The Use of Gamma Irradiation to Induce the Miscibility between Urea-Formaldehyde and Vinyl Acetate Versatic Ester Copolymer Latex Blend

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ABSTRACT: The objective of this research was to investigate the miscibility behavior of urea-formaldehyde (UF) resin and vinyl acetate versatic ester copolymer latex (VAcVe) blends. Blend of various compositions of UF resin as thermoset polymer and VAcVe as thermoplastic polymer were prepared. This study shows how the addition of VAcVe latex can alter the behavior of UF resin toward hardness, press-ability, and inhibition of cracks occurred in the UF resin films and moulds. After that, these blends (UF/VAcVe) were irradiated with gamma rays in different doses. Physical properties such as solubility percent, water absorption behavior in water, and effect of dilute acid and dilute alkali were studied. Thermogravimetric analysis shows that VAcVe is more stable against thermal decomposition than UF resin over the entire temperature range studied. Also, the thermal stability of polymer blends (UF/VAcVe) increases with increasing the ratio of VAcVe component in the blend. The influence of addition of VAcVe on compressive strength was studied. The results showed an improvement with a decrease in compressive strength due to the flexibility, this improvement is related to the amount of VAcVe. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: urea formaldehyde; vinyl acetate versatic ester; radiation; thermal properties

INTRODUCTION

Urea-formaldehyde resins are the most prominent examples of the class of thermosetting resins usually referred to as amino resins. Urea-formaldehyde resins comprise about 80% of the amino resins produced world wide.[1–3] The principal attractions of urea-formaldehyde resins are water solubility before curing, which allows easy application to and with many other materials, colorlessness, which allows unlimited colorability with dyes and pigments, excellent solvent resistance in the cured state, outstanding hardness and abrasion resistance, good heat resistance, and low cost.[4,5] However, the acceptance of urea-formaldehyde as a universal material in many engineering areas is impeded by some of its inherent qualities such as brittleness, poor water resistance, and formaldehyde emission.[6,7] A significant improvement in the durability of urea-formaldehyde (UF) resin would broaden the application and markets for its products.[8] So improving the moisture resistance and toughness of UF resin has been a focus of research for several decades.[9–11] The most successful attempt to modify UF resin appears to be the work of Rachtanapun and Heiden,[12] who introduced different thermoplastics into aqueous UF resin suspensions to improve both the toughness and the hydrolytic resistance of UF resin. Greater moisture resistance has also been reported when additives such as amines were incorporated into the UF resin.[13–15] The future for amino resins seems secure because they can provide qualities that are not easily obtained in other ways. New developments will probably be in the areas of more highly specialized materials for treating textiles, paper, etc., and for use with other resins in the formulation of surface coatings, where a small amount of an amino resin can significantly increase the value of a more basic material. Vinyl acetate versatic ester copolymer (VAcVe) latex having higher bond strength and better film properties has grown considerably in the past two decades in the adhesive, paint, paper, and textile industries.[16] It comes in a white liquid form, an odorless and nonflammable adhesive. Its application is very easy and it does not damage the tools during the cutting process. When polyvinyl acetate was added to melamine-formaldehyde polymer, and the blend used as wood adhesive, the formaldehyde emission was dramatically reduced.[17]

The aim of this work is the study of the miscibility behavior of UF resin and VAcVe prepared blends.

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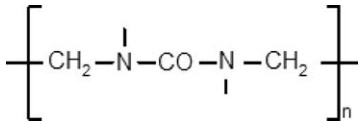
Solubility% of the irradiated prepared blends was calculated, thermogravimetric analysis (TGA) and scanning electron microscope (SEM) to determine the miscibility behavior of UF/VAcVe blend to reduce formaldehyde emission level, cracking, and stiffness. For these purposes, different compositions of VAcVe copolymer latex and UF resin were blended in different ratios and subjected to different gamma irradiation doses.

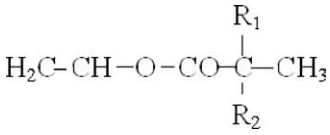
EXPERIMENTAL

Materials

UF was supplied by El-Mansoura for Particle Wood and Resins, Egypt.



VAcVe was purchased from Tibah chemicals, Egypt, which has milky white appearance, pH 5–7, density 1.1 g cm^{-3}, and solid content 50 ± 1%.



Blend preparation

The polymer films were prepared by using casting method. UF solution was prepared by dissolving a known weight of UF in hot water. After complete solubility, UF solution was mixed with VAcVe emulsion with different ratios (0/100, 20/80, 50/50, 80/20, and 100/0) by weight of (UF/VAcVe) polymer blend at room temperature with continuous stirring till obtain a homogenous solution. After that, all the prepared blends were irradiated at different gamma irradiation doses (25, 50, 100, and 200 kGy).

Gamma irradiation

Irradiation to the required doses was carried out with ^{60}Co gamma source (made in India) at the National Center for Radiation Research and Technology, Cairo, Egypt. The polymer blend films were exposed to gamma irradiation in air at a dose rate 6.92 kGy h^{-1}.

Mass loss % determination

The mass loss % was determined by soaking known weight (W_0) of unirradiated and irradiated blends in water for 24 h at 100°C. After that, the samples were taken out and washed with water to remove the soluble parts. The samples were dried and weighed again (W). The mass loss % was determined from the following equation:

$$\text{Mass loss}\,(\%) = (W_0 - W/W_0) \times 100$$

where W and W_0 are the weight of the dried sample after and before extraction, respectively.

Water absorption

A known dry weight of the sample (W_1) was immersed in distilled water for 24 h at room temperature. Then the sample was removed and blotted on filter paper to remove the excess of water on the surface then weighed (W_2). The water absorption percentage is determined by the following equation:

$$\text{Water absorption}\,(\%) = [(W_2 - W_1)/W_1] \times 100$$

where W_1 and W_2 represent the weight of the dry and wet samples, respectively.

Chemical stability toward acid and alkali

The chemical stability of the unirradiated and irradiated blends was tested by soaking in 0.1*N* NaOH and dilutes HCl for 2 h.

IR spectroscopic analysis

FTIR spectrophotometer model Mattson 100, made by Unicam (UK) was used for FTIR measurements over the range 500–4000 cm^{-1}.

Thermogravimetric analysis

The TGA studies were carried out on Shimadzu-30 (TGA-30) at heating rate 10°C min^{-1} in air over a temperature range from room temperature up to 600°C. The weight loss was recorded for pure polymers and blends in the presence of flowing nitrogen gas and using a constant rate of heating.

Scanning electron microscope measurements

SEM was used to examine the morphology of the fracture surfaces of pure polymers and blends. Scanning electron micrographs were taken with a JSM-5400 instrument manufactured by Joel, Japan. A sputter coater was used to precoat conductive gold onto fracture surfaces before observing the microstructure.

Compacting and compressive strengths

The compressive strength test was done using EL39-6155/01 ADR-Auto 250/25 mortar compression machine. Samples were prepared by pouring

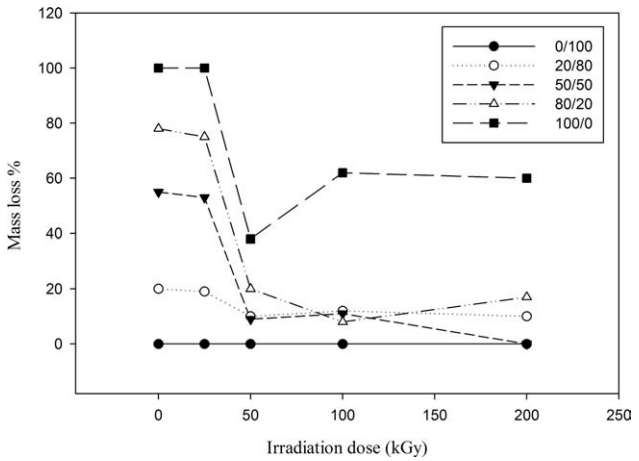


Figure 1 Effect of different gamma irradiation doses on mass loss % of (UF/VAcVe) blends with different compositions.

unirradiated and irradiated blend solutions into standard cubic shelf with dimensions (2 × 2 × 2 cm) then left for 1 day till setting. Samples were taken randomly from shelf and checked for cleanliness. At the age of 1 day, three cubes were removed from the shelf. Each cube was then positioned in the compressive machine with the cast faces in contact with the platens. These procedures were applied onto the remaining two samples, and the average reading was taken as the compressive strength.

RESULTS AND DISCUSSION

One major problem in the uses of UF resin is its limited process ability due to its brittleness and poor water resistance.[6,7] Therefore, it is difficult to make a good film from UF resin for industrial applications. To overcome this problem, VAcVe was mixed with UF resin in different weight ratios and exposing these blends to different doses of gamma irradiation. Many studies were carried out to determine the optimum dose and blend compositions which give a good blend with good properties suitable for industrial applications.

Mass loss %

UF resin is soluble in hot water, whereas VAcVe is insoluble. Therefore, it was necessary to examine the solubility of their blends after being irradiated to different gamma irradiation doses. Hence, pure UF resin, VAcVe and their blends were irradiated to 25, 50, 100, and 200 kGy. The results obtained are shown in Figure 1. From these results, it was noted that the crosslinking of UF resin under the effect of gamma irradiation occur at 50 kGy and increase with increasing gamma irradiation doses. On the other hand, the mass loss % of pure VAcVe is not affected by different gamma irradiation doses that it still insoluble in water and has a mass loss % value equal to (0%). Moreover, it was found that for all blend samples, there is decrease in mass loss % on increasing irradiation doses up to 50 kGy. After that, there is a leveling off in mass loss % values. Also, increasing the UF resin content in the blend results in mass loss % increase for all the unirradiated and irradiated blends but not with the same rate.

The results of mass loss clearly demonstrate that the ionizing radiation could induce the crosslinking between the blend components at all composition ratios. Gamma irradiation may stimulate the formation of radicals from UF resin and also sustained the life of radicals longer which results in high efficiency of crosslinking in the blends. Also, mass loss % results gave a good indication for the compatibility between the two polymers could be achieved and confirmed.

The mass loss study reveals that the optimum conditions for preparing (UF/VAcVe) blend are blend composition (20/80) and irradiation dose 50 kGy.

TABLE I
Water Absorption % of UF/VAcVe Blend with Different VAcVe Content as a Function of Irradiation Doses

	Water absorption % at different irradiation doses (kGy)			
Blend compositions	0	50	100	200
UF 20 : VAcVe 80	18.8	7.6	7.5	7.4
UF 50 : VAcVe 50	15.6	7.4	6.5	6.5
UF 80 : VAcVe 20	12.2	4.1	3.8	3.6

Water absorption

The water absorption % of UF/VAcVe blend with different VAcVe content as a function of irradiation doses are shown in Table I.

Generally, the water absorption percent of all unirradiated and irradiated blend compositions posses a low values independent on blend composition. On the other hand, there is a decrease in the water absorption percent after irradiation to 50 kGy for all the blend compositions. More increase in the irradiation doses to 100 and 200 kGy leads to a partially leveling off in the water absorption percent values. Thus, the lower water absorption ratios observed in the blend systems might be explained by the occurrence of hydrogen

TABLE II
Chemical Stability of UF/VAcVe Blends Toward 0.1*N* NaOH

	Swelling % at different irradiation doses (kGy)			
Blend compositions	0	50	100	200
UF 20 : VAcVe 80	17.2	7.6	5.3	7.5
UF 50 : VAcVe 50	14.3	4.4	4.4	2.7
UF 80 : VAcVe 20	13.2	2.7	2.7	1.7

TABLE III
Chemical Stability of UF/VAcVe Blends Toward Dilute HCl

	Swelling % at different irradiation doses (kGy)			
Blend compositions	0	50	100	200
UF 20 : VAcVe 80	5.4	3.9	2.3	1.2
UF 50 : VAcVe 50	5.8	2.1	1.1	1.1
UF 80 : VAcVe 20	8.8	0.5	0.7	0.6

bonding between UF resin and VAcVe which leads to a sort of physical crosslinking.[18]

Chemical stability toward acid and alkali

Tables II and III show the chemical stability of UF/VAcVe blends toward 0.1*N* NaOH and dilutes HCl for 2 h of immersion time period.

The treatment with either 0.1*N* NaOH or dilute HCl shows low swelling values which permit the use of this blend as joint filler in the flooring without any susceptible damage from the usage of acidic or alkaline detergent.

FTIR analysis

FTIR is a particularly suitable method to determinate the presence of specific interactions between various groups in polymer blends from the force constants, and it is sensitive to both intermolecular and intramolecular interactions.[19] Figure 2 represents FTIR spectra of unirradiated pure UF, VAcVe, and their blends with different ratios. The IR spectrum of UF resin is characteristic with the following stretching vibration bands as N—H stretching vibration at 3400 cm^{-1} which is confirmed by its bending band at 850 cm^{-1} and the C—H stretching of the methelyene group at 2950 cm^{-1} which is confirmed by its bending band at 780 cm^{-1}. The carbonyl group C=O appeared at 1680 cm^{-1} with some lower frequency due to some keto-enol toutomerism structure with neighboring groups as N—H group. Furthermore, C=N has a vibrational stretch at 1590 cm^{-1}. Single stretching vibration bands appear for C—O and C—N stretching at 1400 and 1150 cm^{-1}, respectively. The IR spectrum of VAcVe copolymer latex shows the bands at 820 and 690 cm^{-1} are attributed to C—C and C=C stretching vibrations. The absorption bands at 1090 and 1730 cm^{-1} are due to stretching vibration of C=O group. The bands at 1408 and 2900 cm^{-1} are due to the asymmetrically stretching vibration of C—H group. The absorption bands 1190 cm^{-1} is assigned to ether linkage.

In fact, most of the thermosetting polymer blends studied so far are found to be immiscible except in the presence of favorable intermolecular specific

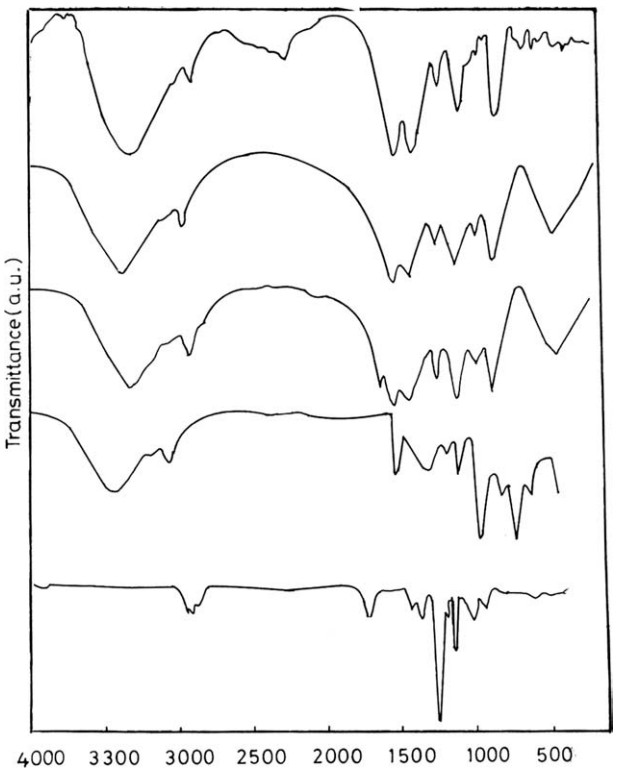


Figure 2 FT-IR spectra of unirradiated pure UF, (80% UF/20% VAcVe), (50% UF/50% VAcVe), (20% UF/80% VAcVe) and pure VAcVe (from up to down).

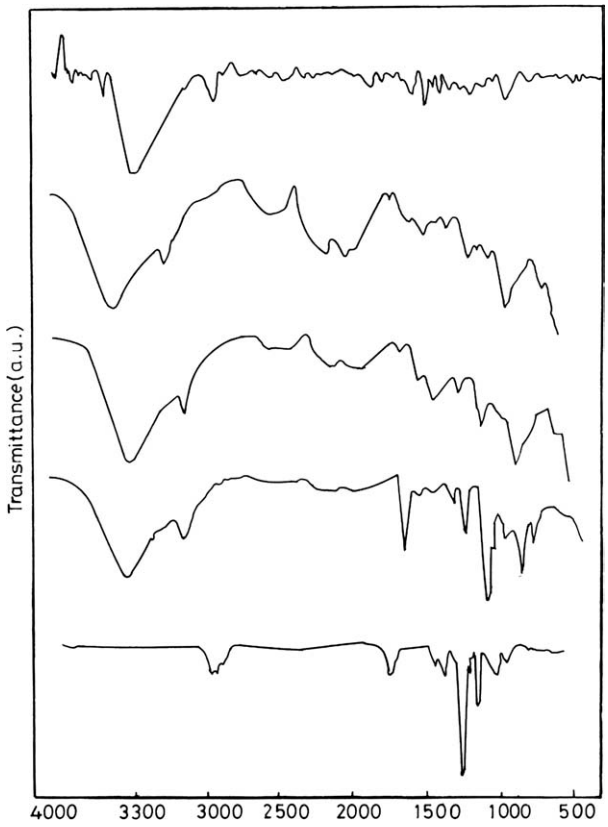


Figure 3 FT-IR spectra of irradiated pure UF, (80% UF/20% VAcVe), (50% UF/50% VAcVe), (20% UF/80% VAcVe) and pure VAcVe (from up to down).

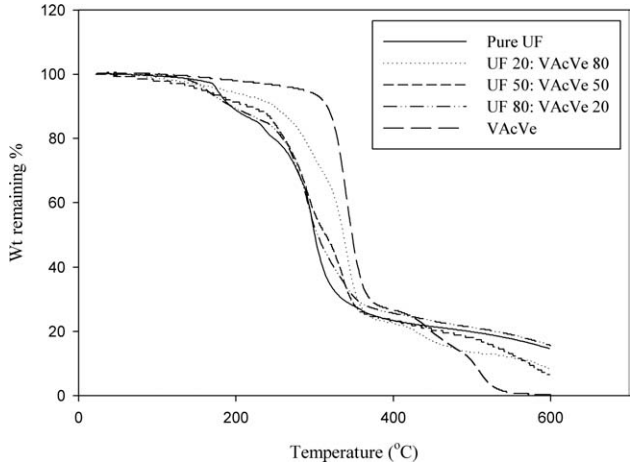


Figure 4 TGA thermograms of unirradiated UF/VAcVe polymer blends.

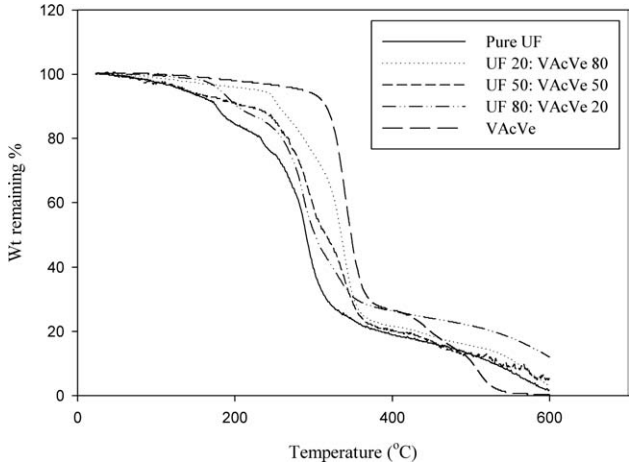


Figure 6 TGA thermograms of different UF/VAcVe polymer blends irradiated to 100 kGy.

interactions (e.g., hydrogen bonding), and these intermolecular-specific interactions have been taken as the driving force for miscibility in some thermosetting polymer blends.[20] Figure 3 represents FTIR spectra of irradiated pure UF, VAcVe, and their blends with different ratios. From this figure, it can be observed that C=O peak disappeared in the pure irradiated UF resin and all irradiated blends. This phenomenon reveals that a new pattern of hydrogen bonding formation results from the competition between amine–amine and amine–carbonyl interactions. Therefore, the amine group of the UF resin and the carbonyl group of VAcVe have strong hydrogen bonding. In general, FTIR results indicated the interactions between functional groups in UF resin and VAcVe.

Thermal analysis

Thermal decomposition behavior (TGA)

The thermal decomposition behavior of unirradiated and irradiated pure UF resin and VAcVe and their blends with different ratios was studied, and the results obtained are shown in Figures 4–6. Table IV summarizes the weight loss % at different decomposition temperature range up to 400°C for the unirradiated and irradiated pure UF resin and VAcVe and their blends with different ratios. It can be seen that unirradiated pure UF resin and VAcVe lose about 52.5 and 5.6% of their weight at 300°C. Thus, it may be concluded that the unirradiated VAcVe is more stable against thermal decomposition than the unirradiated UF resin over the entire range of studied temperature. Moreover, it was noted that there is no marked effect of irradiation at different doses on both pure UF resin and VAcVe. Unirradiated and irradiated UF/VAcVe blends with all its ratios had a higher thermal stability than pure UF resin especially polymer blends rich in VAcVe. For unirradiated and irradiated blends, there is an increase in

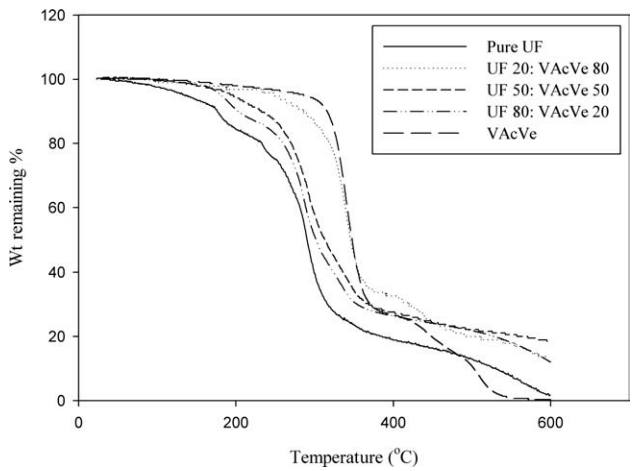


Figure 5 TGA thermograms of different UF/VAcVe polymer blends irradiated to 50 kGy.

TABLE IV
The Weight Loss Percent of Unirradiated and Irradiated Pure UF, VAcVe, and Their Blends with Different Ratios at Different Decomposition Temperatures

Blend composition (UF : VAcVe)	Irradiation dose (kGy)	Weight loss (%)			
		100°C	200°C	300°C	400°C
(100 : 0)	0	2.5	9.6	52.5	81.8
	50	2.4	15.5	60.5	81.2
	100	0.57	11.3	50.4	76.7
(80 : 20)	0	0.27	10.5	47.7	74.4
	50	0.4	9.4	49.1	73.7
	100	1.2	10.3	51.8	77.4
(50 : 50)	0	2.2	8.9	43.5	76.8
	50	0	5.4	42.2	72.4
	100	2.7	8.9	41.5	79.5
(20 : 80)	0	1.3	5.8	25.9	77.7
	50	1.1	3.2	13.7	67.4
	100	1.1	4.1	12.5	78.3
(0 : 100)	0	0	1.4	5.6	74.3
	50	0	2.03	6.1	73.2
	100	0	0.78	4.3	71.8

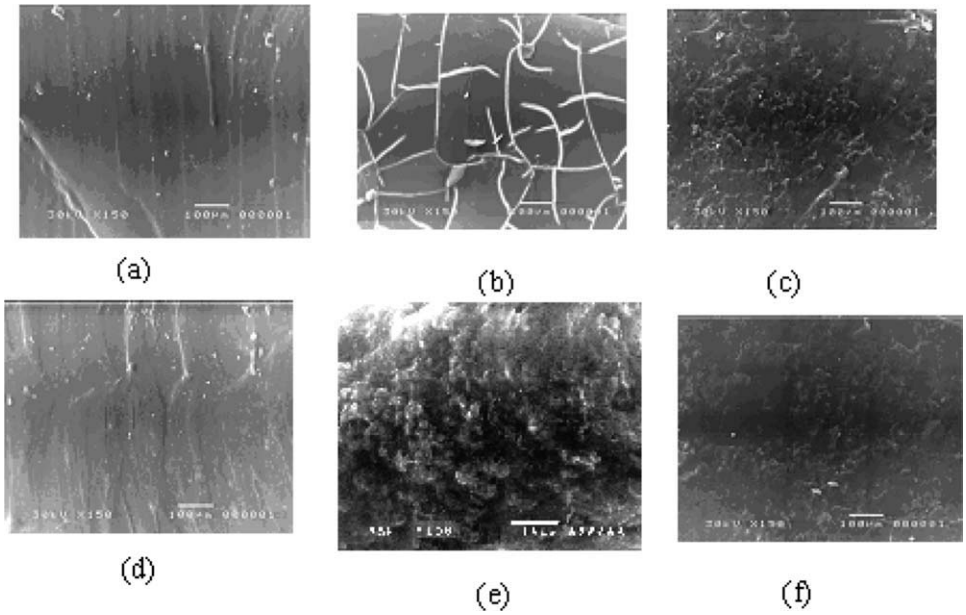


Figure 7 Scanning electron micrographs of (a) unirradiated VAcVe, (b) unirradiated UF, (c) unirradiated 20% UF/80% VAcVe blend, (d) irradiated VAcVe, (e) irradiated UF, (f) irradiated 20% UF/80% VAcVe blend.

the thermal stability at 100, 200, and 300°C on increasing VAcVe content. Also, the values of weight loss % are lower for the irradiated blend than unirradiated ones which reveal higher thermal stability of the irradiated blends. An important remark is that blend which contains UF/VAcVe (20/80) irradiated at 50 kGy posses the higher thermal stability at all decomposition temperature, as for example, the weight loss % at 300 and 400°C is equal to 13.7 and 67.4%, respectively, which is the lowest values than all other unirradiated and irradiated blends. This thermal stability may be due to the nature of VAcVe as thermoplastic polymer which posses a combination of physical and rheological properties that are unavailable in pure UF resin.[21]

Scanning electron microscopy

From Figure 7, it can be seen that micrographs (a, b, and c) represents the fracture surface of unirradiated pure VAcVe, UF resin, and (UF : VAcVe 20 : 80) blend. From which it can be observed that pure VAcVe appears as a blank homogeneous phase, whereas pure UF resin micrograph indicates clearly longitudinal cracks which run through the UF matrix. While the micrograph of (UF : VAcVe, 20 : 80) blend shows a homogeneous phase between the two polymers which indicates the compatibility between the blend components because the addition of VAcVe increase the blend elasticity which may be act as crack inhibitor.

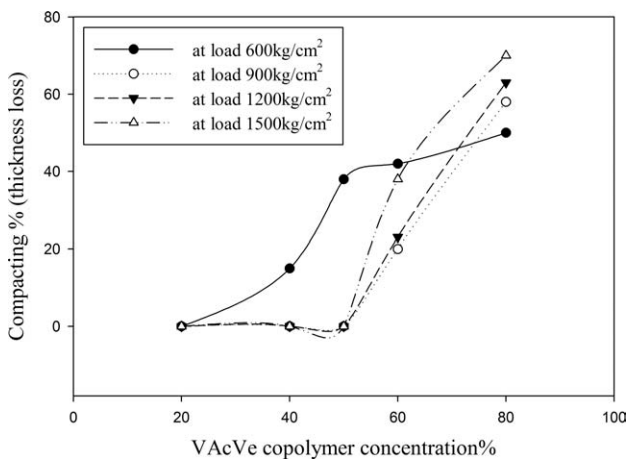


Figure 8 Effect of VAcVe ratio on compacting percent (thickness loss) at different loads of unirradiated UF/VAcVe blend mold.

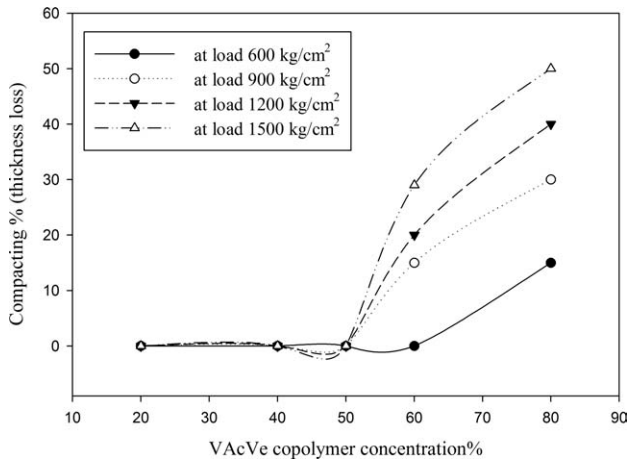


Figure 9 Effect of VAcVe ratio on compacting percent (thickness loss) at different loads of irradiated UF/VAcVe blend mold at 50 kGy.

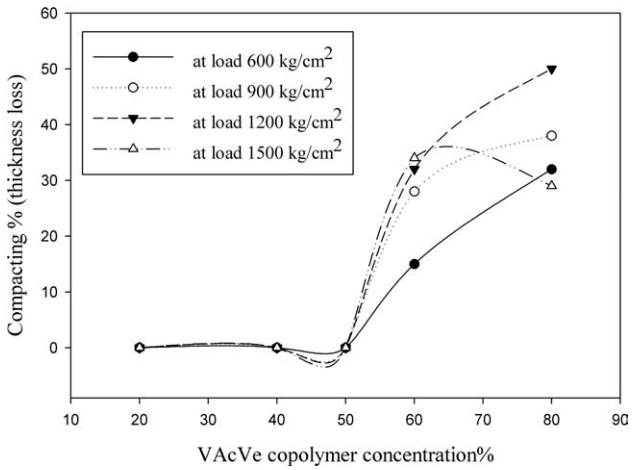


Figure 10 Effect of VAcVe ratio on compacting percent (thickness loss) at different loads of irradiated UF/VAcVe blend mold at 200 kGy.

Micrographs (d, e, and f) represents the fracture surface of irradiated pure VAcVe, UF resin, and (UF : VAcVe 20 : 80) blend at 50 kGy. From which it can be observed that irradiation has no effect on the homogeneity of fracture surface of VAcVe. While in case of irradiated UF resin, there is a clear rearrangement in the structure of the polymer due to the occurrence of some sort of crosslinking. Moreover, in micrograph (f), a large plate appeared after irradiation of the VAcVe/UF blend giving a pronounced crosslinking between UF resin and VAcVe which give more compatibility.

Compacting and compressive strength

This study offers a compatible blend of thermoset/thermoplast as a mold able to compact without breakness up to 80% decrease in the thickness from the initial thickness of the original mold (expressed as thickness loss after pressing).

Figure 8 shows the effect of VAcVe composition on compacting percent (thickness loss) at different loads of unirradiated UF/VAcVe blend mold. This figure indicates that the blends possess compacting behaviors which increase with increasing of VAcVe content in the blend. VAcVe changes the thermosetting behavior of UF resin to be more elastic due to the incorporation of chemically reactive groups into copolymer's main chain, the crosslinking reactions between latex particles and UF resin. This change from hard to elastic is confirmed a physicochemical compatibility between UF resin and VAcVe. On the other hand, the increase of UF content in the blend increase the compressive strength, where the increase of UF resin leads to more hardness that cause the blend to be more brittle and sensitive to induce the breakness at the same load of compacting, where the compression at break began after the ultimate compacting had been achieved.

Figures 9 and 10 show the effect of VAcVe on compacting percent (thickness loss) at different loads of irradiated UF/VAcVe blend mold at 50 and 200 kGy. It was shown that the irradiation doses do not affect the compacting and compressive strength showing that the blend has a stable mechanical behavior toward the exposure to irradiation.

CONCLUSIONS

This work describes the preparation of UF/VAcVe blend which has been blended with different ratios and subjected to different gamma irradiation doses. Mass loss %, water absorption, morphological, thermal, and mechanical properties of the blends were investigated. The results presented confirm that the addition of VAcVe to UF resin made a significantly improvement in UF resin properties. Also, changes the thermosetting behavior of UF resin to be more elastic. Thermal analysis showed that all blends, especially blends with high VAcVe ratio, displayed a high thermal stability than pure UF. From this study, it can be concluded that blend composed of 20% UF : 80% VAcVe irradiated at 50 kGy is the best prepared blend. The study offers different properties and applications from the prepared blend that could be as the following: reducing the release of formaldehyde emission; the resistively toward hot water, acid, and alkali media; the mechanical stability toward the radiation environment that let the blend to be recommended for exterior environmental application.

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