



# Upcycling of waste polyethylene and cement kiln dust to produce polymeric composite sheets using gamma irradiation

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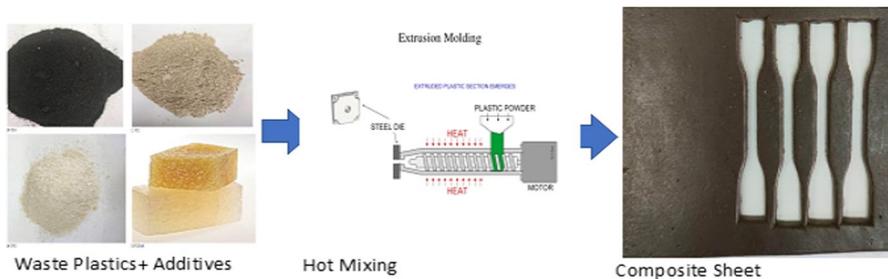
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## Abstract

Cement kiln dust (CKD) is a residue produced during the manufacture of cement that contains hazardous solid waste of high toxicity that affects the environment and public health. In this study, the possibility of using CKD as a filler in the plastic and rubber industry was studied. The effect of CKD concentration and gamma irradiation dose on the mechanical and physico-chemical properties of the composite containing waste polyethylene/devulcanized rubber/EPDM rubber (named blank) was investigated. Different concentrations of CKD, namely 10, 15, 20, and 30 phr (part per hundred part of composite), were used. The results indicated that this composite (blended with CKD) properties were improved. The most significant improvement was achieved by using CKD concentration of 20 phr at the dose of 100 kGy of gamma irradiation. These findings were demonstrated by scanning electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, and thermogravimetric analysis.

## Graphical abstract



**Keywords** Recycling · Waste plastics · Waste rubber · Composite · Ionizing radiation

Extended author information available on the last page of the article

## Introduction

With the increasing use of polymers, especially plastic and rubber around the world due to their unique characteristics such as tensile strength, flexibility, lightweight, cheapness, and versatility in all aspects of life, whether it is domestic, agricultural, industrial, or even medical, production is increasing in large quantities steadily, and hence, the amounts of waste polymers generated from consumption also rapidly increased [1, 2]. The negative impact on the environment increases also with the increase in polymer waste, making the recycling of waste polymers a challenging topic. One of the most common types of these polymers is polyethylene, which with its various types makes up the largest proportion of plastic waste and it is not a biodegradable polymer [3]. The opportunity is good in recycling waste polyethylene due to its nature as a thermoplastic polymer. However, repeated recycling of polyethylene causes decreases in molecular weight due to degradation and poor mechanical properties [4], and therefore, polyethylene waste prefers to be recycled by mixing with organic or inorganic materials to raise and improve its properties [5, 6].

Rubber tire waste is the most difficult to recycle due to the triple entanglement resulting from the vulcanization process, which makes the recycling process in this case neither possible nor bad because the vulcanized rubber is unable to form new bonds [7]. Therefore, the devulcanization process is necessary for recycling and becomes able to regenerate with new materials to improve their properties and exploit these very large quantities of waste rubber [8]. Devulcanization of waste tire rubber refers to a process of cleaving the polysulfide bonds crosslinks of vulcanized rubbers [9, 10]. After the devulcanization process not before, the waste rubber can react with new polymers forming new bonds [10–12]. Many studies have been done in this part, including devulcanization and blending with different percentages of new polymers to produce a new blend close to the new product in properties that can be used in different applications. (Jiang et al. [13] prepared devulcanized waste tire rubber/high-density polyethylene blends by the devulcanization of waste tire rubber with tetraethylenepentamine followed by grafting of HDPE with styrene and glycidyl methacrylate which led to the homogeneity of d-GTR/HDPE blend and the improvement in the mechanical properties clearly [13]. Sutanto et al. [14] studied the mixing of reclaimed and devulcanized EPDM with virgin EPDM to enhance and improve the mechanical properties of waste rubber. And since the devulcanized rubber contains a large percentage of carbon, so when re-merging, the process will not need carbon, so a new filler such as cement kiln dust can be added to improve the properties and reduce the cost [15, 16]. Cement kiln dust (CKD) is an inorganic alkaline fine powder that is produced as a by-product of cement production in large quantities in most cement plants all over the world. CKD affects negatively the environment because it is easily released into the atmosphere causing air pollution and contains a high concentration of many metals such as As, Cd, Pb, Cr, and Ni known to have toxic effects not only on plants and animals but also on humans. Because of the high content of lime which prevents the setting process of concrete production, the

recycling of cement kiln dust (CKD) is so difficult [17]. From X-ray diffraction (XRD) analysis, it contains mainly lime, CaO, SiO<sub>2</sub> and minor elements such as Al<sub>2</sub>O<sub>3</sub>, MgO, Fe<sub>2</sub>O<sub>3</sub>, ZnO, Cr<sub>2</sub>O<sub>3</sub>, KCl, NaCl, and K<sub>2</sub>SO<sub>4</sub> [18–21]. In this study, we used the ionizing radiation as an alternative, cheap and easy-to-use technique to obtain a good three-dimensional cross-linking of the rubber plastics through free radicals which formed when the polymer is exposed to ionizing radiation, through which the polymer can combine with the new polymers and form a strong crosslinking with good specifications [22]. In this work, we will study the possibility of making a composite of polyethylene waste with devulcanized waste rubber with the addition of a small portion of new rubber EPDM to increase the compatibility between these polymers and the ease of the mixing process [13], accompanied by a study of the effect of adding different concentrations of cement dust on the mechanical and thermal properties of composite materials.

## Experimental techniques

### Materials and methods

Virgin Ethylene-Propylene-Diene- Monomer (EPDM) commercial trade was obtained from Exxon Chemical Company (Belgium). Waste tire rubber powder (WR) of particle size of about 80 meshes produced from the recycled tire was provided by Narobine industries company, Cairo, Egypt. Waste polyethylene (WPE) from transparent bags was provided by a local supplier, in Cairo, Egypt. Cement kiln dust (CKD) is a mixture of metal oxides (clay minerals); its composition is listed in (Table 1). Cement dust is produced as an undesired by-product of cement industries; it was kindly provided by El-Sweedy cement company, Sues, Egypt, fine powder of particle size about 50 μm. Dioctyl phthalate (DOP) as a lubricants oil and compatiplizing agent, zinc oxide (ZnO), lead oxide (PbO), and stearic acid to facilitate and enhancement the plasticity of the compounding process were purchased from Loba-chem (India). Benzoic acid and hydroquinone were purchased from Loba-chem (India) for the devulcanization process. Resin (Rosin), a natural polymer that can interact with the semi-devulcanized rubber and enhance the processability of the milling handle of waste rubber, was provided by a local supplier in Cairo, Egypt [9, 23–25].

### Devulcanization of waste rubber

Devulcanization process is to cleavage the sulfur S–S bonds which crosslink bonds in the vulcanized rubber, totally or partially through chemical interaction under mild milling and temperature around 70 °C [9]. It was carried out in both

**Table 1** Chemical composition of cement kiln dust (CKD)

Oxides elements	Ca	Si	Al	Fe	Mg	S	K	Cl
Conc. (%)	52.1	24.5	4.42	3.69	2.06	2.56	6.62	1.36

plasticoder (hot mixer) and roll mill. Waste rubber powder (200 g) is mixed with an adjusted amount of benzoic acid (3%wt) as a proton donator which enhances the cleavage of sulfur bonds into a hot mixer at 30 rpm screw speed at 120 °C for 20 min. The output of extrusion is poured into a roll mill at 20 rpm speed and 50 °C for 30 min., stearic acid (3% wt) and zinc oxide (2% wt) were added to the mixture to rebuild new bonds between macromolecules which lead to the capability of devulcanized rubber to interact with new materials [26] and hydroquinone (1% wt) acts as chain transfer of macromolecule chains of polymer (inhibitor) that prevents reattachment of sulfur radicals (S–S) with each other before the proton donor attaches itself to the sulfur to achieve devulcanization process. Rosin as a kind of thickening agent can stick to the rubber powder and prevents it from slipping until the devulcanization process is completed and the devulcanized rubber flakes are successful [24].

### Preparation of (WPE/DWR/EPDM)/CKD composite sheets

Polyethylene was melted in a hot mixer twin-screw with a speed of 80 r/min at 120 °C for 5 min. Then, the prepared flakes of devulcanized waste rubber (DWR), EPDM, and CKD were added, respectively, for 20 min until complete homogeneity of the composite mixture. During the mixing process, laxatives like stearic acid and di-octyl phthalate (DOP) are added to the mixing process. Different concentrations of (WPE/DWR/EPDM)/CKD were used to produce the composites, as shown in (Table 2). The mixed composite samples were pressed to sheets using Carver hydraulic hot press at 120 °C and 160 kg/cm<sup>2</sup> on the mold surfaces for at least 5 min. The prepared composite sheets were subjected to <sup>60</sup>Co-gamma rays at irradiation doses 25, 50, 75, 100, and 150 kGy with a dose rate of ≈1.4 kGy/h.

### Gamma irradiation

Exposure to gamma irradiation was carried out in the Cobalt-60 source of gamma Chamber-4000A installed at National Center for Radiation Research and Technology, Cairo, Egypt. The compounds were subjected to gamma irradiation in the air at room temperature. The irradiation was carried out at a dose rate of 1.4 kGy/h.

**Table 2** Formulation of plastic-rubber composites

Sample no	WPE (g)	DWR (g)	EPDM (g)	CKD (phr)	ZnO (phr)	PbO (phr)	Stearic acid (phr)	DOP (mL)
Blank	100	10	10		5	5	1	3
Composite 1	100	10	10	10	5	5	3	3
Composite 2	100	10	10	15	5	5	3	3
Composite 3	100	10	10	20	5	5	3	3
Composite 4	100	10	10	30	5	5	3	3

## Analysis and measurements

### Fourier transform infrared spectroscopy (FTIR)

FTIR studies of samples were recorded on Bruker, Unicomb infra-red spectrophotometer, Germany, in the range of 400–4000  $\text{cm}^{-1}$ . The composite samples were prepared as a thin film before the transmission measurements could be made, except CKD powder, which was measured as it without a press with KBr.

### EDX measurements

Cement kiln dust (CKD) analysis was carried out by EDX unit (ISIS Oxford) attached to scanning electron microscopy (ZEISS EVO-15, UK).

### X-ray diffraction analysis (XRD)

The XRD patterns of cement kiln dust (CKD), (WPE/DWR/EPDM) polymer blend, and (WPE/DWR/EPDM)/CKD composite samples were measured using an X-ray diffractometer (Shimadzu 6000, Japan) with a copper target ( $\lambda = 1.542 \text{ \AA}$ ) at operating voltage of 40 kV, an electric current of 30 mA, and the scan speed of 8°/min. The average particle size of the (CKD) was calculated using the Debye–Scherrer formula [27] as shown in Eq. 1:

$$D = k\lambda / (\beta \cos \theta) \quad (1)$$

where  $D$  is the mean particle size,  $k$  is the Scherrer constant defined as the crystallite shape and is approximately equal to 0.9,  $\beta$  is the full width of the peak at half of the maximum intensity (rad) (FWHM),  $\lambda$  is the wavelength of the monochromatic X-ray beam, and  $\theta$  is the peak diffraction angle (rad)

### Scanning electron microscope (SEM)

A scanning electron microscope (SEM) was used to study the morphological structure of the prepared composite sheets and the grain size of CKD as a filler used in the prepared composite, using (ZEISS EVO-15, UK).

### Mechanical measurements

Standard mechanical tests were conducted on dumbbell-shaped specimens of standard width of 4 mm and length of 15 mm using tensile testing control unit of Hung-Ta Model HT-9112 (Taiwan). The crosshead speed was 500 mm/min. The recorded values of the mechanical properties were the average of five measurements.

## Thermogravimetric analysis measurements

The thermal characteristics of WPE, (WPE/DWR/EPDM) and (WPE/DWR/EPDM)/CKD composite samples have been investigated using the thermogravimetric analysis (TGA) technique with the TG-50 instrument Shimadzu; (Japan). This technique was used to measure the thermal stability of the samples at a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ .

## Physico-chemical properties

**Soluble fraction (SF)** Soluble fraction measurement of the prepared composite sheets was carried out with toluene as a suitable solvent for rubber, with heating under reflux for 24 h. After extraction, the samples were dried to constant weights in a dry oven at  $50\text{ }^{\circ}\text{C}$ . The soluble fraction can be calculated as follows:

$$\text{SF} = W_o - W_1/W_o \quad (2)$$

where:  $W_o$  and  $W_1$  represent the dried weight of the sample before and after extraction, respectively.

**Swelling** The swelling properties of the prepared samples were studied by placing them ( $W_1$ ) in a beaker covered with solvent for 24 h and then weighing again ( $W_2$ ) and calculating the degree of swelling as follows.

The swelling number (S) is given by:

$$S = W_2 - W_1/W_1 \quad (3)$$

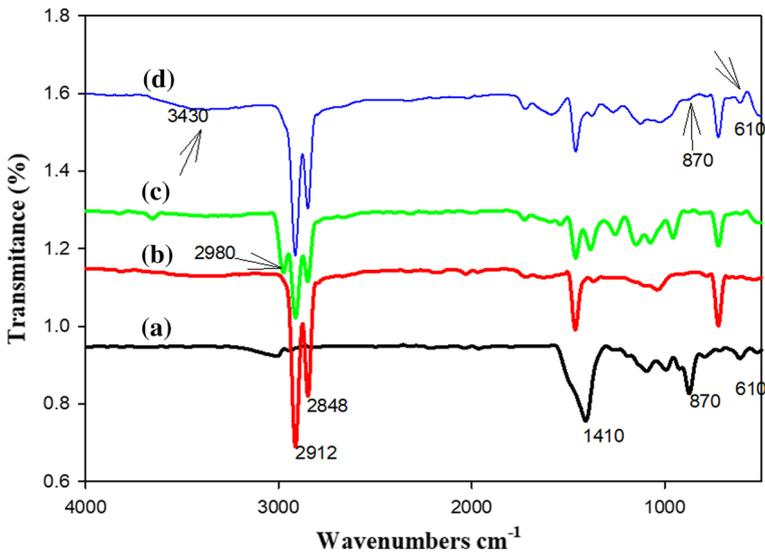
**The volume fraction of rubber in a swollen gel ( $V_r$ )** The volume fraction of rubber in a swollen gel ( $V_r$ ) was calculated according to the following Eq. (5):

$$V_r = \frac{\frac{W^1 - W^0 f}{\delta_r}}{\frac{W^1 - W^0 f}{\delta_r} + \frac{W^2 - W^1}{\delta_s}} \quad (4)$$

where  $W^0$  = original weight,  $W^1$  = de-swollen weight (weight after extraction and drying),  $W^2$  = weight after swelling,  $f$  = weight fraction of insoluble components,  $\delta_r$  and  $\delta_s$  the density of the rubber and solvent, respectively.

**Determination of crosslinking density ( $\nu$ )** The equilibrium swelling in toluene was used to calculate the cross-link density, which is the number of network chain densities, by applying the Flory–Rehner equation as follows:

$$\nu = \frac{1}{V_s} \left\{ \frac{[Ln(1 - V_r) + V_r + xV_r 2]}{[(V_r)1/3 - V_r/2]} \right\} \quad (5)$$



**Fig. 1** FTIR spectra of **a** CKD powder **b**WPE, **c** (WPE/DWR/EPDM) blend, and **d** (WPE/DWR/EPDM)/CKD (composite No. 3) all samples gamma irradiated at 100 kGy

where  $V_s$  is the molar volume of the solvent,  $V_r$  is the volume fraction of rubber in the swollen gel, and  $x_1$  is the polymer–solvent interaction parameter, which is equal to 0.351 for EPDM in toluene.

**Statistical analysis**

All measurements were carried out at least in triplicate, and the data were analyzed with (spss version 16.0, USA). The data were analyzed using the analysis of variance technique for comparing the average value of the parameters and were presented as a mean  $\pm$  standard deviation. Duncan’s multiple range test (DMRT) evaluated the significant difference between the studied samples.

**Results and discussion**

**Fourier transform infrared (FT-IR) spectroscopy**

Figure 1 shows the FTIR spectra of CKD, WPE, WPE/DWR/EPDM (blank sample), and WPE/DWR/EPDM/CKD composite (Sample No. composite 3), all samples are gamma-irradiated at 100 kGy. FTIR spectrum of CKD (Fig. 1a) showed that peaks at about  $870\text{ cm}^{-1}$  representing the bending vibration of the long alkyl chain bonded to the surface of  $\text{CaCO}_3$ [28] and peaks at  $1410\text{ cm}^{-1}$  could be assigned to metal–oxygen stretching vibration mode. A characteristic absorption band appeared around  $610\text{ cm}^{-1}$  which is the characteristic peak of Fe–O bonds confirming that CKD is incorporated in the composite samples [29]. FTIR

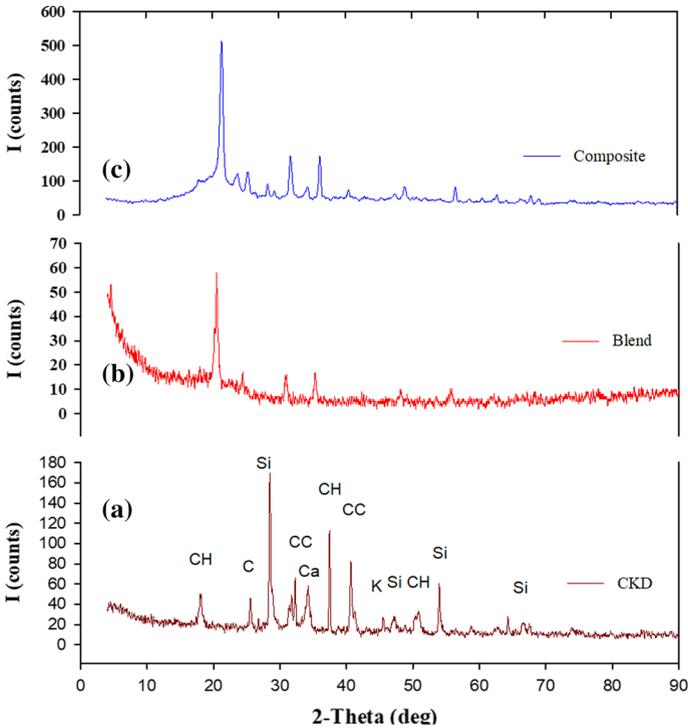
spectrum of WPE (Fig. 1b) showed strong two peaks at 2912 and 2848  $\text{cm}^{-1}$  due to C-H stretching vibration mode. The band observed at 1462 and 726  $\text{cm}^{-1}$  corresponded to  $\text{CH}_2$  bending and rocking, respectively; these observed peaks were assigned to WPE. In the spectrum of WPE/DWR/EPDM (Fig. 1c), a new peak appeared at 2980  $\text{cm}^{-1}$  ascribed to aromatic C-H stretching vibration may be due to the benzene ring in SBR reclaimed rubber as the main elastomer of the devulcanized rubber DWR [9]. A new peak at 1375  $\text{cm}^{-1}$  has also appeared, characteristic of  $\text{CH}_3$  bending in polypropylene as the main component of the EPDM rubber used in the blend preparation. For (WPE/DWR/EPDM)/CKD composite sample (Fig. 1d), the peak at 2980  $\text{cm}^{-1}$  which appeared in (Fig. 1c) could be masked by the shoulder between 2964 and 3008  $\text{cm}^{-1}$  due to the addition of CKD. The weak broad band at 3430  $\text{cm}^{-1}$  could be assigned hydrogen bonded to the OH group of silica present in CKD filler. Peaks at 610, 870, and 1410  $\text{cm}^{-1}$  could be assigned to the metal–oxygen vibration bands confirming the homogeneity of CKD in the composite samples.

### Energy dispersive X-ray (EDX)

Table 1 represents the EDX analysis of CKD powder. The EDX analysis confirmed the results of the XRD measurement, as the results showed the presence of calcium compounds by 52% and a high percentage of quartz (silicon cpds) estimated at 24.5%, and different ratios of other minerals such as iron, aluminum and a small percentage of potassium and chlorine.

### X-ray diffraction (XRD) analysis

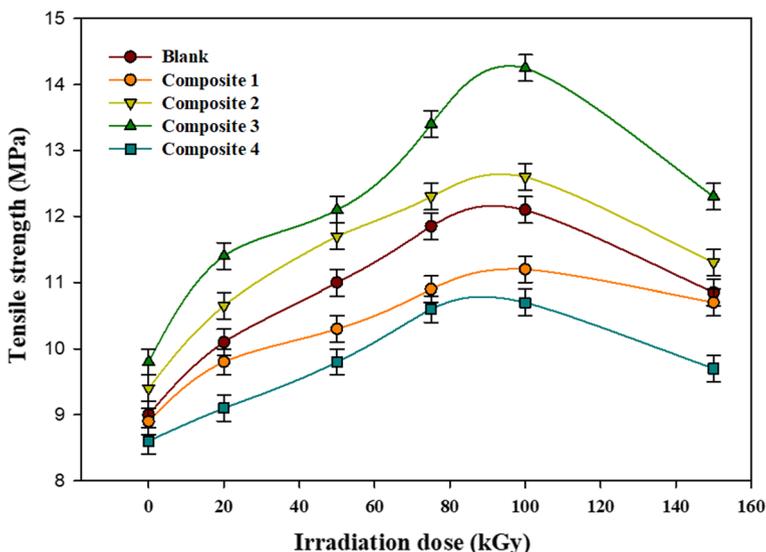
Figure 2a shows the XRD pattern of CKD. From it can be seen that, high content of lime and CaO at peaks 18, 25.5, 32, 34, 37, 41, and 51 2-Theta. It also shows a high content of quartz (Silicon oxides) at peaks 28.4, 47.4, 54, and 66 2-Theta and low content of K at  $2\theta = 45.5$ [30]. The average particle size of CKD nanoparticles was determined from the broadening in the XRD pattern utilizing Eq. (1). The particle size of the CKD used as a filler in composite sheet preparation at triple theta values ranged 38, 49, and 34 (nm) with an average particle size of 41 (nm.). In Fig. 2b, the XRD pattern of (WPE/DWR/EPDM) irradiated at 100 (kGy) shows that the characteristic peaks are identified at 21 and 24.2 2-Theta confirmed the partial crystallinity of the polymer which are in a good agreement with the literature for pure low-density polyethylene which is the main constituent of the blend and compatible with the formulation of EPDM that peaks lie around 20–26 in the literature [31, 32]. In Fig. 2c, the XRD pattern of (WPE/DWR/EPDM)/CKD polymer composite which was irradiated at 100 (kGy) and loaded with 20 phr of CKD shows that the intensity is much higher when compared with the polymer blend unloaded with CKD and this may be due to decrease in cross-linking with the increment of filler content (CKD) which interferes between the polymer chains, reducing crosslinking.



**Fig. 2** The XRD patterns of **a** CKD powder, **b** WPE/DWR/EPDM blend, and **c** (WPE/DWR/EPDM)/CKD composite (samples No. 3), all samples irradiated at 100 kGy

### Mechanical properties

Figure 3 shows the effect of gamma irradiation dose on the tensile strength (TS) of WPE/DWR/ EPDM rubber (named blank) loaded with different concentrations of CKD, namely 10, 15, 20, and 30 phr. From the figure, it can be seen that the values of TS for all compositions increase with increasing irradiation dose reaching its maximum values at about 100 kGy. After that, the values of TS decrease on increasing the irradiation dose up to 150 kGy. As shown in Table 3 which represents the variations between the effect of different irradiation doses and the tensile strength (TS) values obtained for the 5 compositions in three replications, it can be seen that the same composition with different irradiation doses is statistically significant. This behavior is due to the increase in the intensity of the crosslinking by increasing the radiation dose and the degradation prevalent at higher doses of radiation, where the breakage of the carbon–carbon prevalent at the main rubber chain may occur at a higher rate than the crosslinking process [33]. Also, from Fig. 3, it can be seen that the addition of CKD leads to a relative increase in TS values (especially at 20 phr from CKD). The reason for this is due to the large number of interconnections between the composite chains and CKD



**Fig. 3** Tensile strength of WPE/DWR/EPDM (as a blank) and (WPE/DWR/EPDM)/CKD composite samples loaded with different concentrations of CKD

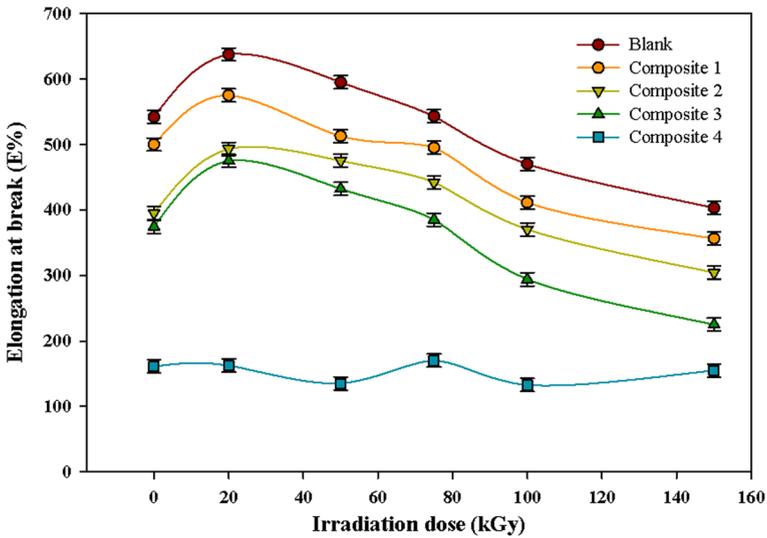
**Table 3** Effect of polymer composition and irradiation dose on tensile strength of (WPE/DWR/EPDM) blend and (WPE/DWR/EPDM)/CKD composite sheets (mean  $\pm$  SD,  $N=3$ )

Irradiation dose	Blank	Composite 1	Composite 2	Composite 3	Composite 4
0	9 $\pm$ 0.2 A	8.9 $\pm$ 0.18 B	9.4 $\pm$ 0.0.19 C	9.8 $\pm$ 0.0.18 D	8.6 $\pm$ 0.0.17 E
20	10.1 $\pm$ 0.2 A	9.8 $\pm$ 0.18 B	10.65 $\pm$ 0.19 C	11.4 $\pm$ 0.18 D	9.1 $\pm$ 0.17 E
50	11 $\pm$ 0.25 A	10.3 $\pm$ 0.19 B	11.7 $\pm$ 0.18 C	12.1 $\pm$ 0.18 D	9.8 $\pm$ 0.17 E
75	11.85 $\pm$ 0.25 A	10.9 $\pm$ 0.20 B	12.3 $\pm$ 0.18 C	13.4 $\pm$ 0.2 D	10.6 $\pm$ 0.17 E
100	12.1 $\pm$ 0.23 A	11.2 $\pm$ 0.22 B	12.6 $\pm$ 0.2 C	14.25 $\pm$ 0.2 D	10.7 $\pm$ 0.19 D
150	10.85 $\pm$ 0.21 A	10.7 $\pm$ 0.19 B	11.3 $\pm$ 0.2 C	12.3 $\pm$ 0.2 D	9.7 $\pm$ 0.19 D

\*Values followed by the same letters (S) mean no difference significantly at 5%

as a result of the material's characteristics in terms of a small granular size that increases the surface area of diffusion and thus creates a greater amount of synaptic bonds with composite chains.

Figure 4 shows the effect of  $\gamma$ -rays on the elongation at break (E%) of the above-mentioned samples. It can be seen that the E% was increased with irradiation dose up to 25 kGy and then decreased progressively by increasing the CKD content and irradiation dose up to 150 kGy. This behavior can be explained as follows increasing the radiation dose and the filler content, the prepared compound increases crosslinking, and the samples relatively harden, which leads to a decrease in the mobility of the molecular chains and thus reduce the elongation properties [34, 35]. Table 4 represents the variations between the effect of



**Fig. 4** Elongation at the break of WPE/DWR/EPDM (as a blank) and (WPE/DWR/EPDM)/CKD composite samples loaded with different concentrations of CKD

**Table 4** Effect of polymer composition and irradiation dose on elongation at break (E%) of (WPE/DWR/EPDM) blend and (WPE/DWR/EPDM)/CKD composite sheets (mean ± SD, N = 3)

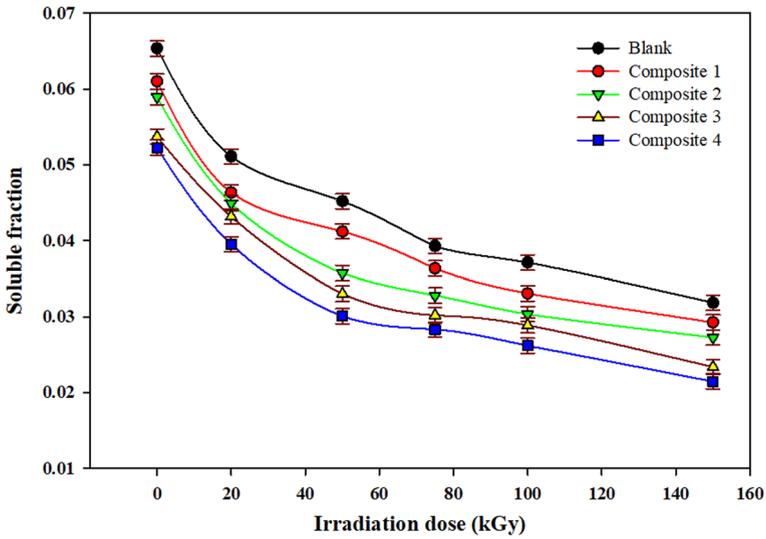
Irradiation dose	Blank	Composite 1	Composite 2	Composite 3	Composite 4
0	542 ± 10 A	500 ± 9.7 B	395 ± 8.5 C	374 ± 8.2 D	161 ± 6.4 E
20	637.5 ± 10.5 A	575 ± 9.7 B	493 ± 9 C	475 ± 8.5 D	162.5 ± 6.4 E
50	595 ± 10 A	512.5 ± 9.7 B	475 ± 9 C	432 ± 8.5 D	135 ± 6 E
75	543 ± 10 A	495 ± 9.5 B	442 ± 9 C	385 ± 8.2 D	170 ± 6.5 E
100	470 ± 9.5 A	411 ± 9.5 B	370 ± 8.5 C	294 ± 7.5 D	132.5 ± 6 E
150	403 ± 9.5 A	356 ± 9.4 B	304 ± 8.5 C	225 ± 7.5 D	155 ± 6 E

different irradiation doses and the values of elongation at break (E%), and there are statistically significant for the same composition.

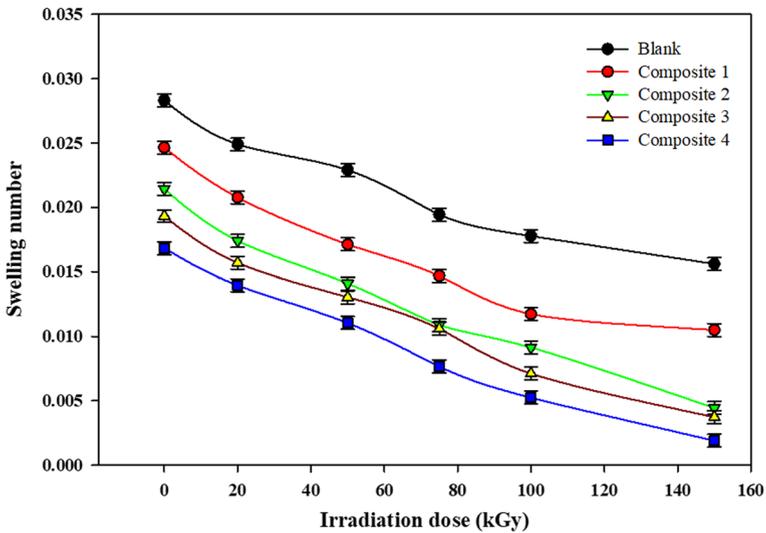
### Physical properties

#### Soluble fraction and swelling number

Figures 5 and 6 show the variation of soluble fraction and number of swelling in toluene as a function of irradiation dose and CKD concentrations. The results indicate that by increasing the radiation dose, the values of the soluble fraction and swelling number for all samples gradually decrease. These results are attributed to the difficulty of diffusion of the solvent through the films due to the increased cross-linking in the samples due to exposure to ionizing radiation. We can also see from

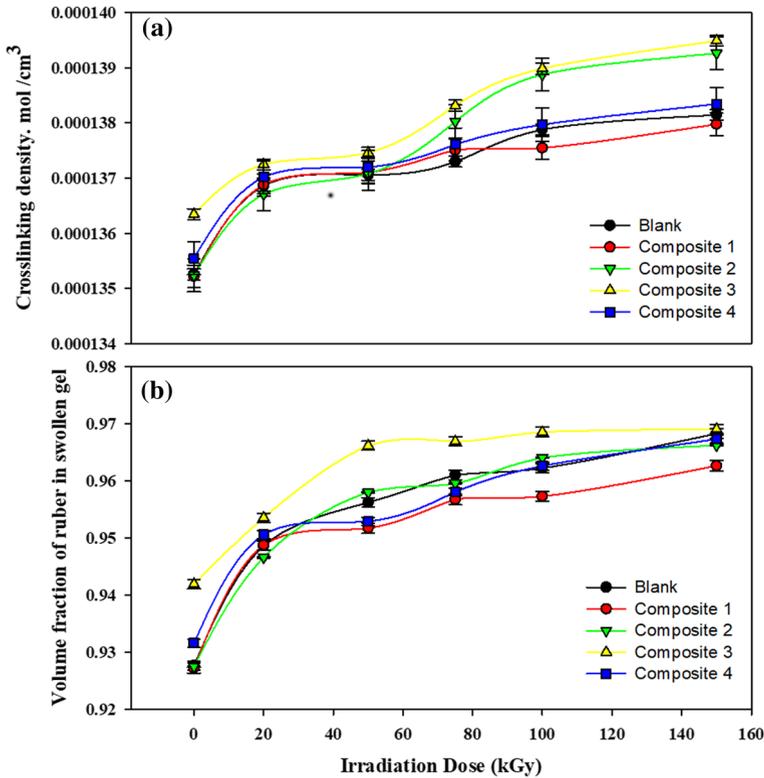


**Fig. 5** Soluble fraction of WPE/DWR/EPDM (as a blank) and (WPE/DWR/EPDM)/CKD composite samples loaded with different concentrations of CKD



**Fig. 6** swelling number of WPE/DWR/EPDM (as a blank) and (WPE/DWR/EPDM)/CKD composite samples loaded with different concentrations of CKD

the figures that the samples treated with cement dust (CKD) decreased the percentage of soluble fractions and the number of swelling. This results in less diffusion of the solvent within the material. The same explanation can be given, increasing the cross-link density to reduce the soluble fraction with increasing radiation dose [15].



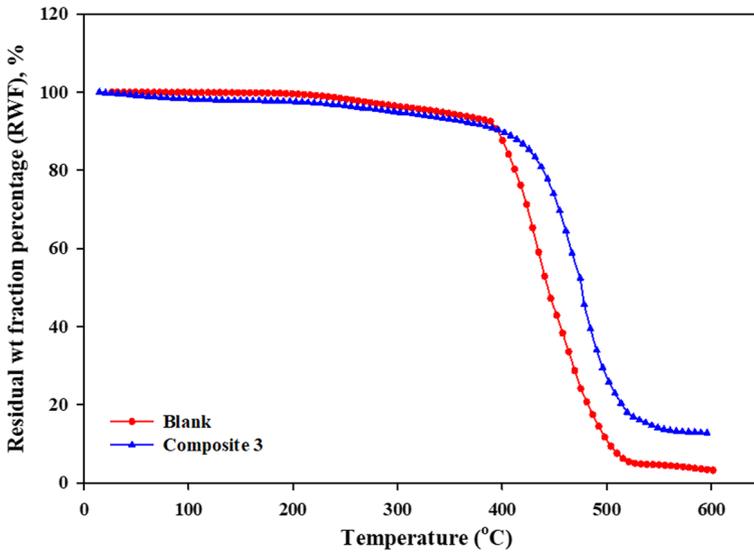
**Fig. 7** Volume fraction and cross-linking density of rubber in swollen gel of WPE/DWR/EPDM (as a blank) and (WPE/DWR/EPDM)/CKD composite samples loaded with different concentrations of CKD

**Volume fraction of rubber ( $V_r$ ) and crosslinking density**

Figure 7 shows the effect of irradiation dose on the volume fraction and cross-linking density as a function of irradiation dose and CKD concentrations. The results showed that both volume fraction and cross-linking density increase gradually with gamma irradiation increases, and the highest value is for composite 3, which gives more cross-linking than the blank sample (un-loaded with CKD) due to the reinforcement effect of polymer with CKD during vulcanization and the action of gamma-ray which increase the adhesion force between the components.

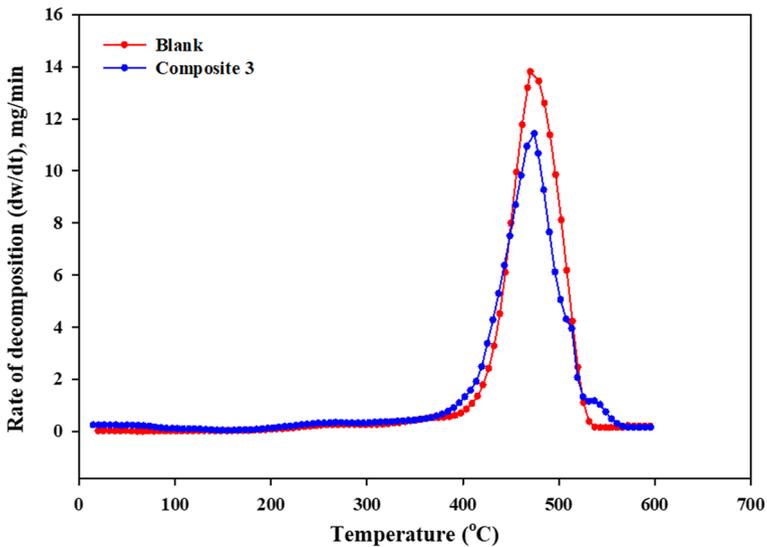
**Thermal gravimetric analysis (TGA)**

Thermogravimetric analysis is widely used to study the degradation of different polymeric materials at a wide range of temperatures. The thermal stability was studied for the blank sample (WPE/ DWR/ EPDM rubber), and the blank loaded with 20 phr CKD all was gamma-irradiated at 100 (kGy). Figure 8 shows the TGA thermograms of the above two formulations. The corresponding rate of thermal



**Fig. 8** Residual weight fraction percentage against the temperature of (WPE/DWR/EPDM) (as blank) and (composite 3), all irradiated at 100 kGy

decomposition reaction curves for these formulations is shown in Fig. 9, and Table 5 shows the weight loss (%) at different heating temperatures and the temperatures of the maximum rate of the thermal decomposition reaction of the above-mentioned two formulations.



**Fig. 9** Rate of decomposition against the temperature of WPE/DWR/EPDM (as blank) and (composite 3) all irradiated at 100 kGy

**Table 5** Weight loss (%) and temperatures of the maximum rate of the thermal decomposition reaction of the prepared composite at different heating temperatures, all samples were gamma-irradiated at 100 kGy

Sample	Weight loss					$T_{\max}$ (°C)
	100 °C	200 °C	300 °C	400 °C	500 °C	
Blank	0.3	0.5	5	12.9	89.4	470
Composite 3	1.9	2.3	5.6	9.8	74.3	474

As shown in Fig. 8, there are slight differences in the thermal stability between the two formulations based on the remained weight (%) within the temperature range (0–300 °C). Meanwhile, within the temperature range (350–550 °C), the blank sample loaded with 20 g (phr) CKD displayed higher thermal stability than the blank only.

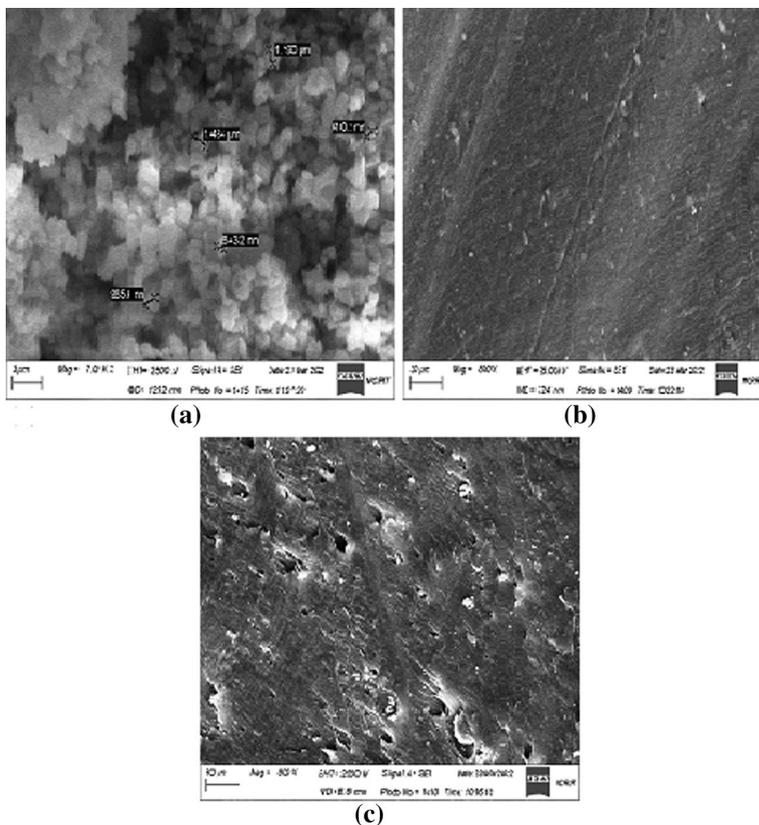
As shown in Fig. 9 and Table 5, the thermal stability of the maximum rate of the thermal decomposition reaction ( $T_{\max}$ ), for the loaded sample with 20gm (phr) CKD (composite 3), has  $T_{\max}$  higher than the blank sample.

### Scanning electron microscope (SEM)

SEM images were used to investigate the microstructure of CKD and the morphology of the prepared composite sheets. Figure 10a illustrates the grain size of CKD that showed the typical shape of calcite, the main component of cement, which resembles the shape of popcorn, which tend to agglomerate more together as specific small nanoparticles. Figure 10b represents the topographic surface of (WPE/DWR/EPDM) blend which illustrates good mixing and complete homogeneity and coherence between the mixed polymers, with no cracks or fractures on the surfaces. Figure 10c shows the micrograph of the composite after adding filler (CKD) (composite 3), which showed the presence of tiny particles of filler, penetrating the surface of the composite and leading to some cracks and irregularities in the surface. However, it is clear that the fabric is cohesive and strong.

### Conclusions

With the increase in human use of plastic and rubber products, waste increases enormously, affecting the environment and heat emissions. Therefore, interest is growing every day in trying to recycle plastic waste and rubber safely and economically. With the steady increase in construction and cement production, what is known as alkaline cement kiln dust (CKD) is formed as a by-product that is difficult to use in construction operations, which is a big problem, especially for cement producing countries due to its super smoothness and volatility, which is a serious environmental problem. In this research, we succeeded in incorporating cement kiln dust (CKD) as filler to produce rubber and plastic in large quantities, reaching 40%. For the waste mixing process to be successful, the waste rubber



**Fig. 10** Scanning electron micrograph of **a** CKD powder, **b** (WPE/DWR/EPDM) polymer blend **c** (WPE/DWR/EPDM)/20CKD all composites irradiated at 100 kGy

should be recycled through the devulcanization process by thermomechanical methods with the addition of rosin during extrusion to promote the devulcanization process. We succeeded in producing flexible plastic sheets (WPE/DVWR/EPDM) loaded with CKD that have good thermal tolerance and strong tensile properties. Statistical analysis was studied on different composites under the influence of radiation, which showed that the tensile strength and elongation at break are statically significant for the same compositions. The crosslinking was done by exposure to gamma rays. The surface was examined with a microscope, and no cracks or fractures appeared. Mechanical and thermal measurements proved that the cement kiln dust could be used as filler in the production of plastic and rubber industries in a good way.

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## Declarations

**Conflict of interest** The authors have no relevant financial or non-financial interests to disclose.

**Data availability** Data are available under request.

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