Effect of Ionizing Irradiation and Blending of Natural Rubber Latex on Polyvinylalcohol Gelation by Using Chemical and Freezing–Thawing Processes for Use in the Field of Construction Engineering

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ABSTRACT: The aim of this work is to study the gelation behavior of polyvinylalcohol (PVA) and natural rubber latex (NRL) using two methods: The first was chemical gelation by adding sodium borate as a crosslinking to obtain a modeling clay gel able to draw easily under tension (using drum mill) or by using hand pressing. Irradiation was then applied at 2.5 Mrad to possess more crosslinking effect, where stable and rubbery-gel shape in the dimension was obtained. The second method, where samples of liquid PVA were frozen and thawed for three consecutive cycles. The obtained gel was quite rubbery but completely soluble in hot water at 70°C. Irradiation was performed at 2.5 Mrad to produce a highly rubbery gel and resistant to boiled water. Also, blending of NRL with PVA induced a significant increase in gel-elasticity and resistivity to boiled water. Factors affecting the properties of the prepared gel such as gel draw ability and gel strength were studied. The study was supported with thermal and scanning electron microscopy (SEM) to investigate the modification of PVA-gel behavior through irradiation and blending with NRL processes. The results indicated that the PVA-gel obtained by chemical method or blended with NRL through freezing–thawing gelation gave a superior ability for cement loading. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1073–1080, 2010

Key words: blend; gelation; radiation

INTRODUCTION

Polymer hydrogels have proposed for many applications such as the artificial muscles, sensor systems, and purification of waste water.[1–3] The gelation process of locust bean gum aqueous solution has been prepared and dependent on repeating cycles of the freezing–thawing process and freezing speed. When freezing–thawing was repeated more than three times, the dynamic rigidity of the hydrogel was about 50% more than that of the original polymer solution.

Furthermore, the storage modulus was greater for the hydrogel prepared by 12°C min^{-1} freezing than that by 1°C min^{-1} freezing. These observations are explained in terms of the formation of ice crystals during the freezing process.[4] Dea and coworkers have prepared hydrogels of various polysaccharides by freezing–thawing processes.[5,6] They investigated the gel forming ability in relation to the chemical structures of polysaccharides.

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Polyvinyl alcohol gels play an important role in numerous industrial and environmental applications. The irradiation technique seems to be promising for the preparation of polyvinylalcohol (PVA) gels because the gel is not contaminated with foreign additives and the crosslinking must be composed of chemically stable C—C bonds.[7]

The elastomers of PVA gel were made from the PVA polymer, with boric acid added as a crosslinking agent. Based on these, the PVA shows a good rubber-like elastic.[8,9]

In the field of tissue engineering, PVA scaffolds were prepared by freeze–thaw and progeny (glycerol) methods. The samples were frozen and thawed for three consecutive cycles at −25°C (90 min) and room temperature (60 min).[10]

PVA gels are hydrophilic polymer networks, which have a high capacity to absorb a substantial amount of water. On contrary, natural rubber latex (NRL) gels are hydrophobic polymer networks, which have a high resistivity to swell in or absorb water. Therefore, the PVA/NRL blends at different ratios may offer a partially hydrophilic gel with a new elastomeric properties.

The study discusses the preparation of PVA and NRL gels with two different methods: chemical and freeze–thaw processes and the effect of ionizing

irradiation on each process separately. Also, the effect of blending of NRL with PVA to increase the elastomeric properties of the obtained gel will be investigated. The use of PVA gel and PVA/NRL blend gel for cement loading application will be also discussed.

EXPERIMENTAL

Materials

PVA (MW 70,000–10,000 gm/mol) with degree of hydrolysis 96–98% was purchased from Sigma. NRL with trade name of TOPTEX contains 50% solid content, Malaysia.

Preparation of PVA solution

Homogenous solutions of 10% by weight polymer in water were obtained by first adding the powder in water at ambient temperature, and then heating under reflux and moderate stirring of the solution over 2 h.

Preparation of NRL-PVA blend

The blend of NRL and PVA was carried out by mixing different ratios from NRL and PVA as follows:

25% NRL-75%PVA, 50% NRL-50%PVA, and 75%NRL-25%PVA.

Stirring was applied using mechanical stirrer for 5 min at room temperature.

Cement loading process

Cement loading was applied by using drum mill at 1 mm width to draw PVA gel and adding cement during multidrawing process.

Chemical gelation of PVA and NRL

PVA or PVA/NRL blend and borax solutions at different ratios (1–12%) were applied separately, where a glass or wooden rode was dipped in PVA or PVA/NRL blend solution then in borax solution a complex gel formation occurs on the substrate.

Freezing-thawing gelation of PVA and NRL

Solution of PVA was frozen in a freezer (about $-15^{\circ}C$) for $\sim$ 18 h and was then thawed slowly at room temperature (about 25°C) for at least 6 h. This process is defined as a single freezing–thawing cycle in this study.

Gelation observation

An appropriate amount of a polymer gel sample was placed in a 20 mL glass container with $\sim$ 10 g of deionized water and heated at 105°C for 30 min. The glass container had inner and outer lids, so that the evaporation of water during the heating was assumed to be negligible.

Gel determination

A dried gel was extracted with distilled water for 24 h at 100°C to extract the insoluble parts of gel. The insoluble parts were taken out and washed with hot distilled water for removing the soluble parts and then dried and weighed. This extraction cycle was repeated until the weight became constant. The gel yield in the gel was determined as follows:

$$\text{Gel } (\%) = (W_e/W_d) \text{ X } 100$$

where W_d and W_e represent the weights of the dry gel and the gelled part after extraction, respectively.

SEM

The surface morphology indicated by scanning electron microscopy technique, Jeol (Japan) took the micrographs with a JSA-5400 instrument.

Thermogravimetric analysis

A shimodzu TGA-50 system in a nitrogen atmosphere (20 mL/min) was used. The temperature range was from the ambient temperature to 500°C at a heating rate of 10°C/min.

Gel strength (compression set)

The property is defined as the residual thickness in a gel mold test piece after it has been held under compression to a given thickness for a given time and then allowed to recover for a given time, the temperature being held substantially constant during the test. The result is calculated as the difference between the original thickness of the test piece and after recovery, expressed as percentage of the initial applied compression. The test was carried out using Instron (Model-1195), UK, at a cross speed of 50 nm min^{-1}.

Draw ability % (extended strain)

Defined as the ultimate extension percent of initial strain of the gel after it has been held under compression and tension (drawing) by using drum mill at room temperature.

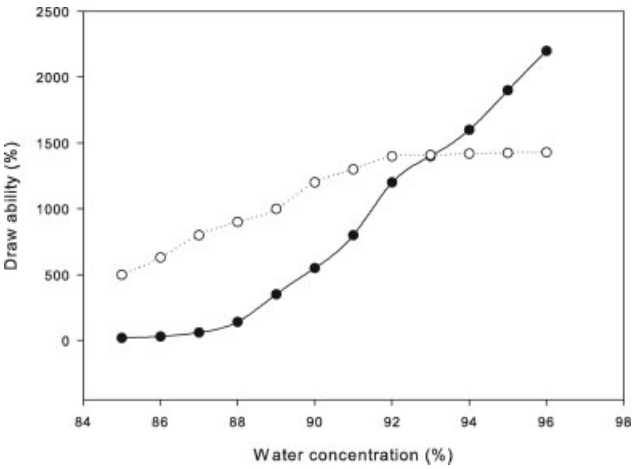

Figure 1 Effect of water concentration percent on draw ability at 2% borax concentration.

Ionizing irradiation

The equipment used for ionizing irradiation was electron accelerator (USA) operating at 1.5 MeV. The samples were put on a mobile plate in the electron accelerator and the selected dose was obtained by varying the number of passages through the scanned electron beam. Every passage resulted in a dose of 2.5 Mrad.

RESULTS AND DISCUSSION

Chemical gelation of PVA and NRL and draw ability behavior

Borax is a particularly effective gelling agent for polyvinyl alcohol solutions giving a modeling clay gel type and PVA/NRL blend giving an elastic gel.

Chemical gelation enhances the performance of the PVA gel to draw and crosslink. The experimental results showed that water exists in PVA gel in a suit amount in different states through hydrogen bonds with PVA and borax concentration added influence the draw ability of PVA gel. But in case of PVA/NRL gel, the draw ability is different as it possesses an elastic behavior giving rubbery properties.

Figure 1 shows the effect of the bounds water ratios with PVA, and PVA/NRL blend gels where, the draw ratio of the PVA gel was quite large because of the effects of the bound water with PVA gel, as well as the plasticization of free water. With the increase of the water content in PVA gel, the free water content and draw ratio of the gel increased. PVA/NRL blend showed an increase in draw ability than PVA till 92% of water content in PVA and then gave a slight stability with further increase of water added.

On contrary, with the increase of the borax content in PVA gel and in PVA/NRL blend, the draw ratio of the gel decreased in PVA/NRL blend and sharply decreased in PVA gel as shown in Figure 2.

Figure 3 shows that the maximum draw ratio was at zero irradiation dose and with increasing the irradiation dose the crosslinking was decreased where, no draw at 5 Mrad was observed. But in case of PVA/NRL blend gel the decrease of draw was limited and slightly stable at 3 Mrad.

Freezing-thawing gelation of PVA and NRL

It is well known that an aqueous solution of PVA forms a flexible gel by freezing and thawing.[11–14] Gel forming properties are closely related to the molecular mobility of polymer chains associated with bound water molecules. At the same time, the role of free water (bulk water) during the gelation is also important. It is thought that molecular chains of PVA are too mobile in excess amounts of water to stabilize junction zones. But in case of NRL the gelation by freezing and thawing process occurs by the

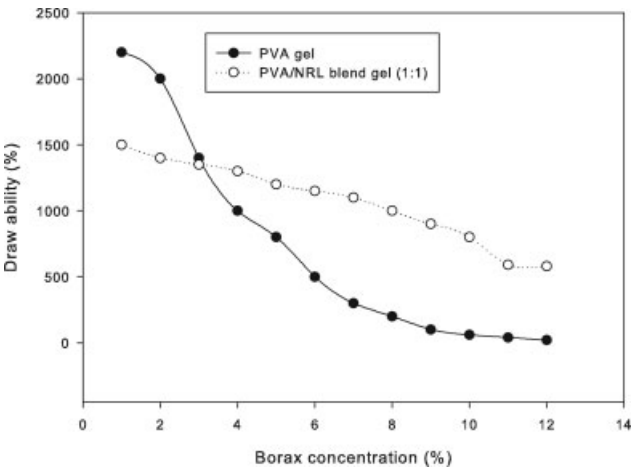

Figure 2 Effect of borax concentration percent on draw ability.

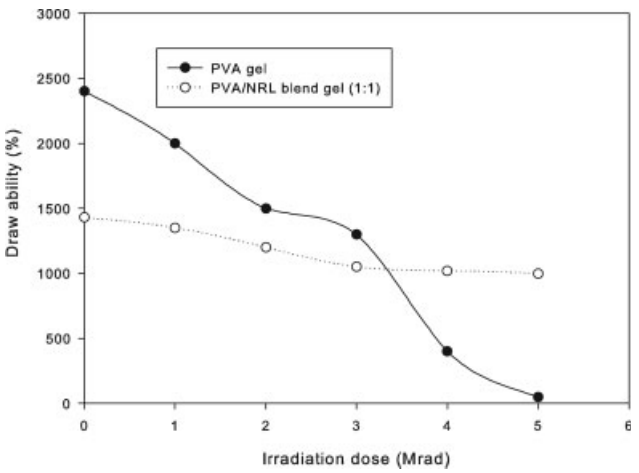

Figure 3 Effect of irradiation dose on draw ability.

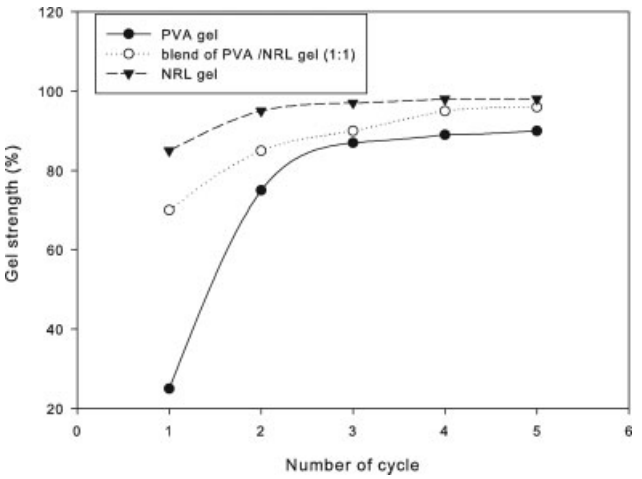

Figure 4 Effect of number of cycle of freezing-thawing on gel strength at 4% concentration of PVA solution.

physical contraction during the freezing process where, the molecules of NRL approach to the critical distance possessing in sequence the coagulation process.[15] For this reason, it is considered that a freezing–thawing process is an appropriate method to investigate the gel formation in both PVA and PVA/NRL blend.

The interaction becomes stronger, probably involving more hydroxyl groups of the polymer molecules, when the freezing–thawing process is repeated. The strengthening is quite large during the first three freezing–thawing cycles and becomes stable or negligible after the fourth cycle, irrespective of the original concentration of the PVA or NRL solution as shown in Figure 4.

Solubility in hot water

Figure 5 shows the effect of irradiation process on solubility of PVA gel, where the effect of temperature(hot water) on weight loss percent of PVA gel obtained from freeze–thaw process possessed a full solubility at 70°C but the irradiated samples at 2.5 Mrad have not possessed full resistance to boiled water. Figure 6 shows the effect of NRL concentration on solubility of NRL/PVA blend gel in boiled water, where at 40% of NRL a full resistance was observed. Also, the irradiated blend samples showed a full resistance toward the boiled water with any ratios of blending at 2.5 Mrad.

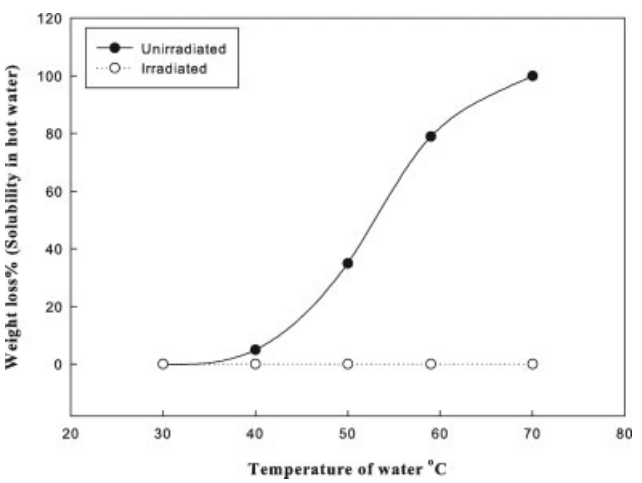

Figure 5 Effect of temperature (hot water) on weight loss percent of PVA gel (unirradiated and irradiated frozen-thawed sample).

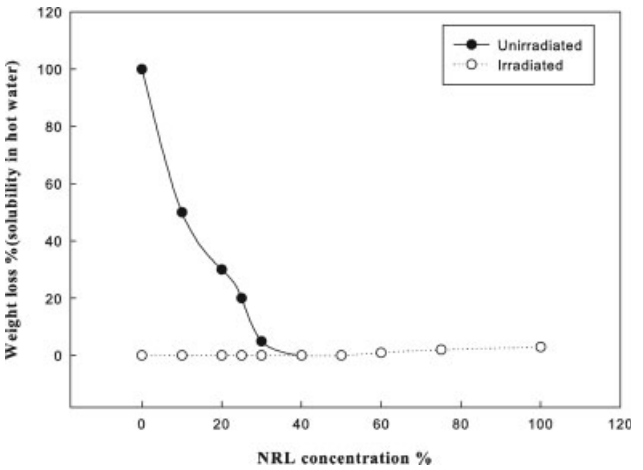

Figure 6 Effect of NRL concentration on solubility of NRL/PVA blend gel in hot water (unirradiated and irradiated frozen-thawed sample).

Figure 7 shows the effect of irradiation dose on PVA gel prepared by radiation at 2.5 Mrad, freeze–thaw process, chemical process, and freeze–thaw gelation of 50% NRL/50%PVA. The gel prepared by radiation showed a gel strength 82% and increased in parallel with increasing the irradiation dose giving a maximum gel strength at 7.5 Mrad.

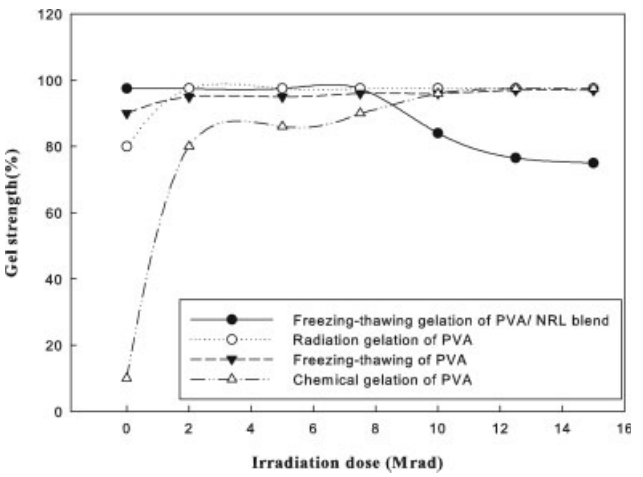

Figure 7 Effect of irradiation dose on gel strength percent.

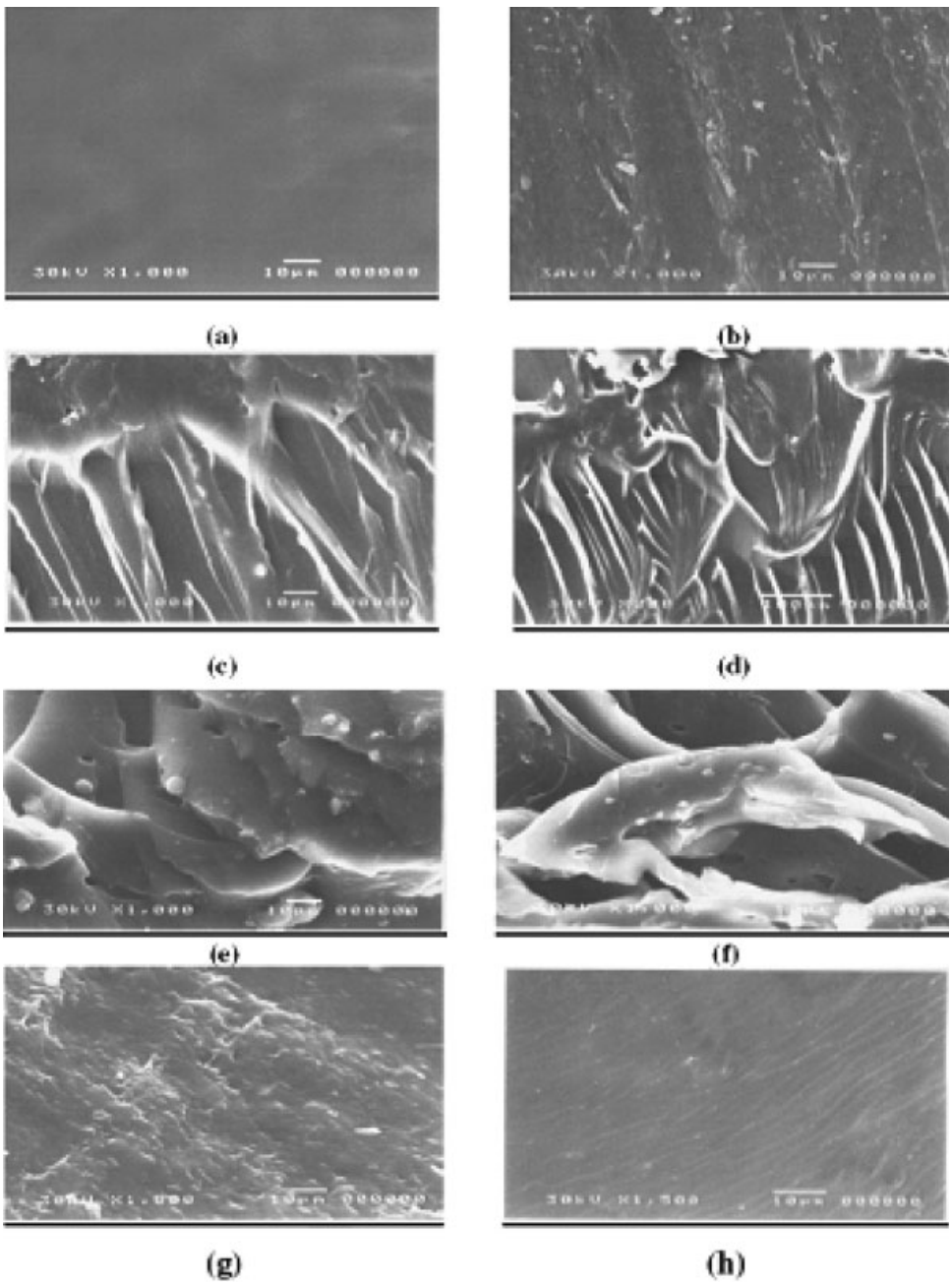

Figure 8 Scanning electron micrographs of PVA as a dry polymer obtained from radiation, chemical and freeze–thaw gelation: (a) PVA dry film by casting, (b) PVA dry gel by electron beam irradiation, (c) PVA dry gel by freeze–thaw process, (d) PVA dry gel by freeze–thaw process and then irradiated by electron beam, (e) PVA dry gel by chemical process, (f) PVA dry gel by chemical process and irradiated by electron beam, (g) NRL dry film by casting, (h) NRL/PVA blend dry film by casting.

The gel prepared by freezing–thawing showed the highest ratio of gel strength 90% and increased by increasing the irradiation dose. On contrary, the gel strength of PVA gel prepared by chemical process showed a very low ratio (not more than 10%) and the effect of irradiation was apparently effective for imparting a highly strength gel. In case of freeze–thaw gelation of 50%NRL/50%PVA, the strength was in a maximum ratio at 7.5 Mrad and started to decrease with the increase of irradiation dose. The figure shows that at 7.5 Mrad the gel strength of the three processes was almostly equal in gel strength ratios.

Morphological properties

Figure 8 represents the scanning electron micrographs of PVA as a dry polymer obtained from

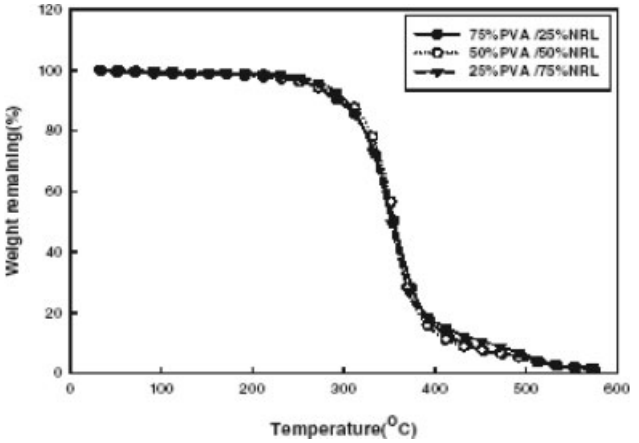

Figure 9 TGA thermograms of unirradiated PVA/NRL polymer blends.

radiation, chemical, and freeze–thaw geleation. Micrograph (a) shows that the surface of the original unirradiated PVA is smooth and no strains or pores was appeared, where in micrograph (b) shows that the molecular chains are compacted and oriented parallel to each others due to the crosslinking occurred by irradiation process. Micrograph (c) shows a parallel uncrosslinked rods shape due to freeze–thaw gelation, the fracture was slightly rough and shallow ridges was observed. But in micrograph (d) a crosslinking has apparently appeared after irradiation where, overlapped rods have observed and fracture surface became rougher and more rigid giving insoluble gel in boiled water. Micrograph (e) shows the chemical gelation of PVA as alternated muscle shape arranged in succession and in pseudo-homogeneous structure which can easily changing its mold dimension by a sensitive hand pressing, on contrary, micrograph (f) shows a large coiled muscle shape due to irradiation crosslinking which gave a stable shape in dimension and a rubber-gel phase was obtained. Micrograph (g) shows the original NRL fracture film appears as a corrugated surface

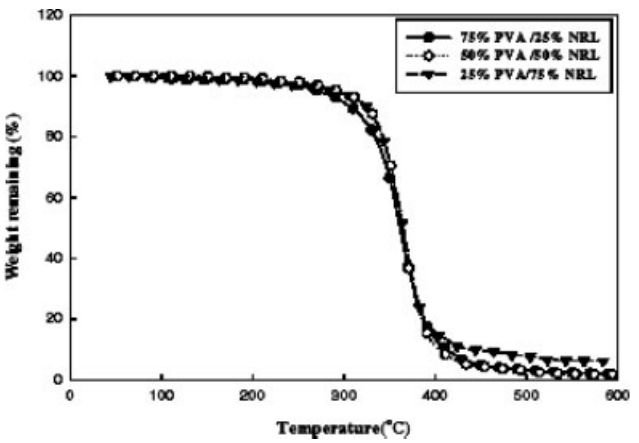

Figure 10 TGA thermograms of PVA/NRL polymer blends irradiated at 2.5 Mrad.

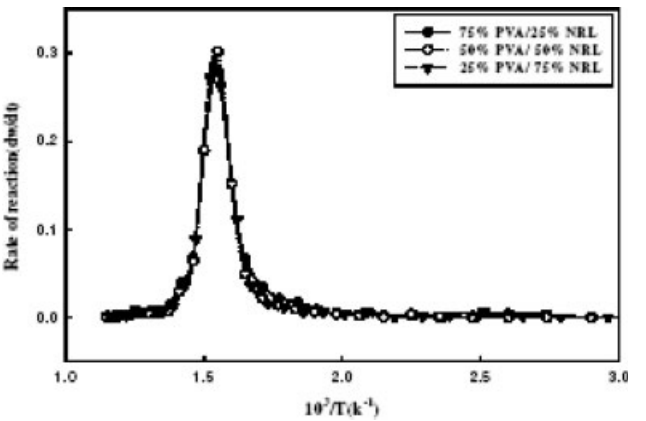

Figure 11 Rate of reaction curve of unirradiated PVA/NRL polymer blends.

which gave after blending with PVA a regular and parallel thin strains at blending ratio of 25% NRL and 75% PVA as shown in micrograph (h).

THERMAL PROPERTIES

The thermal decomposition behavior of unirradiated and irradiated polymer blends PVA/NRL were investigated. The initial TGA thermograms over the temperature range (0–600°C) at a heating rate of 10°C/min before and after exposure to 2.5 Mrad are shown in Figures 9 and 10. The rate of thermal decomposition reaction and the maximum reaction rate temperature are shown in Figures 11 and 12.

Figure 9 shows the dependency of thermal decomposition on the composition of blends. Within the stage above 250°C the thermal stability of different unirradiated blends follows the order:

$$25\%\text{PVA}/75\%\text{NR} > 50\%\text{PVA}/50\%\text{NR} > 75\%\text{PVA}/25\%\text{NRL}$$

This order showed that the thermal stability increases as ratio of the NRL increases in the blend as shown in Table I.

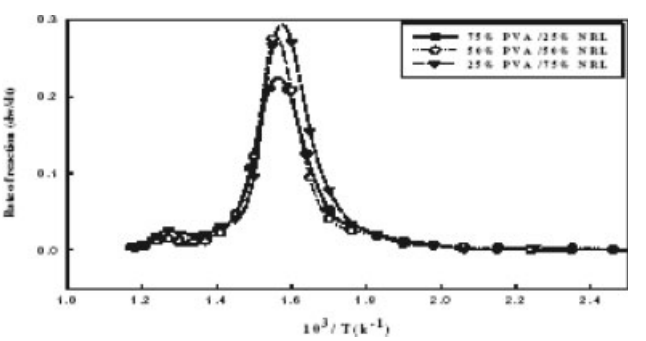

Figure 12 Rate of reaction curve of PVA/NRL polymer blends irradiated at 2.5 Mrad.

TABLE I
Weight Loss (%) at Different Decomposition Temperatures for Polymer Blends of Various Ratios of PVA and NRL Unirradiated and Irradiated at 2.5 Mrad

Composition of polymer blend	Irradiation dose (Mrad)	Weight loss (%)									
		210°C	230°C	250°C	270°C	290°C	310°C	330°C	350°C	370°C	390°C
75% PVA/25% NRL	0	1.47	2.26	3.57	5.72	9.08	14.54	27.71	49.64	71.67	82.85
	2.5	1.73	2.09	3.03	4.8	6.95	10.75	17.73	33.58	62.62	82.38
50% PVA/50% NRL	0	2.22	2.83	3.66	5.56	8.13	12.29	21.95	43.35	71.62	84.17
	2.5	0.79	1.29	1.96	3.03	4.60	7.06	12.55	29.51	63.33	84.61
25% PVA/75% NRL	0	1.12	1.59	2.37	4.00	7.01	13.75	27.02	50.31	73.24	81.53
	2.5	1.95	2.36	2.97	3.59	4.71	6.3	9.98	21.35	48.26	76.21

Irradiation of blends to 2.5 Mrad seems to increase the thermal stability as the same order.

A differential plot of the decomposition rates versus temperature yields curve with one several peaks, indicating the temperatures where the most rapid break down occurs as shown in Figures 11 and 12. It can be seen that these types of curves display similar trends in case of unirradiated and irradiated blends as shown in Table II.

This was lead to the conclusion that the compatibility of PVA with NRL induce a significant increase in gel-elasticity and resistivity to boiled water. This is because the crosslinking may have occurred due to the presence of NRL started from the ratio 50% NRL and has mostly stable as the ratio of NRL increases in the blend. Therefore, the thermal analysis data indicate a strong interaction between the blend components. This behavior of the blends allows us to forecast their potential application for possessing a high gel strength and full resistivity toward the boiled water.

Gel-cement composite

A study of the chemical reactions occurring in high strength cements is presented with particular reference to the cement–polymer interaction. PVA is a water-soluble polymer used as cement modifier. An important modification observed by addition of PVA is the increase of the bond strength between cement paste and aggregate. The purpose of this work was to investigate the effect of PVA gel for cement loading for use as wall cracks filling materials.

TABLE II
Temperatures of the Maximum Values of the Rate of Reaction of Unirradiated and Irradiated Polymer Blends PVA/NRL

Composition of polymer blend (%)	Irradiation dose (Mrad)	Treatment of maximum rate of reaction (°C)
75% PVA/25% NRL	0	373
	2.5	370
50% PVA/ 50% NRL	0	375
	2.5	378
25% PVA/ 75% NRL	0	372
	2.5	383

The addition of small amounts (1.6%) of polyvinyl alcohol to the cement retards the normal hydration reactions. At much larger ratios (10%PVA) the crystalline hydrates are completely suppressed and the polymer reacts with the cement solution to form calcium acetate and a crosslinked polymeric product.[16]

Figure 13 shows the effect of gel-draw ability on cement loading, where the increase of draw ability percent of the prepared gel allows the more ratio of cement to load. Also, the blended gel of PVA/ NRL which lead to increase the gel draw ability caused in turn an increase in cement loading.

CONCLUSION

We have studied and reported the behavior of PVA and NRL gelation during irradiation, chemical and freezing processes, respectively, with a view to their possible applications according to their mechanical properties obtained. We found that it is necessary to apply the irradiation process to PVA gel obtained from chemical to possess a stable shape in dimension or blending of NRL to PVA gel obtained from

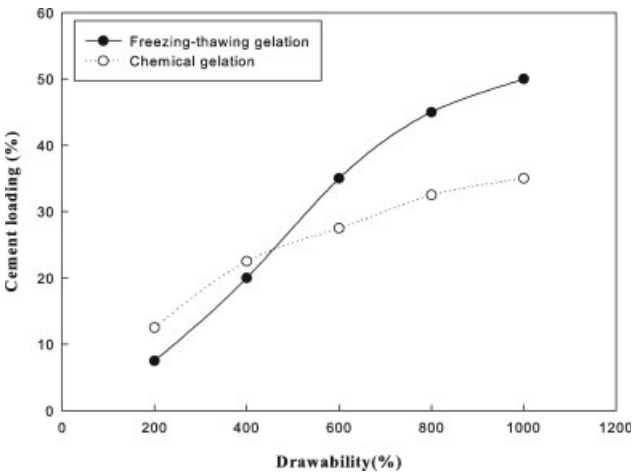

Figure 13 Effect of draw ability on cement loading.

freeze–thaw process to possess a highly resistant gel to boiled water. Where, the irradiation of chemical and frozen gel recorded a more applicable strength and draw ability than PVA-gel which was prepared by irradiation process only. The strength of PVA gel was found to be increased by a repeated freezing–thawing process. The increase of strength was prominent during the first three cycles of the repeat process. The same freezing–thawing process as mentioned earlier was applied to aqueous solutions of PVA/NRL blend. The experimental results showed that polymer concentration influences the draw ability of PVA gel, to possess the properties of the modeling clay. When the polymer content of the gel was less than 5%, the draw ratio of the PVA gel was quite large because of the effects of the bound water with PVA, as well as the plasticization of free water. With the increase of the water content in PVA gel, the free water content and draw ratio of the gel increased but the strength of the gel decreased because of the higher residual water in the gel. NRL added to PVA enhanced a limited draw ability and possessed also an elasticity with improving the gel strength. Radiation process can suppress the behavior of gel–draw ability at 2.5 Mrad due to crosslinking, but on the other hand crosslinking enhances the mechanical strength of PVA gel. The study offers two kinds of gel-cement composite for use as crack filling material (hard and rubbery). The first is PVA gel loaded with cement prepared with chemical method using borax solution. The second type was a blend of PVA/ NRL gel using freezing–thawing gelation.

References

1. El-Hag, A.; Shawky, H. A.; Abd El-Rehim, H. A.; Hegazy, E. A. Eur Polym J 2003, 39, 2337.
2. Hegazy, E. A.; El-Salmawy, K. M.; El-Naggar, A. J App Polym Sci 2004, 94, 1649.
3. Solpan, D.; Duran, S.; Ssaraydin, D.; Guven, O. Rad Phys Chem 2003, 66, 117.
4. Tanaka, R.; Hatakeyama, T.; Hatakeyama, H. Polym Int 1998, 45, 118.
5. Dea, I. C. M.; Morris, E. R.; Rees., D. A.; Welsh, E. J. Carbohydr Res 1977, 57, 249.
6. Dea, I. C. M. In Industrial Polysaccharides: Genatic Engineering, Structure/Property Relations and Applications; Yalpani, M., Ed.; Elsevier: Amsterdam, 1987; pp 207–216.
7. Mahmmoud, Gh. A.; Hegazy, E. A.; Abd El-Wahab, M. J Rad Sci Appl 2008, 21, 237.
8. Berger, L. D.; Ivison, M. T. In Water-Soluble Resins, 1st ed.; Davidson, R. L. I., Sittig, M., Eds.; Reinhold: New York, 1962; p 199.
9. Gimenez, V.; Mantecon, A.; Cadiz, V. J Appl Polym Sci 1996, 59, 425.
10. Ramineh Shariatpanahi, E.; Orang, F.; Shahriar, H.; Naimi, T. J Biomaterials Sci, Polym ed. 2006, 7, 659.
11. Watase, M.; Nishinari, K. Polym Commun 1983, 24, 270.
12. Nagura, M.; Nagura, M.; Ishikawa, H. Polym Commun 1984, 25, 313.
13. Hatakeyma, T. Y.; Hatakeyama, H. Eur Polym J 1987, 23, 361.
14. Nagura, M.; Hamano, T.; Ishikawa, H. Polym Commun 1989, 30, 762.
15. Dessouki, A. M.; Taher, N. H.; El-Nahas, H. H. Polym Int 1998, 45, 339.
16. Rodger, S. A.; Brooks, S. A.; Sinclair, W.; Groves, G. W.; Double, D. D. J Mater Sci 1985, 20, 8.