Hydrogel Coating of RVNRL Film by Electron-Beam Irradiation

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Received 29 May 1998; accepted 31 August 1998

ABSTRACT: The tackiness properties of radiation-vulcanized natural rubber latex (RVNRL) film surfaces coated by various monomers were investigated in order to define the suitable hydrogels which reduce the tackiness of the film. In this context, different types of monomers, namely, *N*-vinyl-2-pyrrolidone (NVP), *N,N*-dimethylaminoethylamide (DMAEA), acrylic acid (AAc), *n*-butyl acrylate (*n*-BA), and 2-hydroxyethyl methacrylate (HEMA) as well as the monomer mixtures were tried with varying degrees of success. Coating the RVNRL film with 80% HEMA/20% *n*-BA by irradiation at 80 kGy using a low-energy electron beam gave a remarkable reduction in the surface tackiness of the RVNRL film. Several other attempts were made such as priming the RVNRL film with acid and aluminum sulfate prior to coating, mixing the aluminum sulfate into the monomer mixtures, and dipping the partially wet RVNRL film into the monomer to enhance the wettability of the monomers with the film. The photomicrographs taken illustrate that the decrease in tackiness with the coating is due to the increase of the surface roughness at an 80-kGy irradiation dose. The studies also revealed that the reduction in the contact angle and the increase in water absorption of the RVNRL film after irradiation are due to the formation of the hydrogel layer. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1421–1428, 1999

Key words: RVNRL film; coating; tackiness; hydrogel; EB irradiation

INTRODUCTION

Radiation vulcanization of natural rubber latex is an emerging technology whereby radiation is used in place of sulfur in the conventional prevulcanization process for the manufacture of dipped natural rubber latex products.[1–4] The radiation-vulcanized natural rubber latex (RVNRL) has many advantages over conventional vulcanizates such as the absence of *N*-nitrosamines, very low cytotoxicity, degradability, transparency, softness, low emission of SO_2, and less formation of ashes when burned.[5] These characteristics of RVNRL suggest its wide application in the medical field. The rise in environmental consciousness coupled with the health-related issues of protein allergy, nitrosamines, and biocompatibility of latex products have further boosted the potential for RVNRL.

With regard to the application of RVNRL in the medical sector such as in surgical gloves, the RVNRL film needs to be "nonstick." Unfortunately, it was found that the tackiness of RVNRL film is inferior to that of the sulfur-vulcanized one.[6,7] Therefore, further research is essential in order to reduce the tackiness of RVNRL film.

Generally, various methods have been utilized and practiced to reduce the surface tackiness of rubber articles.[8] For example, the surface of a

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Contract grant sponsor: IAEA.

rubber glove can be halogenated with bromine or chlorine to make it slippery. Despite the widespread use of chlorination, there are some disadvantages associated with the method, including possible factory health and safety hazards, poor reproducibility of chlorination levels, doubts over the long-term durability of the chlorinated layer, and deterioration in the physical properties such as ozone resistance, fatigue life, and wear.[9] Waxes, silicones, and powders have been used but this provides only a temporary solution as the material rubs off in a very short time. Furthermore, there is always a risk of such lubricants and powders escaping from the interior of the glove to contaminate the surgical field during donning or if the glove is punctured during an operation. In fact, powdered gloves were recognized as one of the major causes of allergic reactions associated with latex products.[10] Cornstarch acts as a vehicle for the transmission of latex proteins and other potential allergens.[11]

Thus, to overcome such problems, protective rubber products coated by hydrogel were developed by a conventional method using sulfur-vulcanized latex.[12,13] Apart from tackiness, the other properties of the RVNRL film surface including wettability and biocompatibility are important for medical applications. Therefore, surface modification of RVNRL film by a suitable hydrogel lining with optimum bulk properties is an efficient way to render it suitable for medical purposes. During the past two decades, radiation-induced graft copolymerization of monomers onto the surface of polymers using energy sources such as gamma rays, electron beams, and UV have been widely developed.[14–16] In this study, an attempt was made to graft a combination of hydrophilic and hydrophobic hydrogel onto RVNRL film using low-energy electron-beam irradiation.

EXPERIMENTAL

The latex used in this work was a high ammonia centrifuged natural rubber latex concentrate produced by Dunlop of Malaysia (Seremban). *N*-Butyl acrylate (*n*-BA), an ammonia solution, anhydrous aluminum sulfate, sulfuric acid, and hydrophilic monomers such as 2-hydroxyethyl methacrylate (HEMA), acrylic acid (AAc), *N*-vinyl-2-pyrrolidone (NVP), and *N,N*-dimethylaminoethylamide (DMAEA) are products of Kanto Chemical (Tokyo). The solvents and monomers used were reagent grade and were utilized without further purification. Inhibitors were removed from the monomers by filtration over aluminum oxide.

RVNRL Preparation

The latex, in a stainless-steel drum, was diluted to 50% total solids content (TSC) by adding 1% ammonia solution while stirring. This was followed by the addition of 0.2 phr of a 10% KOH solution and 5 phr of *n*-BA. The stirring continued for more than 2 h. The irradiation of latex was carried out at a dose rate of 10 kGy/h for 2 h at 20°C. After irradiation, the latex was tightly covered and kept at room temperature.

Films were prepared by casting the latex onto glass plates and air-drying at room temperature until transparent. Then, the films were leached in 1% aqueous ammonia for 24 h and air-dried again until transparent, followed by heating in an oven at 80°C for complete dryness.

Coating of Hydrogel onto RVNRL Film

Various combinations of hydrophilic and hydrophobic monomers (as shown in the Results and Discussion section) were coated onto the RVNRL film by dipping the film into the respective monomers and monomer mixtures. The dipped films were then irradiated using a 300-keV electron-beam accelerator at 150 keV, 30 mA, and 20 kGy/pass. Samples were irradiated at 20-, 40-, 60-, and 80-kGy doses. The irradiated films were leached with water to wash out the unreacted monomers, followed by air-drying at room temperature for 48 h.

To improve the adhesion and wettability between the rubber and the monomers, the following surface treatments were tried independently prior to dipping:

1. The RVNRL films were primed by 5% sulfuric acid followed by rinsing in purified water at 20°C.
2. The RVNRL films were rinsed with a 4% aluminum sulfate solution.
3. Aluminum sulfate, 0.5% w/w, was mixed into the monomer mixtures and dipping was carried out in the usual manner.
4. Partially wet RVNRL films (leaching followed by partial drying) were dipped into the monomer mixture prior to irradiation.

Evaluation of Tackiness

The tackiness of the films was determined using a probe tack tester (Resca Co. Ltd.) with a stainless probe at a preload of 10 gf, a press time of 10 s, and a detach speed of 30 mm/min.

Wettability of the Film After Hydrogel Coating

The hydrophilicity of the treated surfaces was assessed by the contact angle made by a drop of water placed on the surface.[17] A microsyringe was used to dispense accurately 1 μL of water and the contact angle was measured at 20°C under a microscope at different time intervals, observations being made on several drops in order to obtain a representative value.

Water Absorption of RVNRL Film

Coated films of a measured weight were immersed in purified water for 48 h at ambient temperature (20°C). After 48 h, the swollen films were removed and blotted dry between filter paper before weighing. The water absorbed, C, was calculated as

$$C = (W - W_0)/W_0 \times 100 \tag{1}$$

where W_0 is the initial weight of the sample, and W, the weight of the sample after immersion in water.

Tensile Property Measurement

The tensile test was carried out to evaluate the change in mechanical properties during the course of the reactions. Dumbbells were cut from the coated RVNRL film and the tensile strength (Ts) as well as the elongation at break (Eb) were determined in accordance with ASTM D412-C. This was done using a Toyoseiki Strograph–RI universal testing machine at a crosshead speed of 500 mm/min. The dumbbell test pieces were conditioned at 25°C overnight prior to the tensile test measurements.

Extractable Protein Content

Extractable protein determinations were performed with the BCA (bicinchoninic acid) protein assay reagent (Pierce, Rockford, USA) according to the manufacturer's instructions. Two grams of the RVNRL film specimen were extracted with 10-mL portions of phosphate-buffered saline (PBS), pH 7.4, at room temperature for 2 h and the resulting solution assayed by the BCA method. The principle of the test is the reduction of an alkaline Cu(II) solution by proteins, yielding Cu(I) ions which form a colored complex with BCA.[18] The concentration was determined spectrometrically at 562 nm using a Shimadzu UV-visible spectrometer. Calibration was done using known concentrations of bovine serum albumin (BSA). The method is comparable to the widely used Lowry method.[19]

Durability

The coated films were placed in an air-circulating oven at 70°C for 1, 3, 7, and 14 days prior to tackiness testing. To elucidate the peeling of the coated hydrogel layer in hot water, coated films were immersed in hot water at 70°C for 0.5, 1, 2, 3, and 4 h, air-dried for 24 h, and then tested for changes in tackiness.

Surface Topography

An analysis of the surface topography of the hydrogel-coated RVNRL film surfaces was made using a JEOL Superprobe 733 scanning electron microscope (SEM). The coated RVNRL film surfaces were carefully cut out without stretching the surface and sputter-coated with gold. To avoid contamination, the specimens were stored in a desiccator before and after gold coating until the SEM examination was made. All the above tests were repeated on uncoated RVNRL film for comparison purposes.

RESULTS AND DISCUSSION

Tackiness of RVNRL Film

In preliminary studies, hydrophilic monomers such as NVP, AAc, DMAEA, and HEMA were chosen for coating onto the RVNRL film based on the wettability of the respective monomers on the rubber surface by subjective evaluations. Figure 1 shows the variation in tackiness of the coated RVNRL film with respect to the irradiation dose. It is apparent from this figure that the samples coated with AAc show a drastic reduction in tackiness after a dose of 20 kGy. A gradual reduction in tackiness with dose was also observed for the film coated with HEMA. This was followed by DMAEA, which showed only a moderate reduction in tackiness compared with the uncoated film. In contrast, the samples coated with n-BA

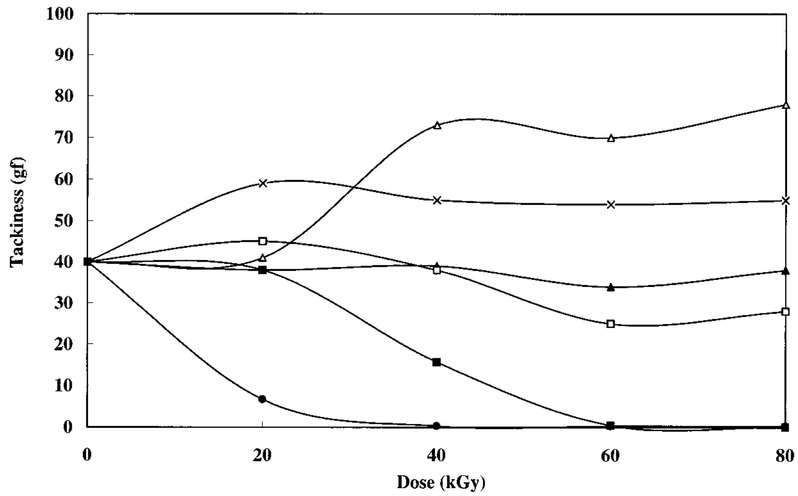

Figure 1 Effect of irradiation on the tackiness of RVNRL film coated with various monomers: (-△-) *n*-BA; (-×-) NVP; (-▲-) uncoated; (-□-) DMAEA; (-■-) HEMA; (-●-) AAc.

showed a drastic increase in tackiness with irradiation, indicating that the poly(butyl acrylate) (p*n*-BA) formed is rather sticky. A similar trend was also observed for samples coated with NVP, suggesting that only AAc and HEMA are likely to be suitable for applications that require low tackiness. However, films coated with AAc gave a hard surface and peeling of the coated layer on stretching. On the other hand, poor wetting of HEMA with the RVNRL film surface was observed.

Considering the above limitations with HEMA and AAc, in order to enhance the compatibility of the above chosen hydrophilic monomers with rubber, which is hydrophobic, an attempt was made to mix the above individual hydrophilic monomers with a hydrophobic monomer, *n*-BA, which is also used as a sensitizer in RVNRL preparation. Furthermore, p*n*-BA possesses a T_g approaching that of natural rubber and this could improve the compatibility between the RVNRL film substrate and the coated layer. The T_g's of natural rubber and p*n*-BA are reported as −72 and −54°C, respectively.[20] Referring to Figure 2, it is clear that the films coated with 80% AAc/20%

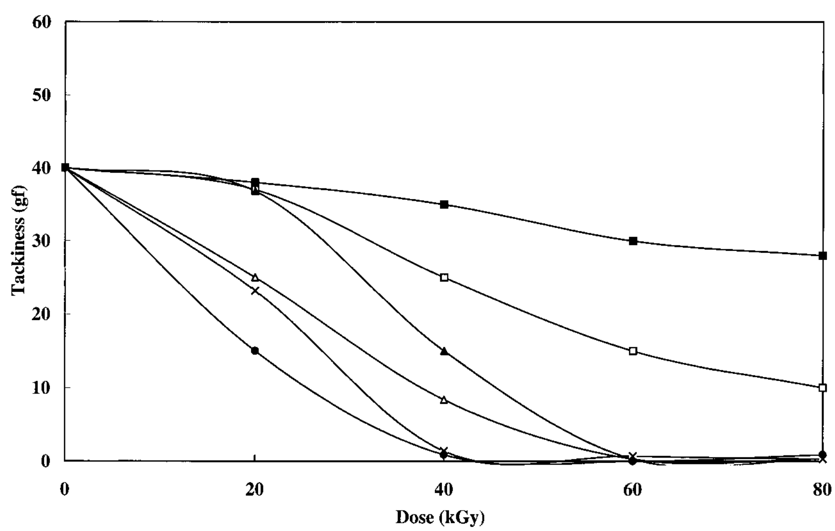

Figure 2 Effect of irradiation on the tackiness of RVNRL film coated with various monomer mixtures: (-■-) 20% HEMA/80% *n*-BA; (-□-) 20% AAc/80% *n*-BA; (-▲-) 50% HEMA/50% *n*-BA; (-△-) 80% HEMA/20% *n*-BA; (-×-) 50% AAc/50% *n*-BA; (-●-) 80% AAc/20% *n*-BA.

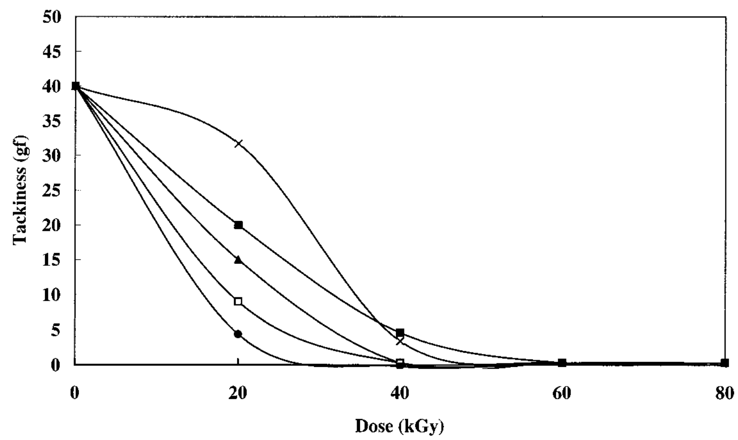

Figure 3 Effect of irradiation on the tackiness of RVNRL film coated with 80% HEMA/20% n-BA: (-×-) control; (-▲-) 5% sulfuric acid; (-●-) wet film dipping; (-■-) 4% aluminum sulfate; (-□-) 0.5% aluminum sulfate (mix).

n-BA and 50% AAc/50% n-BA show a remarkable decline in tackiness with dose, approaching 0 at 40 kGy. Unfortunately, the peeling of the coated layer on stretching coupled with the hard and stiff coated surface was not improved. Interestingly, such problems were not observed for films coated with the 80% HEMA/20% n-BA mixture and an improved wetting of HEMA on the RVNRL surface was noted with the addition of 20% n-BA. Taking the above criteria into consideration, a possible suitable coating material is an 80% HEMA/20% n-BA combination. Thus, from this point, further studies were focused on the coating of 80% HEMA/20% n-BA.

The results on various other methods which were tried to improve further the quality of the coating are plotted in Figure 3. In this experiment, all the samples are coated with 80% HEMA/20% n-BA with respective treatments while the control is the dry RVNRL film coating. It is apparent from Figure 3 that each respective treatment gave a reduction in tackiness to varying extents with irradiation. The improvement with the acid treatment could be because the hydrophobic RVNRL film surface was made more wettable with the monomers by the acid washing. In addition, the rinsing with aluminum sulfate, and the addition of aluminum sulfate into the monomer mixtures, also gave improvement. This result is in line with the hypothesis for trivalent metal ion which has been described elsewhere.[21] In relation to this hypothesis, it is believed that the trivalent aluminum ion in an acidic solution forms a multiplicity of linkages with the hydroxyl group of PHEMA and, on the other hand, with the various nonrubber constituents in the rubber latex film, in particular, with protein substances. Thus, an improved adhesion of the PHEMA on the RVNRL surface was achieved.

Finally, the samples which were produced by dipping the partially wet RVNRL film substrate offered the most promising feature with regard to tackiness. Visual observations also confirm that even coating and the best homogeneity were achieved. This result could be attributed to the accelerative effect of water on the graft polymerization, as already indicated by Sasaki et al.[22] in a similar monomer system. Also, the improved wetting of HEMA on the rubber surface could be due to the interaction by hydrogen bonding between the water present in the rubber film and the OH group of the HEMA at the interface between the RVNRL film surface and the monomer mixture. Taking the above discussions into consideration, efforts on characterization of the coated surface were focused on the RVNRL film coated with 80% HEMA/20% n-BA where the wet film dipping technique was employed prior to irradiation.

Contact Angle and Water Absorption

The results shown in Figure 4 were obtained after 5 min of contact. The principal interest was how the hydrophilicity of the RVNRL film surface changed according to the treatment employed. It was found that the hydrogel coating with 80% HEMA/20% n-BA decreased the contact angle, producing the lowest values at a dose of 80 kGy, implying that higher hydrophilicity was achieved with increasing dose.

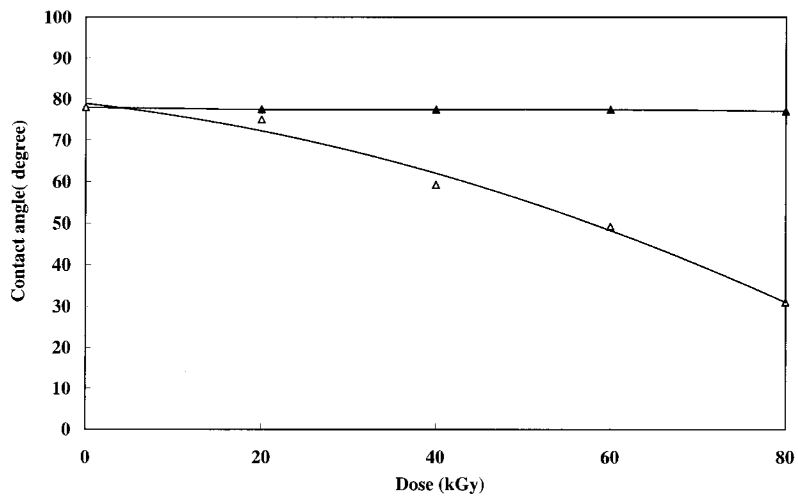

Figure 4 Effect of irradiation on contact angle of coated and uncoated film: (-▲-) uncoated; (-△-) 80% HEMA/20% *n*-BA.

Figure 5 indicates that the water absorption for uncoated film is almost constant (about 1%) with irradiation, whereas for coated samples, there is a gradual increase in the water absorption with irradiation dose, implying that the porosity of the coated layer increases with increasing dose. This correlates well with the contact angle measurements and tackiness which has already been discussed.

Tensile Properties

Due to high molecular weight of polymers, polymers often exhibit drastic changes in their physical properties with only minor modifications. Thus, the tensile properties of coated and uncoated RVNRL films were examined. The data obtained from the tensile strength and elongation-at-break measurements (Fig. 6) indicate that there is no significant difference in the tensile strength and elongation at break between the coated and uncoated film. Hence, this result confirms that the hydrogel layer formed as well as the penetration of the electron beam during irradiation are relatively too thin to cause changes in the tensile properties.

Durability of the Coating

The tackiness of the coated film after accelerated aging and also after immersion in hot water was investigated. In both cases, a 100 ± 0.5% reten-

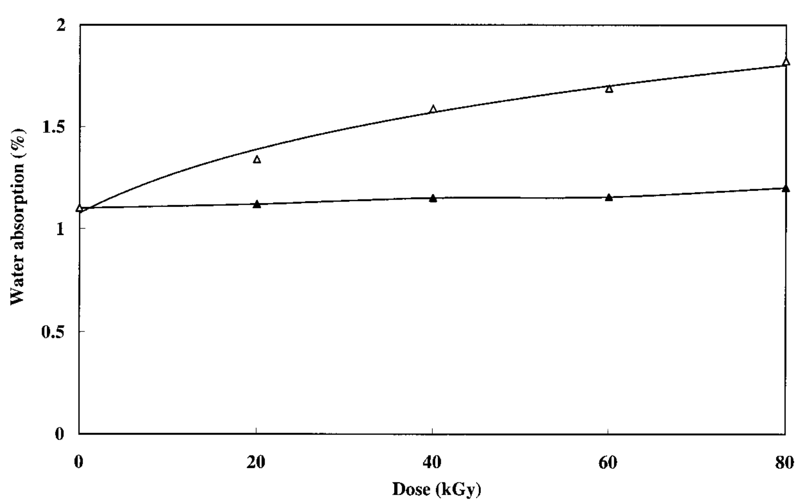

Figure 5 Water absorption of coated and uncoated RVNRL film at various irradiation doses: (-▲-) uncoated; (-△-) 80% HEMA/20% *n*-BA.

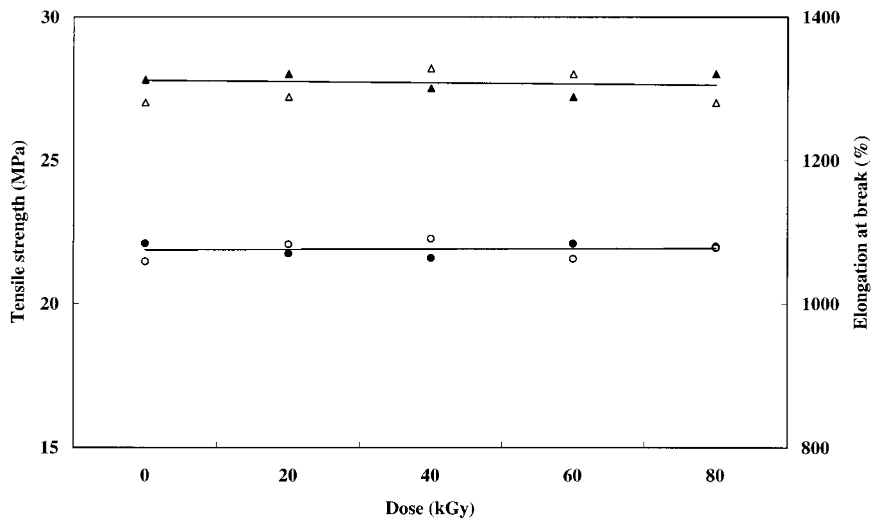

Figure 6 Tensile strength (Ts) and elongation at break (Eb) of coated and uncoated RVNRL film at various irradiation doses: (-▲-) uncoated (Ts); (-●-) uncoated (Eb); (-△-) 80% HEMA/20% n-BA (Ts); (-○-) 80% HEMA/20% n-BA (Eb).

tion in tackiness properties was observed, indicating that the hydrogel layer did not peel off either in hot water or in a hot-air-circulating oven at 70°C.

Extractable Protein

Allergic reactions caused by water-soluble protein in natural rubber latex products are increasing in Western countries. Therefore, the amount of protein extracted from the coated RVNRL films was examined. It was found that the extractable protein for uncoated film was 0.175 ± 0.002 mg/g, whereas the extractable protein for the coated samples was 0.12 ± 0.002 mg/g. Thus, it can be concluded that the hydrogel coating did not cause a remarkable effect on the extractable protein in the RVNRL film. However, the marginal decrease in extractable protein with the coating is believed to be due to the protective effect of the coated layer.

Surface Topography

SEM photomicrographs of the surfaces are shown in Figure 7. It can be noted that the hydrogel-coated surface was rough, whereas the uncoated surface appears to be smooth. Comparing the coated surfaces which were irradiated at 20 and 80 kGy, it is apparent that the roughness of the coating increased with irradiation dose. Accordingly, a close relation between roughness and tackiness is observed; the decrease in tackiness is due to the increase in roughness. This observation is in agreement with that reported by Saito et al.[23] who studied the development of antisticki-

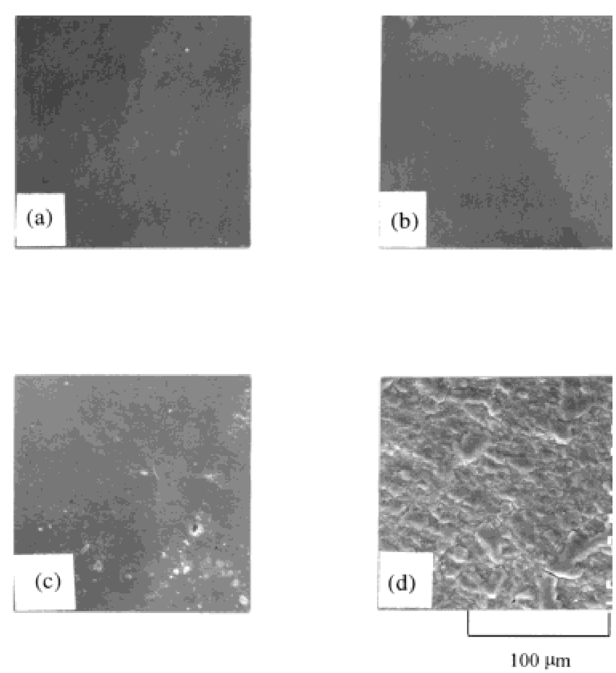

Figure 7 Scanning electron micrograph of hydrogel-coated RVNRL film: (a) uncoated RVNRL film (control); (b) uncoated RVNRL film (irradiated at 80 kGy); (c) coated RVNRL film with 80% HEMA/20% n-BA (irradiated at 20 kGy); (d) coated RVNRL film with 80% HEMA/20% n-BA (irradiated at 80 kGy).

ness of the rubber surface by UV irradiation and sputter-etching treatments.

CONCLUSIONS

Hydrogel coating onto RVNRL film using a low-energy electron beam approach in this study was effective in reducing the tackiness of the RVNRL film where 80% HEMA/20% *n*-BA was found to be the most suitable monomer mixture. Although treatments with acid and aluminum sulfate were studied, these seem unnecessary considering the great improvement in tackiness achieved by dipping the partially wet RVNRL film into the monomer mixtures followed by irradiation. No significant changes in the mechanical properties of the coated film were observed compared to the uncoated one. Furthermore, it is of interest to note the good durability of the coating both in water and hot air. SEM photomicrographs confirm that an 80% HEMA/20% *n*-BA coating at an 80-kGy irradiation dose gave the necessary surface roughness in relation to reduced surface tackiness.

One of the authors (C.T.R.) gratefully acknowledges IAEA for financial support, MINT for giving permission to work at TRCRE, Japan, and JICA for the kind cooperation. Sincere thanks are also due to Dr. T. Sasaki for stimulating discussions, Mr. Shin Hasegawa for his assistance during the experimental work, and Mr. Taro Enjoji for his help during the typing of this manuscript.

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