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ORIGINAL ARTICLE

The effect of gamma irradiation and particle size of $CaCO_3$ on the properties of HDPE/EPDM blends

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Abstract Mechanical blends formed of 50 wt% of high-density polyethylene (HDPE) and 50 wt% of ethylene–propylene–diene-monomer (EPDM) elastomer have been loaded with 50 wt% of three different particle size of $CaCO_3$, namely $CaCO_3$ 300, $CaCO_3$ 700, and $CaCO_3$ 2000 whereby the latter has the smallest particle size of ~311, 82 μm. Mechanical, physico-chemical and thermal properties were followed up as a function of irradiation dose for loaded and unloaded blends. The results obtained indicated that the values of tensile strength, tensile modulus at 50% elongation, gel fraction and decomposition temperature increase with increasing irradiation dose. On the other hand elongation at break, permanent set and swelling number were found to decrease with increasing irradiation dose. Moreover, the effect of particle size of $CaCO_3$ was observed in a limited but apparent upgrading of mechanical, physico-chemical, and thermal properties. The order of semi-reinforcing capacity of three different types of $CaCO_3$ is as follow: $CaCO_3$ 2000 > $CaCO_3$ 700 > $CaCO_3$ 300 > unloaded blend. Whereby $CaCO_3$ 2000 has the smallest particle size.

1. Introduction

Blends of hard thermoplastic such as semicrystalline HDPE with synthetic and totally amorphous soft rubber such as EPDM are widely produced with diverse properties that may found applications mainly in non-tire products as in packing, kitchen wears, toys, furniture, roofing, electric and electronic goods, etc. Such scope of utilization, may be extended by loading such blend of HDPE and EPDM with different types of fillers. Curing of such blends via chemical or radiation techniques may be applied. In this respect, it is known that radiation crosslinking of polymer blends can produce materials with better properties and high stability when subjected to aging, weathering and aggressive media (Shaltout et al., 2003). It is known that both HDPE as well as EPDM are categorized as radiation crosslinking types of polymers due to their chemical structure (Hil et al., 1989). This is due to the occurrence of only ~17% amorphous part in HDPE and the limited amount of diene, offering some unsaturation in EPDM (Abou Zeid, 2007, 2008; Abou Zeid et al., 2008; Machado and van Duin, 2005; Shaltout et al., 2008). It would be expected, therefore, that a limited extent

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of crosslinking would take place on exposing HDPE/EPDM blend to ionizing radiations.

Ground calcium carbonates when used as fillers in elastomeric based composites are economical and higher loadings of 50–150 phr (part per hundred parts of rubber) are common (Shaltout et al., 2003). Such composites process well and still conserve their rubbery behavior. Calcium carbonates, on the other hand, are of limited reinforcing capacity when compared to that of particulate carbon blacks or silica (Abou Zeid et al., 2008; Shaltout et al., 2007). This behavior is attributed mainly to the limited physico-chemical interactions between $CaCO_3$ particles and the polymeric matrix composed of elastomer and thermoplastic (Bandyopadhyay et al., 1995).

Special calcium carbonates with respect to their mean particle diameter may be obtained. In this respect, three types denoted as $CaCO_3$ 300, $CaCO_3$ 700 and $CaCO_3$ 2000 are available having mean particle diameter of 520, 32 μm, 415, 33 μm and 311, 82 μm, respectively.

The aim of the present work is to follow the effect of irradiation dose as well as the particle size of $CaCO_3$ filler on the mechanical, physico-chemical and thermal properties of 50/50 HDPE/EPDM blend.

2. Experimental

2.1. Materials

The polymers used in the blend were: EPDM and HDPE. EPDM rubber was of Vistalone 5600 type from Exxon Chemical, Belgium; and its content in the blend was kept constant at 50 wt%. HDPE was supplied by Dow Chemical Company, Spain. Its specific gravity, melt temperature and crystallinity are 0.96, ~150 °C and ~94%, respectively. Its content was kept constant in the blend at 50 wt%. Three different types of calcium carbonate $CaCO_3$; $CaCO_3$ 300, $CaCO_3$ 700 and $CaCO_3$ 2000 having particle diameter 520, 32 μm, 415, 33 μm and 311, 82 μm, respectively, were all used as fillers. They are purchased from Takehara Chemical Industrial Co., Ltd., Japan. The filler was kept constant at 50 phr. The recipe of this study contained other additives: ZnO, stearic acid and tetrene. The first two additives act as accelerators as well as activators (Babbit Ro, 1978) and their content was 5 wt% and 1 wt%, respectively. Tetrene was kept constant at 1 wt%, it acts as antioxidant. Solvent (benzene) and other chemicals used were of commercial grade and were used as received.

2.2. Preparation of samples and irradiation

The HDPE was mixed first with the raw EPDM and then with the proper additives using plasti-corder PL 2100 from Barabender, Germany; then fitted with mixer of type 350 S. The mixing time was 15 min at 140 °C and 64 rpm speed, followed by rubber milling at 100 °C and gear ratio of 1:1.14 for 5 min. A Carver hot press was applied to make sheets of about 2 mm. thickness at 150 °C for 5 min under 60 kg/cm^2 pressure. Irradiation by gamma ray of ^{60}Co was carried out in atmosphere using a gamma cell type 4000 from Bhabha Atomic Energy Center, Bombay, India, at dose rate of 5.4 kGy/h.

2.3. Measurements

2.3.1. Mechanical properties

Mechanical tests including tensile strength (TS), tensile modulus at 50% elongation (M_{50}), elongation at break (E_b) and permanent set were preformed at room temperature using an Instron Machine (model 1195) employing a crosshead speed of 50 mm/min. The recorded values for each mechanical parameter were the average of five measurements according to ASTM D-638 (ASTM, 2000) standards, in which the standard deviation was ±5%. The samples for tensile measurements were dumbbell shaped having width of 4 mm and length of 50 mm.

2.3.2. Hardness

Samples of at least 1 mm in thickness with flat surface were cut for hardness test. The measurement was carried out according to ASTM D 2240 (ASTM, 2000) using a durometer of model 306L type A Durometer. The unit of hardness is expressed in (A Shore).

2.3.3. Physico-chemical properties

Gel fraction GF, expressed as fraction of insoluble weight was obtained by extracting soluble part in benzene. The extraction was carried out using Soxhlet for 24 h. followed by drying the insoluble part completely in vacuum oven at 50 °C. The GF is given by: Gel fraction (GF) = (W_1/W_0). where,

W_0 = initial weight of samples before extraction,

W_1 = final weight of samples after extraction.

Swelling measurements were performed in benzene on the gel part and is expressed in terms of the swelling number SN that is given by:

Swelling number = $(W_2 - W_1/W_1)$.

where, W_1 = gel weight, W_{2l} = swollen weight.

2.3.4. Thermal analysis

Thermal analysis was carried out using thermal gravimetric analysis (TGA) apparatus, where samples of (0.98–1.5 mg) were encapsulated in aluminum pans and heated from 50 °C up to 455 °C at a heating rate of 10 °C/min under N_2 atmosphere.

3. Results and discussion

Both EPDM and HDPE are considered as a limited crosslinking type of polymers when subjected to ionizing radiation under atmospheric condition (Shaltout et al., 2003; Xu et al., 2009; Markovic et al., 2008). Gamma rays were used in inducing crosslinking of prepared composites.

3.1. Mechanical properties

The change in the TS values as a function of irradiation dose for unloaded as well as loaded blends is shown in Fig. 1.

The value of TS has increased for all composites with irradiation dose up to150 kGy and then decreased. The TS values for the blend loaded with three different types of $CaCO_3$ as natural filler, are higher than the unloaded one over the whole irradiation range. The order for the attained increase in TS for

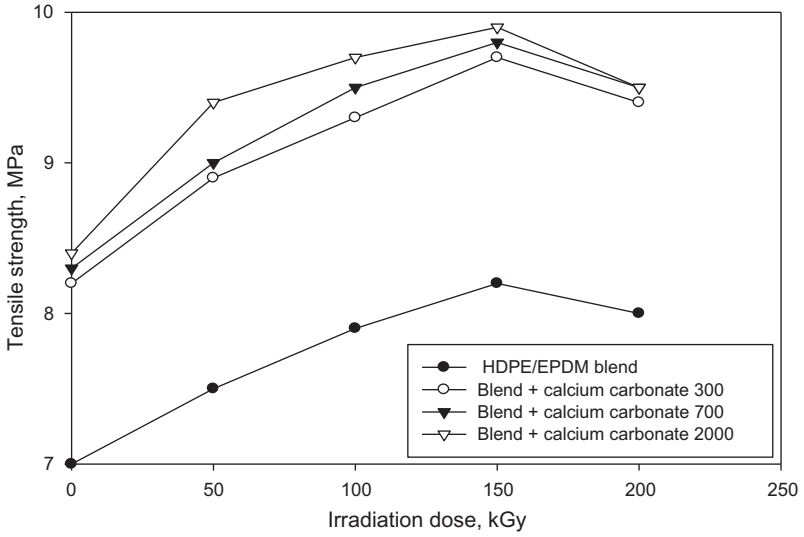

Figure 1 Variation of tensile strength of the 50/50 HDPE/EPDM Blend unloaded and loaded with three different types of $CaCO_3$, with irradiation dose.

the unloaded and loaded samples over the whole irradiation range with respect to type of loading was as follow:

$CaCO_3$ 2000 > $CaCO_3$ 700 > $CaCO_3$ 300 > unloaded blend. This order is apparently correlated with the size of particles of $CaCO_3$ and the smaller the size the larger its reinforcing character (Shaltout et al., 2003).

The increase in TS values with irradiation dose in case of unloaded blend is ascribed to increased magnitude of crosslinking (Corn et al., 1994). For all loaded samples it is essential to assume that the relative improvement in the TS may be due to the semi-reinforcing effect of the $CaCO_3$ besides the increased induced crosslinking by irradiation. The reinforcing effect of the filler mainly depends on its type, composition and surface area (Shaltout et al., 2003). Also, $CaCO_3$ exhibits value of three on Mohs hardness scale (Hancock and Rothon, 1995; Rothon and Hancock, 1995) and its primary particles are spherical which accounts for good dispersion in the polymer matrix. Moreover, the decrease in TS values may be due to degradation as well as disorientation.

Fig. 2 illustrates the variation of M_{50} values for unloaded and loaded blends, with the irradiation dose. Moreover, the values of M_{50} for unirradiated blends are given.

The values of M_{50} for all samples have slightly increased over the whole irradiation dose range as well as with respect to unirradiated ones. Apparently, radiation induced crosslinking has contributed but to limited extent to the values of M_{50}. On the other hand, and for the same irradiation dose, the loaded compositions have attained relatively higher values of M_{50} with respect to unloaded ones, following the same order given above in case of TS. This behavior is affiliated with the

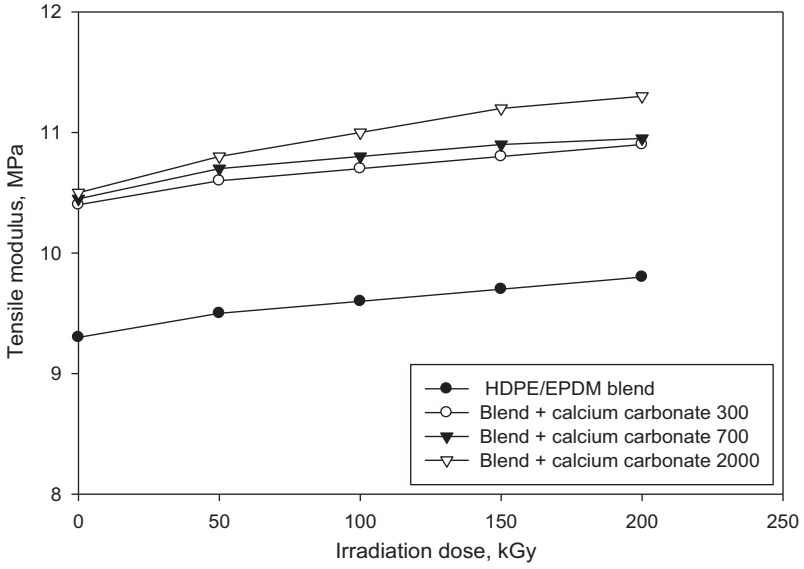

Figure 2 Variation of the modulus stress of the HDPE/EPDM blend unloaded and loaded with three different types of $CaCO_3$, with irradiation dose.

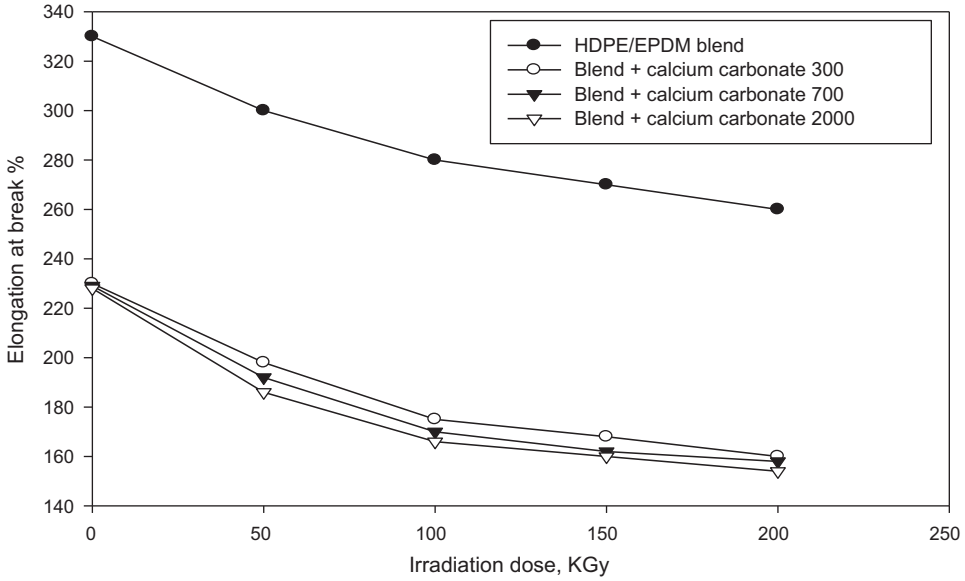

Figure 3 Variation of the elongation at break percentage of the HDPE/EPDM blend unloaded and loaded with three different types of $CaCO_3$, with irradiation dose.

additive nature of M_{50} and hence the contribution from each component and its content (Rothon and Hancock, 1995). Hence, it may be assumed that the filler $CaCO_3$ solid particles has contributed effectively to the value of M_{50} of composites and the magnitude of this contribution is a function of its particle size.

The variation of E_b as a function of irradiation dose for different compositions is illustrated in Fig. 3.

The data for unirradiated samples are also given whereby a considerable decrease in the value of E_b for loaded composites has been attained with respect to that of raw blend, which may be attributed to physical bonding between filler particles and blend components. On the other hand and as expected, the value of E_b for irradiated compositions decreases with relatively moderate rate for doses up to 100 kGy, whereas for higher doses, the value of E_b decreases relatively slowly. The decrease attained in E_b value of irradiated samples may be ascribed to induced crosslinking which increased in magnitude with the irradiation dose in case of loaded composites to an extent effective enough to retard reorientation process as needed for elongation.

Fig. 4 shows the effect of $CaCO_3$ as well as the irradiation dose on the values of the hardness. All composites whether irradiated or unirradiated have attained relatively higher hardness values with respect to those attained by unloaded blend.

Moreover, the hardness values of unirradiated composites are almost the same as those of irradiated ones, where they did not practically change over the whole range of irradiation. Apparently, the hardness of composites is affiliated mainly

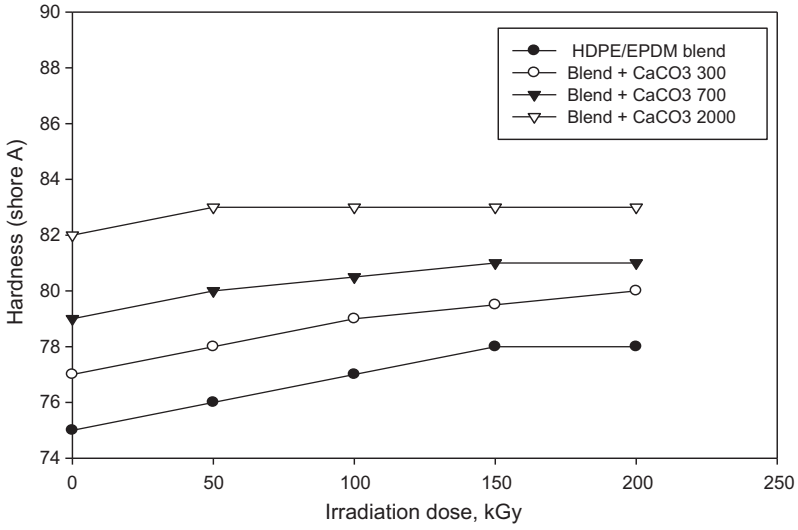

Figure 4 Variation of hardness of the HDPE/EPDM blend unloaded and loaded with three different types of $CaCO_3$, with irradiation dose.

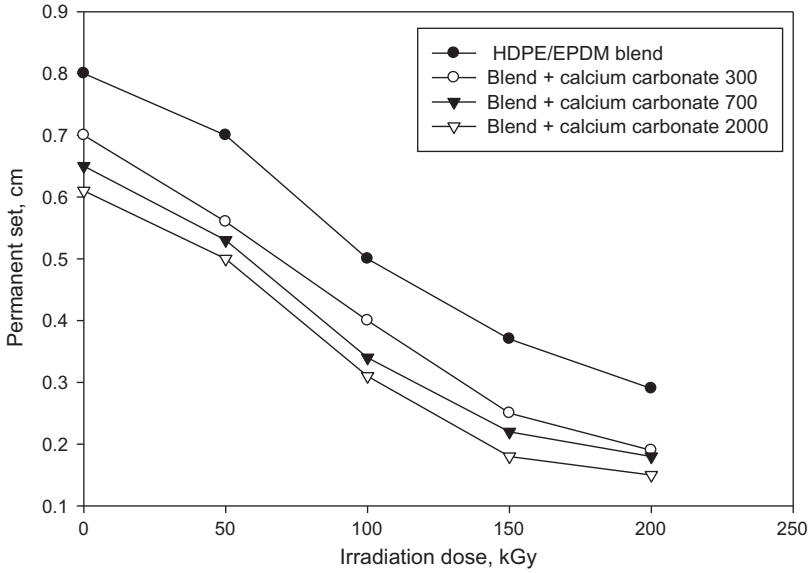

Figure 5 Variation of the permanent set of the HDPE/EPDM blend unloaded and loaded with three different types of $CaCO_3$, with irradiation dose.

with the hardness of $CaCO_3$ as solid filler. In this respect, apparent increase in hardness values of composites has been attained with decreasing the size of $CaCO_3$ particles which accounts for an increased area of contact between them and matrix components.

Fig. 5 shows the variation of the PS as a function of irradiation dose. PS values generally decrease with increasing the irradiation dose up to 200 kGy. Also, the order for the attained decrease of the PS values for unloaded and loaded samples over the whole range of irradiation dose was as follows according to the type of filler:

$CaCO_3$ 2000 < $CaCO_3$ 700 < $CaCO_3$ 300 < unloaded blend.

3.2. Physico-chemical properties

Physical properties; gel fraction GF and swelling number SN are affiliated mainly with induced crosslinking as well as with the different types of linking that may take place at the interface between particulate fillers and polymeric matrix phase. Whereas mechanical properties are indication for the extent of crosslinking and degradation processes that take place simultaneously on irradiation of polymeric materials. Hence, it is always appropriate to follow physical properties.

Variation of GF values as a function of irradiation dose for unloaded as well as loaded blends is shown in Fig. 6. The values of gel fraction increase with increasing irradiation.

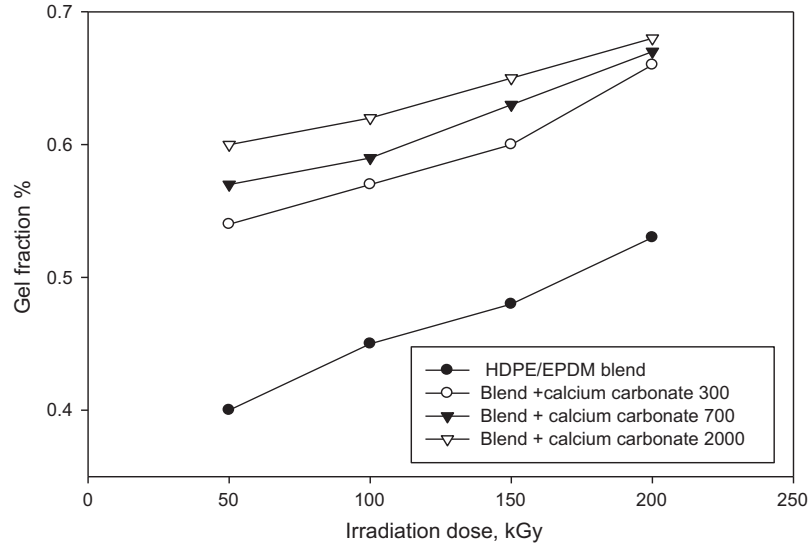

Figure 6 Variation of the gel fraction of the HDPE/EPDM blend unloaded and loaded with three different types of $CaCO_3$, with irradiation dose.

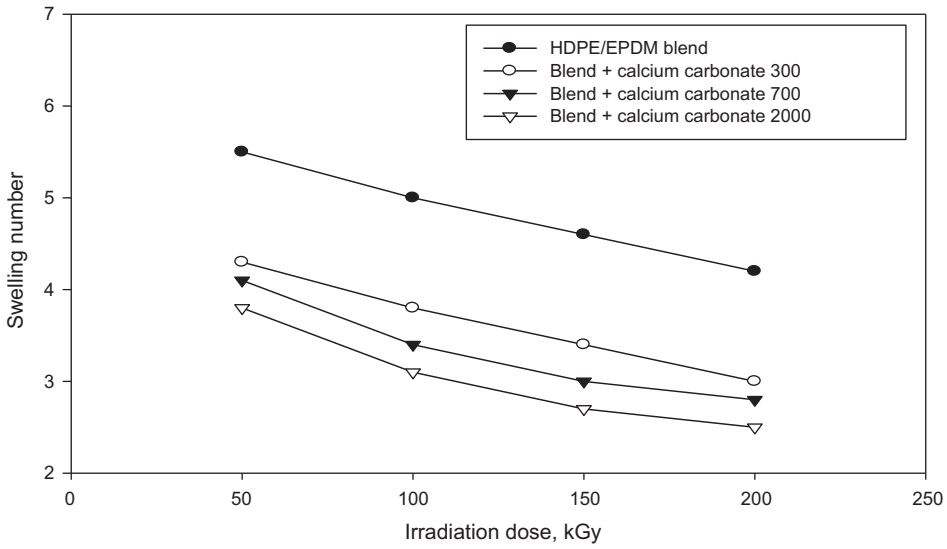

Figure 7 Variation of SN as a function of irradiation dose for unloaded blend as well as loaded ones with three different types of $CaCO_3$, with irradiation dose.

Dose up to 200 kGy for all composites. Moreover, a considerable increase in the value of GF of loaded composites has been attained with respect to that of unloaded blend, where the magnitude of this increase is a function of the type of filler. This increase in GF values may be due to the induced crosslinking by irradiation as well as the reinforcing effect of the $CaCO_3$ fillers. Also, the increase in GF values follow the following order with respect to the type of the filler: $CaCO_3$ 2000 > $CaCO_3$ 700 > $CaCO_3$ 300 > unloaded blend.

Swelling number value decreases as the irradiation dose increases up to 200 kGy for all compositions, as shown in Fig. 7. This result was expected as the relation between the SN values and induced crosslinking is reversible. The order of the attained decrease in SN values follows the following order with respect to the different particle size of $CaCO_3$: $CaCO_3$ 2000 < $CaCO_3$ 700 < $CaCO_3$ 300 < unloaded blend.

Also, the decrease in SN values may be attributed to the semi-reinforcing effect of fillers as well as the induced crosslinking by irradiation. From the above results it is clear that presence of fillers as well as the induced crosslinking by irradiation result in increasing the values of tensile strength, modulus stress, and GF. On the other hand, their presence results in decreasing the values of PS, E_b, and SN. Moreover, physical measurements have given confirmation to mechanical ones.

3.3. Thermal properties

Thermal analysis has been applied for measuring the thermal resistance of polymers (Rothon and Hancock, 1995; Mark

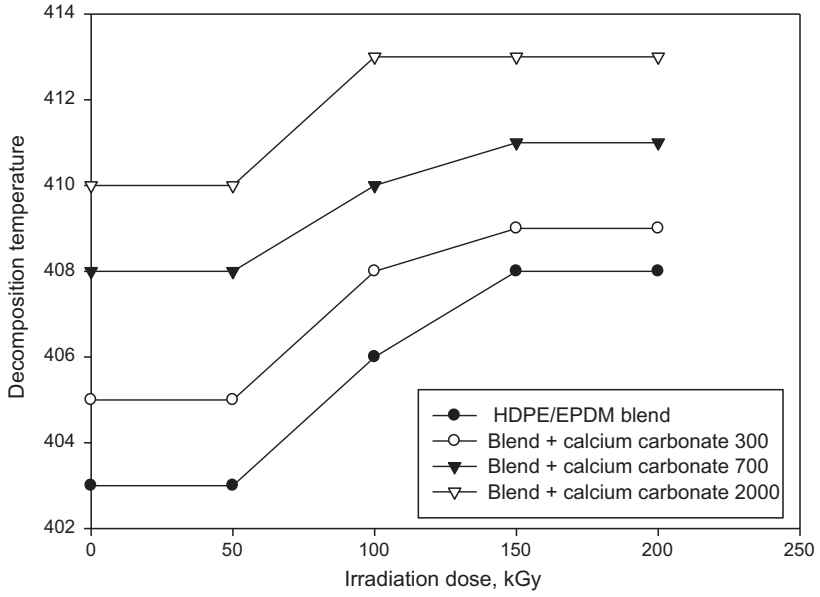

Figure 8 Variation of the decomposition temperature of the HDPE/EPDM blend unloaded and loaded with three different types of $CaCO_3$ with irradiation dose.

et al., 1994; Mucha, 1976). The purpose of the present investigation is to estimate the thermal stability effectiveness of unloaded blend and reinforced blends with different types of $CaCO_3$ and irradiated to a dose up to 200 kGy. The thermo-gravimetric curves were recorded in air. The decomposition temperature, t_i is the initial temperature at the beginning of weight loss. It has been determined for unloaded samples and those loaded with different types of $CaCO_3$ as a function of irradiation dose up to 200 kGy as shown in Fig. 8.

Decomposition temperature increases with increasing the irradiation dose up to 150 kGy, for all samples except for $CaCO_3$ 2000 up to 100 kGy, and the unloaded blends have attained the lowest t_i values over the whole irradiation range. On the other hand, the value of t_i attained by the composites increases with decreasing the particle size of the filler $CaCO_3$; i.e., it follows the same order as mentioned before in case of mechanical and physical properties.

4. Conclusions

Blends of 50/50 HDPE/EPDM and loaded with 50 phr of $CaCO_3$ filler and irradiated by gamma irradiation have attained an improvement in its mechanical, physical and thermal properties with respect to properties of unloaded blends.

The improvement attained increases with increasing the irradiation dose and decreasing the size of the particles of the filler $CaCO_3$.

An irradiation dose 150 kGy is suitable to obtain best combination of mechanical properties.

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