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HYDROGEL COATING OF RVNRL FILM BY ELECTRON BEAM IRRADIATION

PENYALUTAN PERMUKAAN FILEM RVNRL DENGAN MENGGUNAKAN SINARAN ALUR ELEKTRON

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Abstract

The tackiness properties of Radiation Vulcanized Natural Rubber Latex (RVNRL) film surfaces coated by various monomers have been investigated in order to understand 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-dimethyl amino ethyl amide (DMAEA), acrylic acid (AAc), N-butyl acrylate (n-BA) and 2-hydroxyethyl methacrylate (HEMA) as well as monomer mixtures have been tried with varying degrees of success. It was found that coating the RVNRL with 80% HEMA/20% n-BA by irradiation at 80 kGy using low Energy Electron Beam gave remarkable reduction in surface tackiness of the RVNRL film. Several other attempts were made such as priming with acid and aluminum sulfate, mixing the aluminum sulfate into the monomer and dipping the partially wet RVNRL film into the monomer to enhance the wettability of the monomers with the film. Studies on surface topography revealed that the decrease in tackiness with coating is due to the increase of the surface roughness at 80 kGy irradiation dose.

Abstrak

Filem yang disediakan daripada lateks getah asli yang divulkankan dengan menggunakan sinaran (RVNRL) telah disalutkan dengan beberapa jenis monomer dengan tujuan menggurangkan sifat-sifat pelekitan permukaan filem tersebut. Dalam hubungan ini monomer-monomer seperti N-vinyl -2-pyrrolidone (NVP), N,N-dimethyl amino ethyl amide (DMAEA), acrylic acid (AAc), N-butyl acrylate (n-BA), 2-hydroxyethyl methacrylate (HEMA) dan juga campuran monomer tersebut dengan n-BA telah dikaji. Adalah didapati penyalutan permukaan filem RVNRL dengan 80% HEMA/20% n-BA pada 80 kGy dengan menggunakan teknik sinaran alur elektron bertenaga rendah telah berjaya mengurangkan pelekitan permukaan filem RVNRL dengan berkesan. Beberapa percubaan juga telah dibuat untuk meningkatkan pembasahan di antara monomer dengan filem seperti membasuh permukaan filem dengan acid dan aluminium sulfat, mencampurkan aluminium sulfat ke dalam monomer dan juga mencelupkan filem RVNRL yang separa basah ke dalam monomer. Kajian permukaan filem dengan menggunakan mikroskop elektron imbasan (scanning elektron microscope) menunjukkan penurunan dalam pelekitan pada 80 kGy untuk filem yang disalut dengan 80% HEMA/20% n-BA adalah disebabkan oleh peningkatan di dalam kekasaran permukaan filem.

INTRODUCTION

The radiation vulcanized natural rubber latex (RVNRL) has the following advantages over the conventional vulcanizates (Makuuchi 1996) ;

1)Absence of N-nitrosamines
2) Very low cytotoxicity
3) Less protein allergy response
4) Degradability
5)Transparency and softness
6) low emission of SO_2 and less formation of ashes when burned.

These characteristics of RVNRL suggest wide applications of RVNRL in medical field. With regard to this, the first application of RVNR latex was in medical use, optical laser balloon (optical endoscopic balloon) (Shimamura 1989). Indeed, one of the products fabricated from RVNRL are gloves, have been produced successfully from RVNR latex in several countries (Makuuchi et al. 1990; Devendra et al. 1993). However it was found that beside aging , the tackiness of RVNRL fim is also inferior to that of sulfur vulcanized one (Haque et al. 1995).

Generally, various methods has been utilized and practiced to reduce the surface tackiness of rubber articles (Waddell et al. 1992). For example, the surface of rubber glove can be halogenated with bromine or chlorine to make it slippery. However, this treatment may result in very poor aging properties, discoloration and embrittlement. Waxes, silicones and powders have been used but this provide only temporary solution as the material rub off in a very short time. Further more, 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 order to overcome such problem , protective rubber products coated by hydrogel were developed by conventional method using sulfur vulcanized latex (Goldstein et al. 1984; Goldstein et al.1986). Apart from tackiness , the status of RVNRL film surface including wettability and biocompatibility are important for medical applications. Therefore, surface modification of RVNRL film by suitable hydrogel lining with optimum bulk properties is an efficient way to render it suitable for medical purpose. During past two decades , radiation induced graft co polymerization of monomers onto the surface of polymers using energy sources such as gamma rays, electron beams and UV have been widely developed (Chapiro 1962; Ratner et al.1974; Muherjee et at. 1985). In this studies attempt was made to graft a combination of hydrophilic and hydrophobic hydrogel onto the RVNRL film by using Low Energy Electron Beam Irradiation.

EXPERIMENTAL

The latex used in this work was a high ammonia centrifuged natural rubber latex concentrates produced by Dunlop of Malaysia. N-butyl acrylate (n-BA), ammonia solution, aluminum sulfate anhydrous, sulfuric acid and hydrophilic monomers such as 2-hydroxyethyl methacrylate (HEMA), acrylic acid (AAc), N-vinyl -2-pyrrolidone (NVP) and N,N dimethyl amino ethyl amide (DMAEA) are products of Japan. The solvents and monomers used were reagent grade and were used without further purification. Inhibitors were removed from the monomers by filtration over aluminum oxide.

RVNRL preparation

The latex, in stainless steel drum was diluted to 50% total solid content, tsc by adding 1% ammonia solution while stirring. This was followed by addition of 0.2 phr of 10% KOH solution and 5 phr n-BA. The stirring continued for more than 2 hours. The irradiation of latex was carried out at a dose rate of 10

kGy / hour for 2 hours at 20°C. After irradiation the latex was tightly covered and kept at room temperature.
Films were prepared by casting the latex on glass plates and air drying at room temperature till transparent. Then the films were leached in 1% aqueous ammonia for 24 hours and air dried again until transparent followed by heating in oven at 80°C for complete dryness.

Coating of hydrogel onto RVNRL film.

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

In order to improve the adhesion and wettability between the rubber and the monomers following surface treatments were tried independently prior to dipping.

The RVNRL films were primed by 5% sulfuric acid followed by rinsing in purified water at 20°C.

The RVNRL films were rinsed with 4% aluminum sulfate solution.

0.5% aluminum sulfate was mixed into the monomer mixtures and dipping were carried out in usual manner.

Partially wet RVNRL films (leaching followed by partial drying) were dipped into the monomers mixture prior to irradiation.

Evaluation of tackiness

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

Surface Topography

Treated RVNRL film surfaces were prepared in the usual manner for scanning electron microscope (SEM) examination.

RESULTS AND DISSCUSSIONS

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 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 also observed for the film coated with HEMA. This is followed by DMAEA which show only moderate reduction in tackiness compared with the uncoated film. In contrast the samples coated with n-BA show a drastic increase in tackiness with irradiation indicating that polybutyl acrylate formed is rather sticky. Similar trend also observed for samples coated with NVP, suggesting that only AAc and HEMA likely to be suitable for applications require low tackiness. However, films coated with AAc rendered hard surface and peeling of the coated layer on stretching .On the other hand poor wetting of HEMA with RVNRL film surface was observed.

Considering above limitations with HEMA and AAc, in order to enhance the compatibility of above chosen hydrophilic monomers with rubber which is hydrophobiv, an attempt was made to mix the above individual hydrophilic monomers with a hydrophobic monomer, n-BA which poses T_g approaching that of natural rubber and also used used as sensitizer in RVNRL preparation. Referring to Figure 2, it is clear that the film coated with 80%AAc/20%n-BA and 50%AAc/ 50%n-BA show remarkable decline in tackiness with dose, approaching 0 at 40kGy. Unfortunately, the peeling of the coated layer on stretching coupled with hard and stiff coated surface were not improved. Interestingly, such problems were not observed for films coated with 80%HEMA/ 20%n-BA mixture and it is noted an improved wetting of HEMA on RVNRL surface with the addition of 20% n-BA. Taking the above criteria into consideration , possible suitable coating material is, 80%HEMA/20%n-BA combinations. Thus from this point further studies were focused on coating of 80%HEMA/20%n-BA.

Results on various other methods which were tried to further improve the quality of the coating were plotted in Figure 3. In this experiment all 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 give reduction in tackiness in varying extent with irradiation. The improvement with acid treatment could be due to the fact that 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 render improvement. This results is in line with the hypothesis for trivalent metal ion which has been described elsewhere(Podell 1986) . In relation to this hypothesis it is believed that the trivalent aluminum ion in an acidic solution , form multiplicity of linkages with, on the one hand , the hydroxyl group of PHEMA and on the other hand , the various non rubber constituents in the rubber latex film- in particular with protein substances. Thus an improved adhesion of the PHEMA on the RVNRL surface have achieved.

Finally, the samples which were produced by dipping the partially wet RVNRL film offered the most promising feature with regard to tackiness. Visual observations also confirms that even coating and best homogeneity is achieved. This results could be attributed by the accelerative effect of water on graft polymerization as already indicated by Sasaki et al.(Sasaki et al.1979) in the similar monomer system. Besides that 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 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 RVNRL film coated with 80%HEMA/20%n-BA where the wet film dipping technique was employed prior to irradiation.

Surface Topography

SEM photomicrographs of surfaces are shown in Figure 4. It can be noted that the hydrogel coated surface were made to rough whereas the uncoated surface is appear to be smooth. Comparing the coated surfaces which were irradiated at 20kGy and 80kGy, it is apparent that the roughness of the coating increasing with irradiation dose. Accordingly, a close relation between roughness and tackiness is observed; the decrease in tackiness is due to increase in roughness. This observation is in agreement with report by Takeiro Saito et al.(Saito et al. 1993) who studied on development of anti-stickiness of rubber surface by UV irradiation and sputter -etching treatments.

CONCLUSIONS

Hydrogel coating onto RVNRL film using Low Energy Electron Beam approach in this study was effective in reducing the tackiness of RVNRL film where 80%HEMA/20%n-BA 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. SEM photomicrographs confirms that, 80%HEMA/ 20%n-BA coating at 80kGy irradiation dose gave the necessary surface roughness in relation to reduced surface tackiness.

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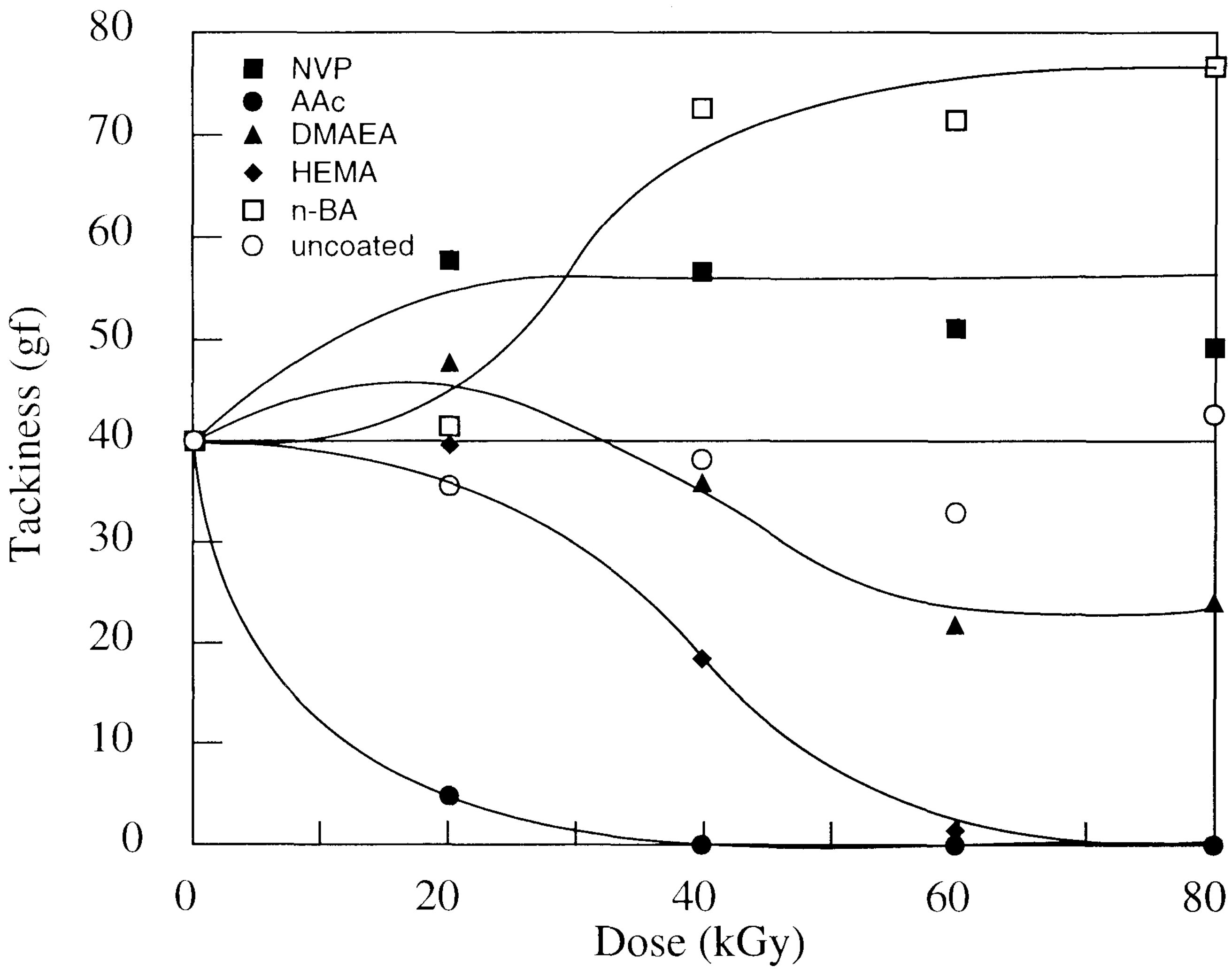

Figure 1. Effect of irradiation on tackiness of RVNRL film coated with various monomers.

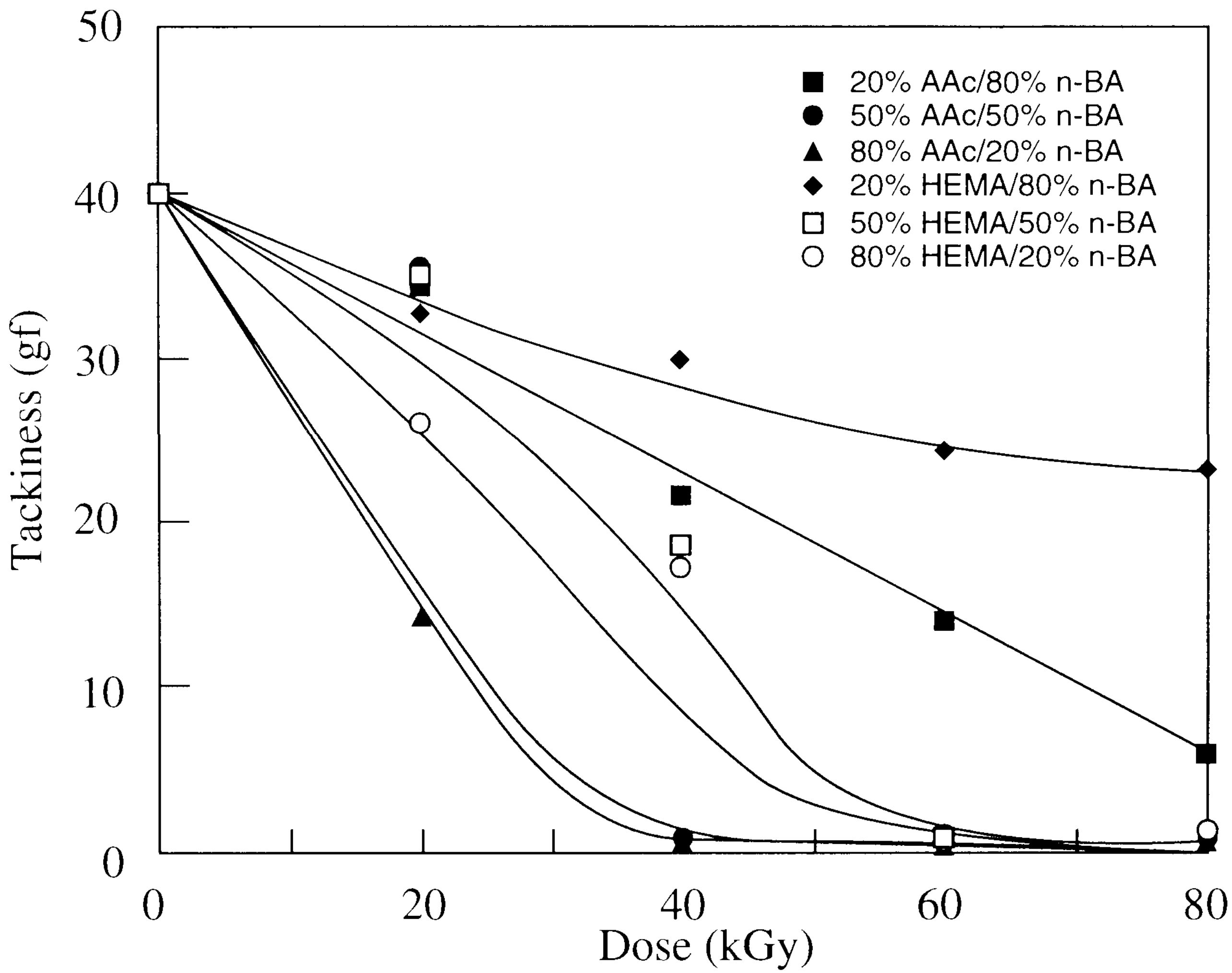

Figure 2. Effect of irradiation on tackiness of RVNRL film coated with various monomer mixtures.

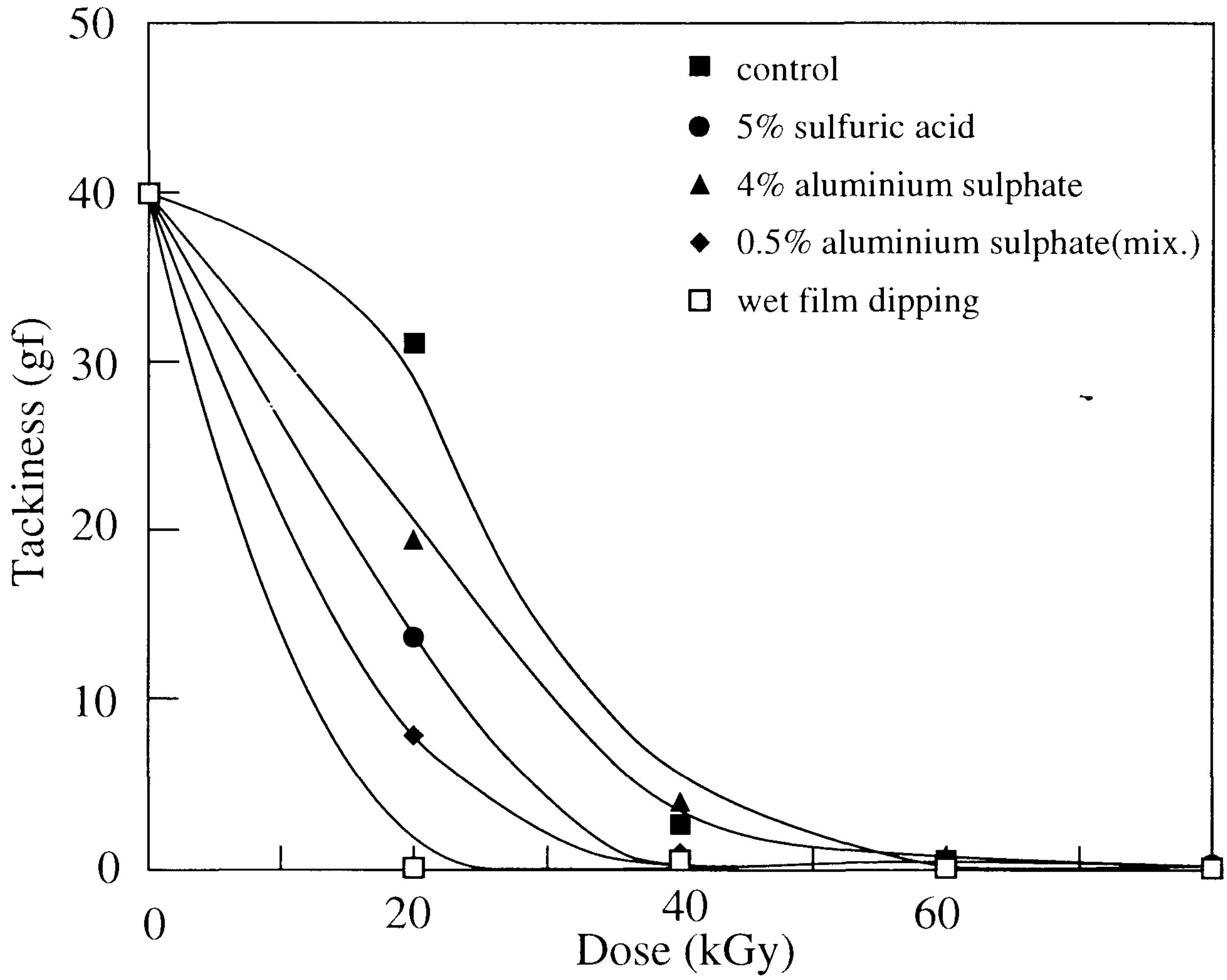

Figure 3. Effect of irradiation on tackiness of RVNRL film coated with 80% HEMA/20% n-BA.

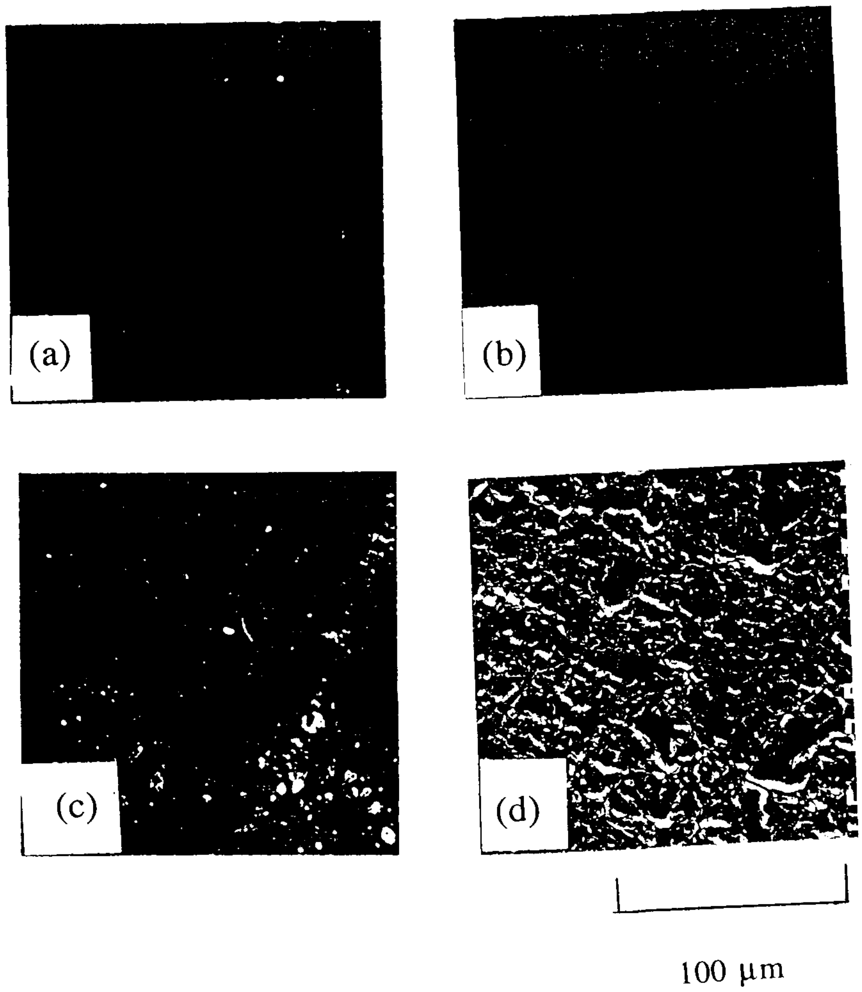

Figure 4 . Scanning electron micrographs of RVNRL film
(a) uncoated RVNRL film (control)
(b) uncoated RVNRL film (irradiated at 80kGy)
(c) coated RVNRL film with 80% HEMA / 20% n- BA (irradiated at 20kGy)
(d) coated RVNRL film with 80% HEMA / 20% n-BA (irradiated at 80 kGy)