into aqueous solution at 70 °C or higher (Pengfi et al., 2005). Therefore, it is interesting to follow the swelling

behavior of γ -radiation-crosslinked SBR/CMC blends, firstly in aqueous solution at room temperature, and secondly after subjecting it to boiling water for 24 h and then following their swelling behavior in water at room temperature.

Fig. 4 illustrates the relation between the swelling number (in distilled water) of SBR rubber loaded with different concentration of CMC and irradiation dose. The swelling is undertaken at room temperature. Also, the values of SN for unirradiated blends under the same conditions are given, whereby they have attained relatively higher values with respect to those of irradiated ones. Moreover, the SN values of the latter samples decrease but slightly with an increasing irradiation dose from 50 kGy to 200 kGy and then increase but slightly at 250 kGy. For one and the same irradiation dose, there is a slight but distinct decrease in SN value with increasing content of CMC in the blend. These data indicate that radiation-induced inter-crosslinking between SBR and CMC has taken place to a noticeable extent on irradiation with the lowest dose of 50 kGy. For doses higher than that and up to 200 kGy, a slight increase in crosslinking has occurred. Apparently, the magnitude of degradation became dominant for the highest dose of 250 kGy as SN values increased slightly. Also, the increase of content of CMC in the blend is accompanied with a slight increase of inter-crosslinking.

The relation between swelling number (in distilled water) of SBR rubber loaded with different concentration of CMC and irradiation dose for blends that have been subjected firstly to boiling water, is given in Fig. 5.

Firstly, it may be observed that SN values of all samples are relatively higher than the corresponding ones shown in Fig. 4, which is an indication that the magnitude of crosslinking is lower for the samples subjected to boiling water. Secondly, the increase in the content of CMC in the blend is accompanied with a decrease in the extent of crosslinking. Apparently, the higher the content of CMC in the blend the higher the magnitude of intra-crosslinking of CMC with respect to the inter-crosslinking of CMC with SBR.

4.2.2. Gel fraction % (GF%)

Fig. 6 illustrates the data obtained for the relation between gel fraction % (in boiling water) of SBR rubber loaded with different concentration of CMC and irradiation dose, whereby the

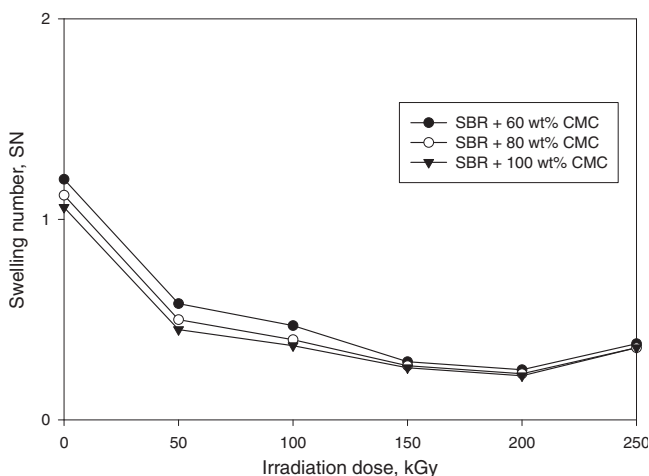


Figure 4 The relation between the swelling number of SBR/CMC blends and irradiation dose.

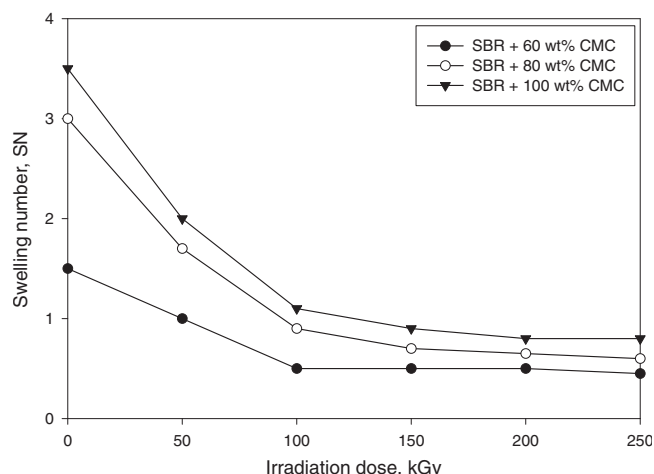


Figure 5 The relation between swelling number of SBR rubber loaded with different concentration of CMC and irradiation dose (the samples subjected to boiling water for 24 h before swelling).

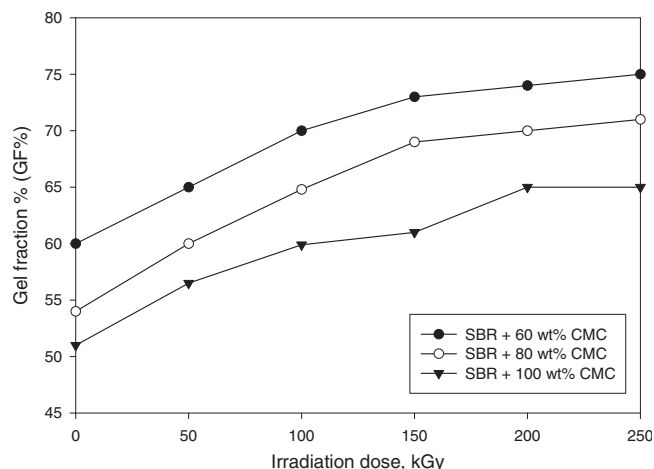


Figure 6 The relation between gel fraction % (in boiling water) of SBR rubber loaded with different concentration of CMC and irradiation dose.

GF% presented is obtained after subjecting the samples to boiling water for 24 h as mentioned before. Also, data for unirradiated samples are given which indicate clearly that almost the total content of CMC in blends has dissolved into boiling water.

On the other hand, the results obtained for gamma-irradiated blends show that radiation-induced crosslinking between blend components has taken place as the value of GF% for the same blend increases with the irradiation dose up to about a dose of 150 kGy and then remains constant for higher doses. Apparently, the obtained increase in GF% may be attributed mainly to crosslinking between CMC and substrate SBR rubber as crosslinked CMC has supposedly dissolved in aqueous boiling water. Accordingly, the higher the amount of SBR with respect to CMC, the higher the extent of radiation-induced crosslinking between blend components. This behavior ac-

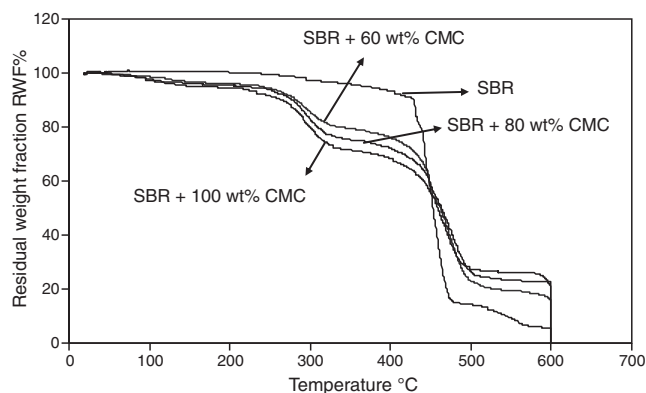


Figure 7 Variation of residual weight fraction (RWF%) with the heating temperature for the SBR rubber and its blends with CMC at 150 kGy.

counts for the obtained results as the GF% increases with decreasing CMC content when comparing its value for different blends at the same irradiation dose.

4.3. Thermal properties

The thermal stability of prepared SBR/CMC blends was followed up by applying the thermal gravimetric analysis (TGA) technique. Fig. 7 shows the data obtained for the variation of residual weight fraction (RWF%) with the heating temperature for the SBR/CC blends whereby all the samples were irradiated with a dose of 150 kGy. Also, included is the thermogram for raw SBR under the same irradiation condition, whereby one thermal decomposition temperature (t_i) is observed that starts at ~ 420 °C indicating the temperature at which SBR starts decomposing and hence losing weight under atmospheric conditions. On the other hand, the thermograms of SBR/CMC blends show two (t_i), the first t_i starts at ~ 260 °C and the second t_i at ~ 420 . This last t_i corresponds, of course, to the component SBR of the blend, whereas the first t_i is affiliated with the CMC component of the blend. As expected, the blend containing the highest content of CMC, i.e. 100% has attained the lowest RWF% values and vice versa, over the temperature range between the two decomposition temperatures.

5. Conclusion

The following conclusions may be derived from the data obtained:

- Gamma rays as ionizing radiations are suitable means for vulcanization of SBR-based blends with CMC as a cellulose derivative. An improvement in mechanical as well as physical properties of blends have been attained with respect to the properties of straight radiation vulcanization of SBR alone.
- The improvement attained is a function of the irradiation dose as well as the content of CMC in the blends.

- The prepared blends, whether unirradiated or irradiated, undergo swelling in water and its magnitude is also a function of irradiation dose and the content of CMC in the blend.
- The swelling behavior of samples in water under atmospheric conditions is different from that of the samples subjected at first to boiling water before undergoing swelling under atmospheric conditions.
- Blends prepared are preferably used under atmospheric conditions without being subjected to boiling water or higher temperature.

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