



Synthesis and Characterization of Poly (vinyl alcohol) / Fullerene C60 Membrane via Chemical and Radiation Crosslinking

Aamer A. M. Alfayyadh^a, Mutasim I. Khalil^b, A. A. Basfar^a and S. Lotfy^{*c}

^a Radiation Technology Center, Nuclear Science Research Institute, King Abdulaziz City for Science and Technology (KACST), Riyadh, Saudi Arabia

^b Department of Chemistry, Faculty of Science, King Saud University, Riyadh, Saudi Arabia

^c Polymer Chemistry Department, National Center for Radiation Research and Technology, Egyptian Atomic Energy Authority, Cairo, Egypt

Received 17 June 2020
Accepted 28 June 2020

Fullerene C60 (FULL-C60) was used as a nano-filler in the preparation of the chemical-crosslinking polyvinyl alcohol (PVA) by glutaraldehyde (Glut) which is copolymerized with acrylate oligomers, 2-carboxyethyl acrylate (CEA) followed by gamma irradiation. The effect of the FULL-C60 content on the gel content and swelling behavior of Glut-(PVA/CEA)-FULL-C60 copolymer hydrogel was investigated. The results revealed an increase in the gel content and a significant reduction in swelling of the nanocomposite material. There are influences for the PVA molecular weight, fullerene content, and absorbed dose on the gel content of the prepared nanocomposite. The irradiation of chemical crosslinked nanocomposites demonstrated approximately a 90% gelation over a range of 50-300 kGy irradiation doses. A scanning electron microscopy (SEM) analysis showed a homogeneous distribution of nanocomposites in the composite matrix. The improvement in the thermal stability of radiation Glut-(PVA/CEA) and Glut-(PVA-CEA)-FULL-C60 was evaluated using the thermogravimetric analysis Technique (TGA). The mechanical properties were examined via dynamic mechanical analysis (DMA) which showed significant variation because of the addition of nanocomposites and irradiation doses.

Keywords: Radiation; Poly (vinyl alcohol); Nanocomposite materials; Fullerene C60

Introduction

Carbon sphere-shaped molecules in the form of a hollow sphere called fullerene were discovered by Kroto et al.[1], which has turned to be a series now. It has nomenclature such as fullerene-60 or fullerene-70, in which all-carbon molecules with closed cage structures, have been found naturally in the Russian metaanthracite Shungite [2,3]. Fullerenes are composed of stacked graphene sheets similar in structure to graphite contain pentagonal or heptagonal rings similar in structure to graphite [4,5]. The interaction of fullerene with a polymer and the duration of fullerene-polymer intermolecular contacts may play an important role

in the modification of properties of polymer systems through the addition of FULL-C60 [6]. Due to the large surface area of FULL-C60 its polymer nanocomposites investigation may get higher performance than usual reinforcement. FULL-C60 is considered perfect strengthening fillers in polymer nanocomposites with multifunction due to its excellent physical properties, nano size in diameter, and low-density. Grafting of the fullerene onto the biocompatible, water-soluble polymer such as PVA was thoroughly investigated in previous studies [7-11]. The polymeric materials' mechanical properties are strongly temperature-dependent[9].

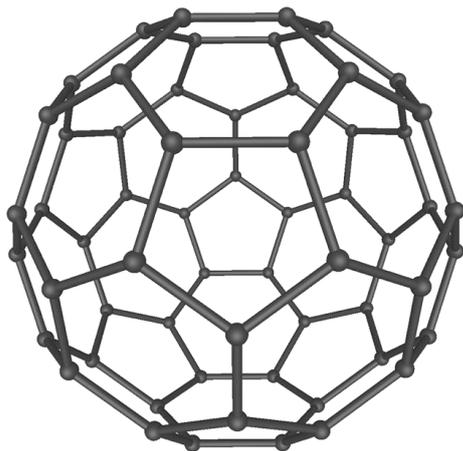


Photo (1): Spherical fullerene molecule with the formula FULL-C60

The stiff amorphous polymer at room temperature could behave in a rubbery manner at higher temperatures (rubbery modulus). The elastic portion of the material and the stored elastic energy modulus are the storage modulus (E'). The viscid portions of the material indicate energy dissipation which results in the loss modulus (E'') [14].

Ionizing radiation is a widely applicable technology in regulating the formation and properties of polymers, and could be used to adjust the achievement of bulk materials or surfaces[12]. Polymer hydrogels demonstrate a controlled gelation process[13]. The dose for which a minimum of the gel is formed can be defined as chemical modification of the gelation nanostructure [16,17]. Gamma irradiation treatment is considered a green technique and a safer non-contact modification, is as a prevalent technique for chemical modification of nanostructures in the fabrication of high-performance polymer composites[19]. Radiation-induced polymerization and crosslinking have advantages over chemical crosslinking and it is widely used in recent years for the synthesis of various hydrogels for biomedical applications[18]. A previous study of chemical and radiation crosslinked (PVA-CEA)-nanocomposites has been reported[18]. The crosslinked density between the polymer chain and nanotubes was improved by the radiation crosslinking of PVA and MWCNTs [19]. A significant reduction in the degree of swelling decreased dramatically up to 25 kGy doses from 2250 to 1000% and the increases of the doses led to decreases in the swelling degree of the prepared nano-composites up to 10 wv-1%, finally, the degree of swelling for the prepared matrices did not increase more than 0.6% [20]. An increase in

the gel fraction that, 100% gelation achieved at 50 kGy of treated material, the authors found promising shape memory behavior [21]. The promising shape memory effect was found for the nano-composites[22].

In the present study of nanocomposites, comprised of PVA and CEA and FULL-C60, Glutaraldehyde is used as a crosslinking agent for (PVA/CEA) and (PVA/CEA)-FULL-C60. It was a challenge to develop high-performance chemical and radiation crosslinked (PVA/CEA) and (PVA/CEA)-FULL-C60 nanocomposites as a hydrophobic polymeric matrix with strong interfacial interactions. In addition, the thermal and mechanical properties of nanocomposites were examined to understand the fundamental scientific drivers necessary to the characterization of the prepared nanocomposites.

Materials and Methods

Materials

2-Carboxyethyl acrylate oligomers (CEA) its molecular weight 170×10^3 g/mole and PVA molecular weight of 16×10^3 g/mole and 146×10^3 g/mole, 87-90% hydrolyzed were purchased from Sigma-Aldrich (St. Louis, USA). Fullerene C60, 99 % (FULL-C60) were procured from Graven Chemical Industries Co. Ancora, Turkey. The anionic surfactant; sodium dodecyl sulfate (SDS) >99% were purchased from Sigma-Aldrich (St. Louis, USA), and all chemicals were used as received.

Synthesis of polymer networks via glutaraldehyde crosslinking

The polymer was prepared using the previously reported procedure[23,24]. PVA solutions of 10 w/v of different molecular weights, were prepared by dissolving PVA in water for 6 hours at 98 °C. The ratio of 9:1 PVA: CEA solutions were mixed then cooled to room temperature. FULL-C60 at 0 to 0.5 w v⁻¹ percentage was dispersed in the previously prepared PVA-CEA solutions of MW 16×10^3 g/mole and 146×10^3 g/mole in the presence of the SDS surfactant as a stabilizing agent at a concentration of 0.5 w v⁻¹ percentage. HCl was used to adjust the pH at 4, then a certain amount of 25 percentage glutaraldehyde[25] was added to the PVA-CEA solutions under stirring conditions. The solution casting technic was used for PVA film preparation by casting the PVA-CEA solution onto a glass Petri dish then dried at 50 °C. The films were left for 36 hours at room

temperature (25 °C) to complete the chemical crosslinking and was carried out for 36 hours at room temperature (25 °C). The obtained films were washed with deionized water until the pH-neutral conditions and dried using a vacuum oven.

Radiation crosslinking

The prepared chemical glutaraldehyde crosslinking films, according to the PVA molecular weight and the FULL-C60 concentrations of 0 to 0.5 w v⁻¹ percentage were packed into polyethylene bags and irradiated to 0, 50, 150, and 300 kGy at room temperature using a 60Co gamma source (Gamma Cell 220; MDS Nordion, Canada).

Swelling studies

Pre-weighed specimens of glutaraldehyde crosslinked (PVA/CEA)-FULL-C60, according to PVA molecular weight and the FULL-C60 concentrations, were allowed to swell up to equilibrium at 37 °C in 50 ml distilled water. After drying the removed specimens from the water by filter papers to remove excess water then the specimens were weighed using a sensitive balance. The averaged values of three specimen's water uptake at equilibrium were reported. The swelling degree (%) was determined from the equation. (1),

$$\text{Swelling degree (\%)} = \frac{W_s - W_o}{W_o} * 100$$

(1)

where W_s and W_o are the weights of the swollen and the dried hydrogel respectively.

Gel fraction

The gel content of the dried specimens of Glut-(PVA/CEA)-FULL-C60 according to PVA molecular weight and the FULL-C60 concentrations were the average values of three specimens gel content were reported. estimated through the determining of its insoluble portion after boiling in distilled water for 48 hours at 60 °C. The averaged values of three specimens of gel content were reported. The gel fraction was calculated according to equation (2).

$$\text{Gel(\%)} = \frac{\text{Mass of residue (g)}}{\text{Original mass (g)}} * 100 \quad (2)$$

The recorded values above 90% considered a good crosslinking yield.

$$100 - \text{Gel(\%)} = \text{sol (\%)} \quad (3)$$

Thermogravimetric Analysis (TGA)

The thermogravimetric analysis (TGA) was executed a TGA apparatus (Perkin Elmer TGA7, USA) from room temperature up to 600 °C under a nitrogen atmosphere at a heating rate of 5 °C/minute.

Dynamic Mechanical Analysis (DMA)

DMA was carried out using PerkinElmer Inc. machine, USA. The specimens were equilibrated thermally at a very low temperatures (-50 °C) for three minutes and then heated up to 280 °C at a rate of 5 °C/minute. The initial conditions of the measurements were the static force equal 110 mN, the dynamic force equal 100 mN, and the frequency equal 1 Hz. Tensile loading was used to determine the peak of the tan delta which defined to be the glass temperature (T_g), the storage modulus (E'), the loss modulus (E''), and the rubbery modulus (E_r) of the specimens.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy was utilized to study the cut edge of the specimens as a cross-sectional and top view using JSM 5800 LV from Joel Co., Japan. The maximum magnification of the SEM was 300,000 at a resolution of 3.5 nm. Before the examination, the specimens were dried under sputters coated gold. All the micrographs were taken on a cut edge of the composites as a cross-sectional and top view.

Results and Discussion

Effect of irradiation dose on the gel fraction of the Glut-(PVA/CEA)-Nano-particles

Figure (1) shows these gel percentages of Glut-(PVA/CEA)-FULL-C60 copolymer of the two molecular weights 16×10^3 g/mole and 146×10^3 g/mole of PVA as a function of irradiation dose and FULL-C60 content. As the FULL-C60, concentration increases, the crosslinking increases leading to more gel formation. The presence of CEA in the three compositions of the Glut-(PVA/CEA) with different fillers play an effective role in the gel formation. These results show the efficiency of radiation crosslinking of PVA and CEA copolymers through their -OH groups and vinyl groups. This is most likely due to the use of the vinyl groups decreases rapidly with increasing γ -radiation dose. [26].

Effect of irradiation dose on the swelling of the Glut-(PVA/CEA)-FULL-C60

Figure (2) shows the equilibrium swelling of Glut-(PVA/CEA)-FULL-C60 copolymer of the PVA two molecular weights as a function of irradiation dose and FULL-C60 content. It is clear that the degree of swelling for Glut-(PVA/CEA)-FULL-C60 copolymers did not exceed 0.5 % for the PVA two molecular weights. The hydrogen bonding between hydroxyl groups of the PVA leads to high physical interactions between the polymer chains. The glutaraldehyde crosslinking decreases the number of hydroxyl groups and weakens the hydrogen bonding interaction [18]. The presence of CEA increases the content of side hydroxyl groups along with the backbone forming attract bound water. When the chemical crosslinked gel exposed to irradiation, the formation of OH radicals and H atoms a result of the radiolysis of

water has occurred. The free hydroxyl group attack by the OH radicals leads to the formation of junction zones inside the gel network [27].

Scanning electron microscope analysis

Figure (3) shows SEM micrographs at an increasing magnification of Glut-(PVA/CEA)-FULL-C60 of the PVA two molecular weights, FULL-C60 content; 0.1 %, irradiated at absorbed doses of 150 kGy. It can be clearly observed that the porous surface of the matrix contains the Full-C60 filler inside its structure which was likely formed as agglomerates of Full-C60. The Full-C60 dispersion in (PVA-CEA) matrix was random. The pores on the surface of the polymer matrix were distributed randomly, the diameters of the pores were affected with the PVA molecular weights. It is evident that interrelated networks have been formed in the final Glut-(PVA/CEA)-Full-C60.

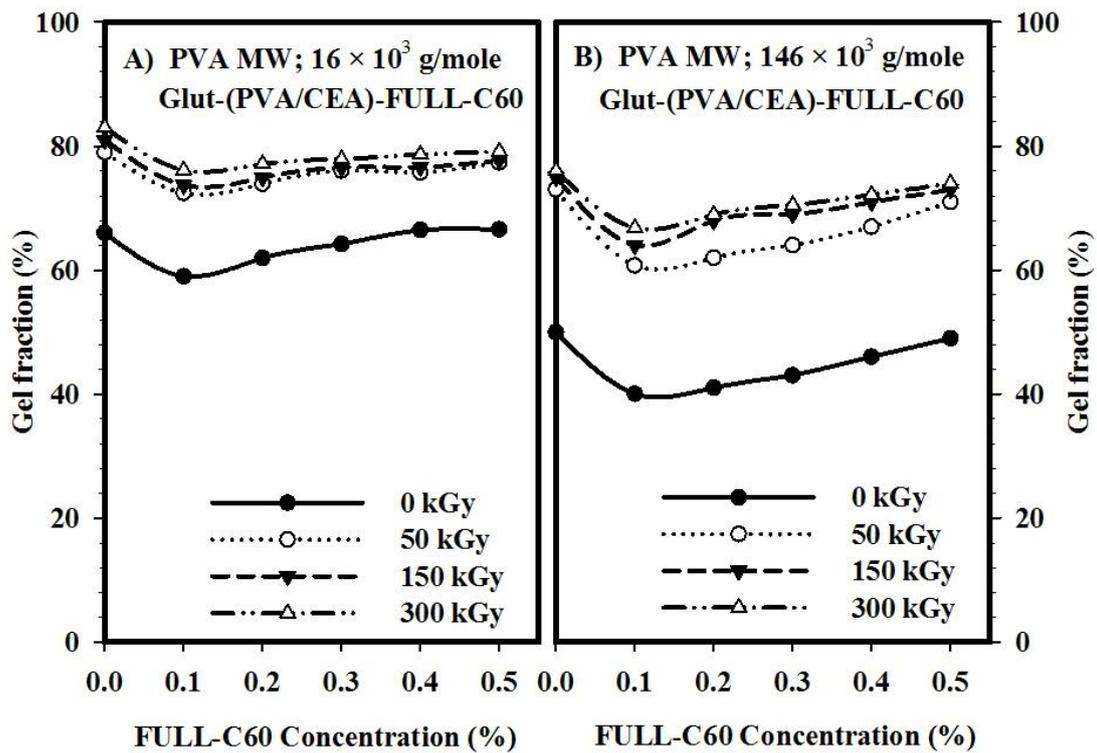


Figure (1): Gel fraction (%) of glutaraldehyde crosslinked of A) PVA molecular weights 16×10^3 g/mole Glut-(PVA/CEA)-FULL-C60, (B) PVA molecular weights 146×10^3 g/mole Glut-(PVA/CEA)-FULL-C60, as a function of irradiation dose and FULL-C60 content

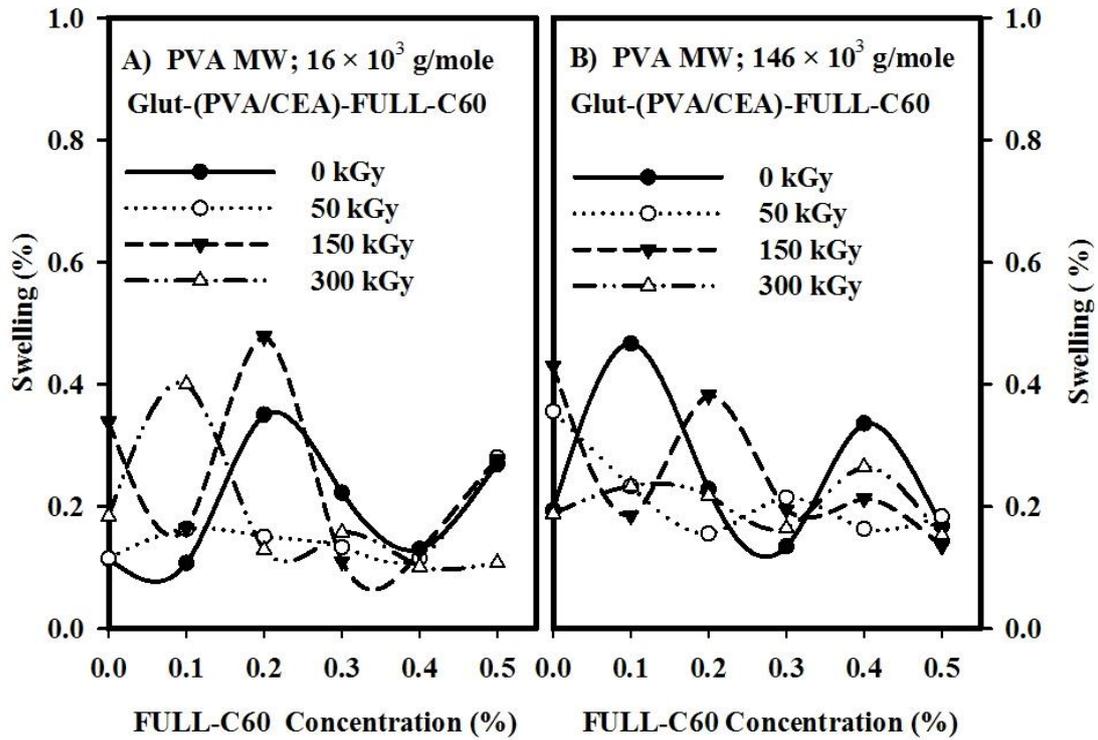


Figure (2): Degree of swelling of glutaraldehyde crosslinked of A) PVA molecular weights 16×10^3 g/mole Glut-(PVA/CEA)-FULL-C60, (B) PVA molecular weights 146×10^3 g/mole Glut-(PVA/CEA)-FULL-C60, as a function of irradiation dose and FULL-C60 content

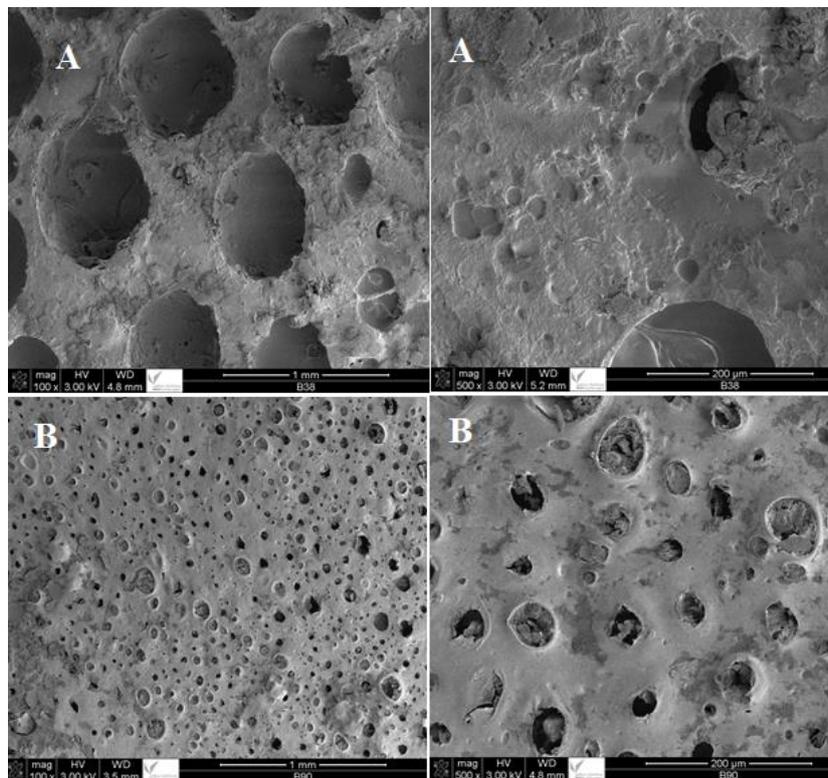


Figure (3): SEM micrographs of glutaraldehyde crosslinked of A) PVA molecular weights 16×10^3 g/mole Glut-(PVA/CEA)-FULL-C60, (B) PVA molecular weights 146×10^3 g/mole Glut-(PVA/CEA)-FULL-C60, FULL-C60 concentration 0.1 %, irradiated to absorbed doses of 150 kGy

Thermogravimetric analysis (TGA)

Figure (4) shows the TGA thermograms of the Glut-(PVA/CEA)-FULL-C60 of the PVA two molecular weights, Fig. 4(A, B) presents the thermograms of Full-C60 content 0-0.5 % at an irradiation dose of 150 kGy. Fig. 4(C, D) shows the thermograms of Full-C60 content 0.5 %, at different irradiation doses up to 300 kGy. The Glut-(PVA/CEA)-Full-C60 at PVA molecular weights 16×10^3 g/mole, shows the three weight-loss stages in the temperature ranges from 31 to 39 °C, 201-272 °C and 449-463 °C as presented in Table (1) as a function of the absorbed doses up to 300 kGy. The absorbed irradiation dose affects the variation of the mass loss. The first weight-loss stage is 0.52–5 weight percent due to the evaporation of the solvent. In the second degradation stage, the mass loss was in the range from 12 to 29 weight percent which results from the degradation of Glut-(PVA/CEA)-FULL-C60 copolymer. The third stage, in the temperature range from 449 to 463 °C, is due to polymer decomposition with mass loss range of 8-13 weight percent. The residual mass percent at 600 °C was found to be in the range of 34-18 weight percent depending on the irradiation dose. The Glut-(PVA/CEA)-FULL-C60 at PVA high molecular weights 146×10^3 g/mole and Full-C60 concentration 0.5 %, exhibits three weight-loss stages in the temperature ranges from 106 to 154 °C, 230-261 °C and 477 to 491 °C as presented in Tables (1 & 2). The weight-loss stages were 0.1-1, 38-60 and 15-24 weight percentages, relative to the irradiation dose up to 300 kGy. The residual mass percentage at 600°C was found to decrease in the range from 19 to 11 weight percentage with increases of the irradiation dose.

The Glut-(PVA/CEA)-FULL-C60 at PVA molecular weight 146×10^3 g/mole at irradiated at 150 kGy, exhibits three weight-loss stages in the temperature ranges from 9 to 170, 250 to 287 °C and 480 to 493 °C as shown in Table (1). The weight-loss stages were 0.1-3, 34-53 and 5-15 of the weight percentage, as a function of the FULL-C60 concentration 0- 0.5 %. The residual mass percentage at 600°C was found to decrease in the range from 7 to 12 of the weight percentage as the irradiation dose increases. This result is in accordance with the gelation results.

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analyses of the composites were directed to study the effect of FULL-C60 inclusion on the storage modulus, loss modulus, and tan delta of the prepared nanocomposite of the two PVA molecular weights.

Tan delta parameters

Figure 5(A, B) presents the Tan δ values of the blank of Glut-(PVA-CEA) and the Glut-(PVA/CEA)-FULL-C60 at PVA molecular weight 16×10^3 g/mole. However, Figure 5(C, D) presents Tan δ values at PVA high molecular weight 146×10^3 g/mole. The Tan δ values were measured as a function of the absorbed doses up to 300 kGy at FULL-C60 concentration of 0.5 %. The Tan δ values of the blank Glut-(PVA/CEA) at PVA low molecular weight cover the temperature ranges from 20, 95, 19, and 14 °C. The Tan δ values of the blank Glut-(PVA/CEA) at PVA high molecular weight cover the temperature ranges from -2, 36, 35, and 31°C as presented in Table(2). The thermal stability of the irradiated composite due to the crosslinking affects the variation in Tan δ values. The Tan δ values of the Glut-(PVA/CEA)-FULL-C60 at low molecular weight cover the temperature ranges of 111, 44, 45, and 82 °C. The Tan δ values of the Glut-(PVA/CEA)-FULL-C60 at PVA high molecular weight cover the temperature ranges of 16, 103, 155 °C and 105°C as presented in Table(2). It is clear that the variation of the Tan δ values was affected by the irradiation doses and the addition of FULL-C60 to the (PVA/CEA) network, compared. In addition, the effect of PVA molecular weight, shift the Tan δ due to interactions between polymer chains and FULL-C60[28]

Storage modulus and rubbery modulus parameters

Figure 6(A, C) presents the storage modulus (E') of the blank Glut-(PVA-CEA) at PVA molecular weight 16×10^3 g/mole and PVA molecular weights 146×10^3 g/mole as a function of the absorbed doses up to 300 kGy, the plots of E' versus temperature. The E' for the blank Glut-(PVA-CEA) composites at 0 kGy are higher than most of the irradiated Glut-(PVA-CEA) composites for both PVA molecular weights and the storage modulus decreased significantly upon increasing the absorbed dose. This result may be due to the degradation process of gamma irradiation as the crosslinking agent. The curves

show three distinct regions, the glassy state, glass to rubber transition region, and the rubbery state.

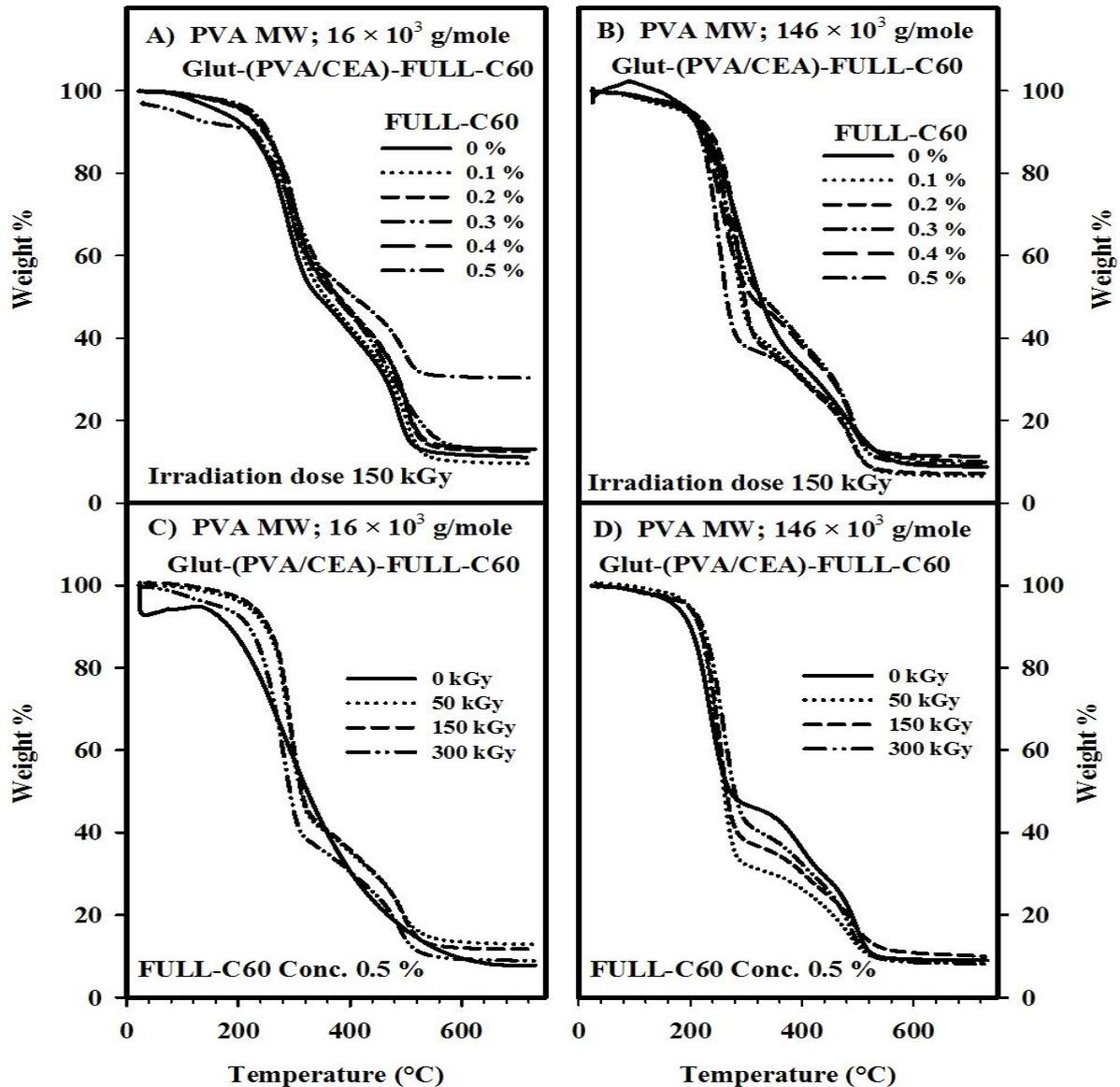


Figure (4): TGA thermograms of glutaraldehyde crosslinked of A) PVA molecular weights 16×10^3 g/mole Glut-(PVA/CEA)-FULL-C60, (B) PVA molecular weights 146×10^3 g/mole Glut-(PVA/CEA)-Full-C60, Full-C60 concentration 0.5 %, irradiated at absorbed doses up to 300 kGy

Table(1): DTG data T_{Onset} and T_{Peak} of Glut-(PVA/CEA)-Full-C60 of A) PVA MW 16×10^3 g/mole, (B) PVA MW 146×10^3 g/mole. Full-C60 concentration 0.5 %, irradiated up to 300 kGy

	Dose kGy	Stage	Glut-(PVA/CEA)-Full-C60 (PVA molecular weights 16×10^3 g/mole)						Glut-(PVA/CEA)- Full-C60 (PVA molecular weights 146×10^3 g/mole)					
			Fillers concentration (%)						Fillers concentration (%)					
			0	0.1	0.2	0.3	0.4	0.5	0	0.1	0.2	0.3	0.4	0.5
T_{Onset} (°C)	0	I	69	70	78	52	87	31	36	107	61	81	62	48
		II	280	273	289	237	271	239	277	235	159	237	186	160
		III	461	471	459	457	453	449	476	456	---	451	452	388
	50	I	23	57	95	87	160	34	50	101	39	67	118	48
		II	272	257	266	221	255	201	207	213	213	221	208	201
		III	545	463	459	466	458	449	420	444	453	458	462	392
	150	I	22	137	104	35	114	39	127	118	54	89	89	64
		II	251	260	267	160	242	272	193	251	253	212	204	198
		III	454	456	457	420	462	463	425	454	453	456	444	433
	300	I	62	50	134	58	138	37	70	63	86	129	136	149
		II	172	252	265	216	266	217	261	245	211	228	218	207
		III	----	457	451	455	456	455	467	445	459	444	445	436
T_{Peak} (°C)	0	I	134	116	139	115	107	132	67	112	88	108	117	106
		II	296	314	318	292	313	367	315	282	234	279	237	230
		III	490	505	499	496	497	496	494	496	----	495	493	477
	50	I	64	124	170	114	176	102	62	119	124	140	133	131
		II	286	300	300	272	301	296	282	271	264	274	257	253
		III	487	505	499	496	502	498	482	488	481	489	490	491
	150	I	86	154	176	60	122	148	155	159	170	146	135	99
		II	289	287	299	286	306	290	287	280	282	264	256	250
		III	485	501	501	492	503	497	490	492	490	493	488	488
	300	I	105	103	165	178	166	119	168	159	124	152	163	154
		II	323	293	301	281	300	304	297	276	267	271	267	261
		III	----	503	500	495	503	495	491	482	483	493	488	489

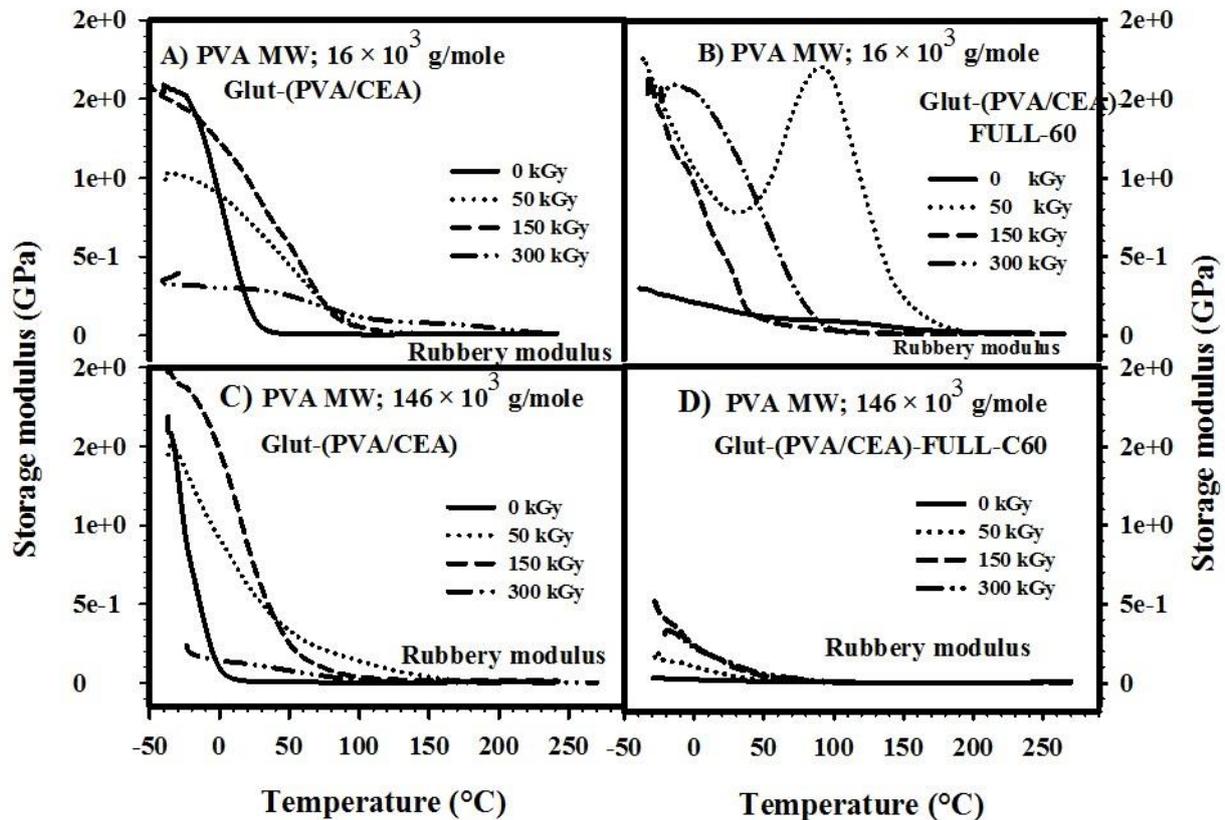


Figure (6): Storage and rubbery moduli of FULL-60 concentration 0.5 % as a function of absorbed dose up to 300 kGy. (A): Blank Glut-(PVA-CEA) of PVA molecular weights 16×10^3 g/mole (B): Glut-(PVA/CEA)-FULL-C60 of PVA molecular weights 16×10^3 g/mole (C): Blank Glut-(PVA-CEA) of PVA molecular weights 146×10^3 g/mole and (D): Glut-(PVA/CEA)-FULL-C60 of PVA molecular weights 146×10^3 g/mole

The storage modulus of the Glut-(PVA/CEA)-FULL-C60 at both molecular weight FULL-C60 concentration 0.5 % as a function of the absorbed doses up to 300 kGy. As shown in Figure 6(B, D) the E' for the Glut-(PVA-CEA)-FULL-C60 composites of PVA low molecular weight are significantly higher than that of PVA high molecular weight Glut-(PVA-CEA)-FULL-C60 composites and the storage modulus increased significantly with increasing the absorbed dose. This result may be due to the crosslinking process of gamma irradiation as a crosslinking agent.

The rubbery modulus (E_r) appears as a plateau in Fig. 6(A, B, C, D). The E_r values in mega Pascal (MPa) at 200 °C of the Glut-(PVA/CEA) at PVA low molecular weight cover the ranges of 1.1, 15, 39, and 12 MPa of absorbed doses up to 300 kGy. The E_r values at 200 °C of the Glut-(PVA/CEA) at PVA high molecular weight cover the ranges of 1.4, 2.6, 4.4, and 0.7 MPa of the same absorbed dose. However, in the case of the Glut-

(PVA/CEA)-FULL-C60 at the PVA low molecular weight the E_r values span, the ranges of 22, 19, 16, and 9.1 MPa. The E_r values at the PVA high molecular weight span in the ranges of 2, 0.7, 0.7, and 0.5 MPa as presented in Table (2). The variation in rubbery modulus is significant and could be attributed to the addition of the CEA. The presence of FULL-C60 acts as fillers, and finally the absorbed dose in kGy. According to these results, the elevated rubbery modulus could be ascribed to the higher crosslink-density in the Glut-(PVA/CEA) and Glut-(PVA/CEA)-FULL-C60, in addition to the effect of the irradiation dose and the PVA molecular weights.

Loss modulus parameters

Figure 7(A, C) presents the loss modulus (E'') of the blank Glut-(PVA-CEA) at PVA molecular weight 16×10^3 g/mole, PVA molecular weight 146×10^3 g/mole and Fig.7(B, D) presents the E'' of the Glut-(PVA/CEA)-FULL-C60 at both PVA molecular weights irradiated at 150 kGy, as a

function of the FULL-C60 concentration 0 - 0.5 percentage. The PVA composites show a peak transition temperature. The irradiated Glut-(PVA-CEA) exhibited a greater E'' than the unirradiated one in both of the PVA molecular weights. This may be due to the crosslinking effect of gamma irradiation.

It is clear that the variance of the loss modulus values is affected by the addition of FULL-C60 to

maximum corresponding approximately to the glass

the (PVA/CEA) network in different concentrations. Also the effect of PVA molecular weights shifts the loss modulus due to interactions between polymer chains and FULL-C60. The filler concentration and PVA molecular weights were effective in the loss modulus values

Table (2): Tan Delta and rubbery modulus of FULL-C60 at concentration of 0.5 % using two molecular weights of PVA as a function of absorbed dose up to 300 kGy for blank Glut-(PVA/CEA) and Glut-(PVA/CEA)-FULL-C60

	Samples detail	FULL-C60 Conc.	Dose kGy	Tan δ °C	Rubbery modulus (MPa) at 150 °C
PVA molecular weights 16×10^3 g/mole	Glut-(PVA/CEA)	0.0	0	20	1.1
		0.0	50	95	15
		0.0	150	19	38
		0.0	300	14	12
	Glut-(PVA/CEA)-FULL-C60	0.5	0	111	21
		0.5	50	44	19
		0.5	150	45	15
PVA molecular weights 146×10^3 g/mole	Glut-(PVA/CEA)	0.0	0	-2	1.4
		0.0	50	36	2.6
		0.0	150	35	4.4
		0.0	300	31	0.7
	Glut-(PVA/CEA)-FULL-C60	0.5	0	16	2
		0.5	50	103	0.7
		0.5	150	155	0.7
		0.5	300	105	0.5

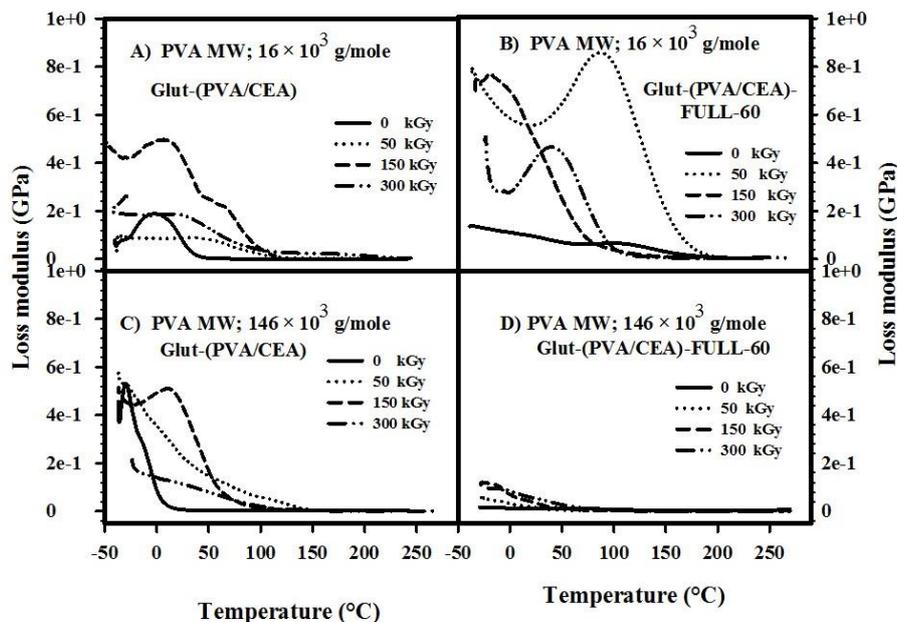


Figure (7): Loss modulus of FULL-60 concentration 0.5 % as a function of absorbed dose up to 300 kGy. (A): Blank Glut-(PVA-CEA) of PVA molecular weights 16×10^3 g/mole, (B): Glut-(PVA/CEA)-FULL-C60 of PVA molecular weights

16×10^3 g/mole, (C): Blank Glut-(PVA-CEA) of PVA molecular weights 146×10^3 g/mole and (D): Glut-(PVA/CEA)-FULL-C60 of PVA molecular weights 146×10^3 g/mole

Conclusions

The preparation and characterization of chemical crosslinked poly (vinyl alcohol) of molecular weights 16×10^3 g/mole and 146×10^3 g/mole in the presence of 2-carboxyethyl acrylate oligomers and fullerene (FULL-C60) fillers followed by gamma irradiation were conducted. The swelling and gelation behavior of the prepared nanocomposite were studied. A significant reduction in swelling and an increase in gelation of both unirradiated and irradiated glutaraldehyde crosslinked nanocomposites were observed. The scanning electron microscopy micrographs of the Glut-(PVA-CEA)-FULL-C60 nanocomposites were investigated showing a homogeneous distribution of composite matrix. The results of TGA analyses indicated that the FULL-C60 addition and the exposure to gamma radiation improve the thermal stabilities of chemical crosslinking polymeric nanocomposites. The dynamic mechanical analysis with the Tan Delta with temperature values around T_g . The storage modulus (E'), loss modulus (E''), and E_r were determined for the irradiated Glut-(PVA-CEA) and Glut-(PVA-CEA)-Fillers. The fullerene C60 and the gamma irradiation improve the thermal and mechanical properties of the chemical crosslinking PVA nanocomposites.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this study.

Acknowledgment

The research team expresses great appreciation to KACST (KACST ASTP-09) for funding this project.

References

1. Kroto H. The Birth of C60: Buckminsterfullerene 1993;117:1–7. https://doi.org/10.1007/978-3-642-85049-3_1.
2. Zuev V V. Polymer nanocomposites containing fullerene C60 nanofillers. *Macromol Symp* 2011;301:157–61. <https://doi.org/10.1002/masy.201150320>.
3. Cadek M, Coleman JN, Barron V, Hedicke K,

- Blau WJ. Morphological and mechanical properties of carbon-nanotube-reinforced semicrystalline and amorphous polymer composites. *Appl Phys Lett* 2002;81:5123–5. <https://doi.org/10.1063/1.1533118>.
4. Sumlo Iijima. Helical microtubules of graphitic carbon. *Nature* 1991;354:56–8.
5. [Iijima S. Direct Observation of the Tetrahedral Bonding in Graphitized Carbon Black By. *J Cryst Growth* 1980;50:675–83.
6. [6] Anufrieva EV, Krakovyak MG, Anan'eva TD, Nekrasova TN, Smyslov RY. Interaction of polymers with fullerene C60. *Phys Solid State* 2002;44:461–2. <https://doi.org/10.1134/1.1462672>.
7. Hurtgen M, Debuigne A, Mouithys-Mickalad A, Jérôme R, Jérôme C, Detrembleur C. Synthesis of poly(vinyl alcohol)/C60 and poly(N-vinylpyrrolidone)/C60 nanohybrids as potential photodynamic cancer therapy agents. *Chem - An Asian J* 2010;5:859–68. <https://doi.org/10.1002/asia.200900277>.
8. Wen X, Min J, Tan H, Gao D, Chen X, Szymańska K, et al. Reactive construction of catalytic carbonization system in PP/C60/Ni(OH)₂ nanocomposites for simultaneously improving thermal stability, flame retardancy and mechanical properties. *Compos Part A Appl Sci Manuf* 2020;129. <https://doi.org/10.1016/j.compositesa.2019.105722>.
9. Fang H, Bai SL, Wong CP. Microstructure engineering of graphene towards highly thermal conductive composites. *Compos Part A Appl Sci Manuf* 2018;112:216–38. <https://doi.org/10.1016/j.compositesa.2018.06.010>.
10. Gandhi M V., Thompson BS, Kasiviswanathan SR, Choi SB. A collage of experimental investigations on smart fibrous composite structures and mechanical systems featuring electro-rheological fluids, piezoelectric materials and fiber-optic sensors. *Compos Eng* 1992. [https://doi.org/10.1016/0961-9526\(92\)90043-6](https://doi.org/10.1016/0961-9526(92)90043-6).
11. Cheng X, Putz KW, Wood CD, Brinson LC. Characterization of local elastic modulus in confined polymer films via AFM indentation. *Macromol Rapid Commun* 2015;36:391–7. <https://doi.org/10.1002/marc.201400487>.
12. Raafat AI, Abd-Allah WM. In vitro apatite forming ability and ketoprofen release of radiation synthesized (gelatin-polyvinyl alcohol)/bioglass composite scaffolds for bone tissue regeneration. *Polym Compos* 2018;39:606–15.

- <https://doi.org/10.1002/pc.23974>.
13. Saif MJ, Naveed M, Asif HM, Akhtar R. Irradiation applications for polymer nanocomposites: A state-of-the-art review. *J Ind Eng Chem* 2018;60:218–36. <https://doi.org/10.1016/j.jiec.2017.11.009>.
 14. Szafulewa K, Wach RA, Olejnik AK, Rosiak JM, Ulański P. Radiation synthesis of biocompatible hydrogels of dextran methacrylate. *Radiat Phys Chem* 2018;142:115–20. <https://doi.org/10.1016/j.radphyschem.2017.01.004>.
 15. A. Abaza, E. A. Hegazy, Ghada. A. Mahmoud, B. Elsheikh. Characterization and Antitumor Activity of Chitosan/Poly (Vinyl Alcohol) Blend Doped with Gold and Silver Nanoparticles in Treatment of Prostatic Cancer Model. *J Pharm Pharmacol* 2018;6:659–73. <https://doi.org/10.17265/2328-2150/2018.07.003>.
 16. Hegazy E-SA, Abd El-Rehim HA, Khalifa NA, Atwa SM, Shawky HA. Anionic/Cationic Membranes Obtained by a Radiation Grafting Method for Use in Waste Water Treatment. *Polym Int* 1997;43:321–32. [https://doi.org/10.1002/\(sici\)1097-0126\(199708\)43:4<321::aid-pi756>3.0.co;2-j](https://doi.org/10.1002/(sici)1097-0126(199708)43:4<321::aid-pi756>3.0.co;2-j).
 17. Ali AEH, Raafat AI, Mahmoud GA, Badway NA, El-Mottaleb MA, Elshahawy MF. Photocatalytic Decolorization of Dye Effluent Using Radiation Developed Polymeric Nanocomposites. *J Inorg Organomet Polym Mater* 2016;26:606–15. <https://doi.org/10.1007/s10904-016-0346-2>.
 18. Du H, Zhang J. Shape memory polymer based on chemically cross-linked poly(vinyl alcohol) containing a small number of water molecules. *Colloid Polym Sci* 2010;288:15–24. <https://doi.org/10.1007/s00396-009-2117-x>.
 19. Dubey KA, Bhardwaj YK, Chaudhari C V, Sabharwal S. LDPE / EVA / PCR / MWNT Nanocomposites : Radiation Crosslinking and Physicomechanical Characteristics 2011. <https://doi.org/10.1002/pc>.
 20. Lotfy S, Atta A, Abdeltwab E. Comparative study of gamma and ion beam irradiation of polymeric nanocomposite on electrical conductivity. *J Appl Polym Sci* 2018;135:46146. <https://doi.org/10.1002/app.46146>.
 21. Basfar AA, Lotfy S. Radiation-crosslinking of shape memory polymers based on poly(vinyl alcohol) in the presence of carbon nanotubes. *Radiat Phys Chem* 2015;106:376–84. <https://doi.org/10.1016/j.radphyschem.2014.08.024>.
 22. Ge Q, Luo X, Rodriguez ED, Zhang X, Mather PT, Dunn ML, et al. Thermomechanical behavior of shape memory elastomeric composites. *J Mech Phys Solids* 2012;60:67–83. <https://doi.org/10.1016/j.jmps.2011.09.011>.
 23. Alfayyadh AAM, Lotfy S, Basfar AA, Khalil MI. Influences of poly (vinyl alcohol) molecular weight and carbon nanotubes on radiation crosslinking shape memory polymers. *Prog Nat Sci Mater Int* 2017;27. <https://doi.org/10.1016/j.pnsc.2017.04.015>.
 24. Du H, Zhang J. Solvent induced shape recovery of shape memory polymer based on chemically cross-linked poly(vinyl alcohol). *Soft Matter* 2010;6:3370. <https://doi.org/10.1039/b922220k>.
 25. Hirai T, Maruyama H, Suzuki T, Hayashi S. Effect of chemical cross-linking under elongation on shape restoring of poly(vinyl alcohol) hydrogel. *J Appl Polym Sci* 1992;46:1449–51. <https://doi.org/10.1002/app.1992.070460815>.
 26. Andersson MG, Jarvid M, Johansson A, Gubanski S, Foreman MRSJ, Müller C, et al. Dielectric strength of γ -radiation cross-linked, high vinyl-content polyethylene. *Eur Polym J* 2015;64:101–7. <https://doi.org/10.1016/j.eurpolymj.2014.11.042>.
 27. Cui H, Yan X, Monasterio M, Xing F. Effects of Various Surfactants on the Dispersion of MWCNTs–OH in Aqueous Solution. *Nanomaterials* 2017;7:262. <https://doi.org/10.3390/nano7090262>.
 28. Zhogova KB, Davydov IA, Punin VT, Troitskii BB, Domvachiev GA. Investigation of fullerene C60 effect on properties of polymethylmethacrylate exposed to ionizing radiation. *Eur Polym J* 2005;41:1260–4. <https://doi.org/10.1016/j.eurpolymj.2005.01.010>.