# Study of Radiation-Induced Graft Copolymerization of Butyl Acrylate onto Chitosan in Acetic Acid Aqueous Solution

**Li Yu, Yu He, Liang Bin, Fang Yue'e**

*Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China*

**ABSTRACT:** The graft copolymerization of butyl acrylate onto chitosan in acetic acid aqueous solution was investigated, using the γ-ray of $^{60}$Co γ-irradiation method. Fourier transform infrared spectra analysis, X-ray diffraction analysis, and scanning electron microscopy characterized the graft copolymer. The effect of synthesis variables in the graft copolymerization have been discussed in the light of grafting efficiency, grafting percentage, and homopolymer percentage. Hydrophilicity and impact strength of the films formed from copolymer solution were tested and their feasibility as seed coating was studied. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2855–2860, 2003

**Key words:** chitosan; butyl acrylate; graft copolymerization; γ-ray irradiation; seed coating

## INTRODUCTION

Chitin is an abundant organic material that can be obtain from the shellfish waste of crab or shrimp. Chitosan is a polyaminosaccharide that can be easily derived from chitin by N-deacetylation. Because of its biocompatibility, biodegradability, and avirulence, chitosan has been widely used on biomedical and agriculture. Since chitosan is easily dissolved in dilute organic acids such as acetic or formic acid, it has been utilized as films[1] and fibers.[2] Seeds treated with biological chitosan films can promote seed germination and seeding growth, and improve plants' stress-resistance ability.[3] However, because of their brittleness and poor water-resisting properties, it is necessary to modify chitosan films.

The chemical combination of natural and synthetic polymer is a promising method for the preparation of new materials that could have desirable properties. Recently, there has been a growing interest in grafting modification of chitosan for biomedical, industrial, and agriculture applications. Graft copolymerization of chitosan with acrylonitrile, methylmethacrylate (MMA), methylacrylate, and vinyl acetate using azobisisobutyronitrile (AIBN) as an initiator has been studied.[4] Grafting of acrylamide and 2-hydroxyethlymethacrylate (HEMA) onto chitosan was studied used ceric(IV) salt as redox initiator.[5,6] Graft copolymerization of HEMA onto chitosan was studied using thiocarbonation–potassium bromate as redox initiator.[7] Graft copolymerization of styrene, vinylacetate, acrylamide, MMA, HEMA, and *N,N'*-dimethylaminoethylmethacrylate onto chitosan using $^{60}$Co γ-irradiation has been reported in the literature.[8–10]

In this work, we studied the modification of chitosan by γ-ray irradiation-induced graft copolymerization with butyl acrylate. The effect of synthesis variables in the graft copolymerization have been discussed in the light of grafting efficiency, grafting percentage, and homopolymer percentage. Butyl acrylate was selected because it is hydrophobic and soft monomer, which grafted onto the chitosan, is expected to increase the hydrophobicity and flexibility of macromolecule. Hydrophilicity and impact strength of the films formed from graft copolymer solution were tested and their feasibility as seed coating was studied.

## EXPERIMENTAL

### Materials

Chitosan was obtained from San Huan Ocean Biochemical Co. Ltd. (China). Its degree of deacetylation and the apparent viscosity were determined as 91.2% and 30 MPa s. Butyl acrylate (BuA) was chemical grade. Other chemicals used were analytical grade and used without any further purification.

### Graft copolymerization and treatment of copolymer

In a typical grafting reaction, an exact amount of dry chitosan was first dissolved in 1% acetic acid using a

50 cm$^3$ stoppered bottle, follow by the addition of monomer (BuA). After stirred 10 min constantly, the system was deoxygenated by slow bubbling of nitrogen gas through the solution for 5 min. The sample bottles were irradiated for a specified time in a $^{60}$Co γ-ray source chamber. After completion of the reaction, the contents were cooled and cast on a polytetrafluoroethylene (PTFE) plate and evaporating the solvent under an infrared lamp in order to obtain grafted films. The grafted films were then dried to a constant weight under vacuum at 60°C for 6-7h in order to remove water and unreacted monomer.

The homopolymer of butyl acrylate was removed from the crude graft copolymer films by exhaustive Soxhlet extraction with toluene for 48 h. The graft parameters [grafting percentage (G%), grafting efficiency (E%), homopolymer percentage (H%)] used to characterize the nature of the copolymer are defined and calculated as follows:

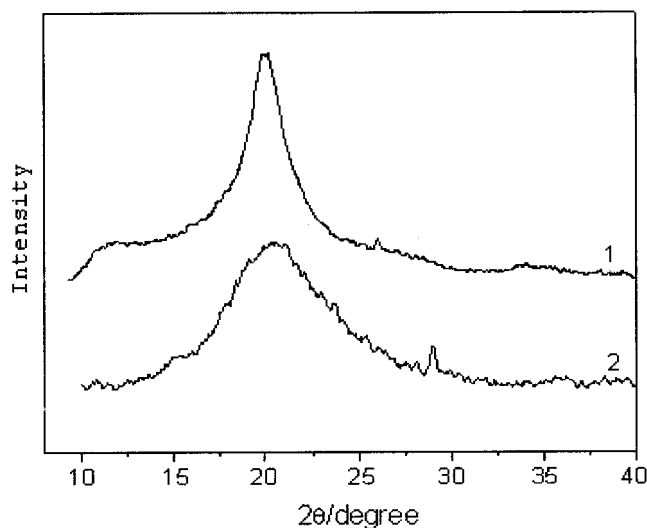$$G\% = \frac{W_g - W_0}{W_0} \times 100$$

$$E\% = \frac{W_1}{W_2} \times 100$$

$$H\% = \frac{W_H}{W_2 + W_3} \times 100$$

where $W_g$ is weight of graft copolymer, $W_0$ is weight of chitosan, $W_1$ is weight of grafted monomer (BuA), $W_2$ is weight of reacted monomer (BuA), $W_3$ is weight of unreacted monomer (BuA), and $W_H$ is weight of homopolymer.
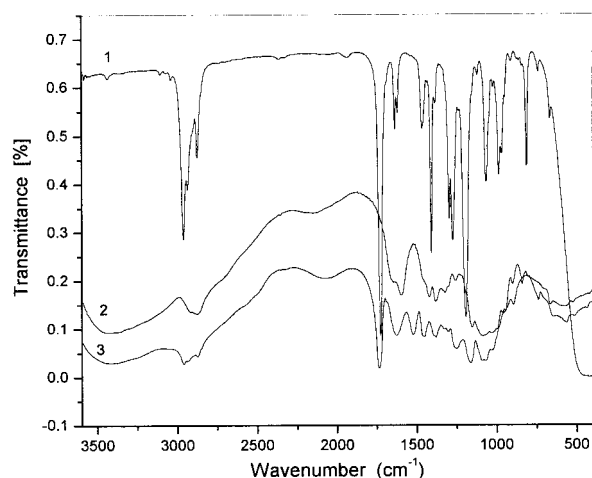


**Figure 1** IR spectra of chitosan, BuA, and chitosan-g-PBuA. (1) BuA, (2) chitosan, and (3) chitosan-g-PBuA (grafting percentage 273.06%).



**Figure 2** X-ray diffraction patterns. (1) Chitosan and (2) chitosan-g-PBuA (grafting percentage 273.06%).

## Characterization

X-ray diffraction patterns were obtained by using a Japanese Rigaku D/max γ$_A$ X-ray diffractometer equipped with graphite monochromatized CuKα radiation (λ = 0.154178 nm). The scanning range was 1.5°–10° with a scanning rate of 2°/min.

Infrared (IR) spectrum was recorded on a Bruker Vector-22 Fourier transform infrared (FTIR) spectrometer scanning from 4000 to 400 cm$^{-1}$ at room temperature. The samples were ground with KBr crystal and the mixture of them was pressed into a flake for IR measurement.

The microstructure of graft copolymer was imaged using a X-650 scanning electron microscope.

## Water absorption measurements

The clean, dried grafted films of known weights were immersed in distilled water at 25°C until equilibrium was reached (almost 24 h). The films were removed, blotted quickly with absorbent paper, and then weighed. The absorption percentage of these samples was calculated using the following equation:

$$X\% = \frac{M_1 - M_0}{M_0}$$

where $M_0$ and $M_1$ are the weight of dry and swollen samples, respectively.

## Hydrophilicity studies

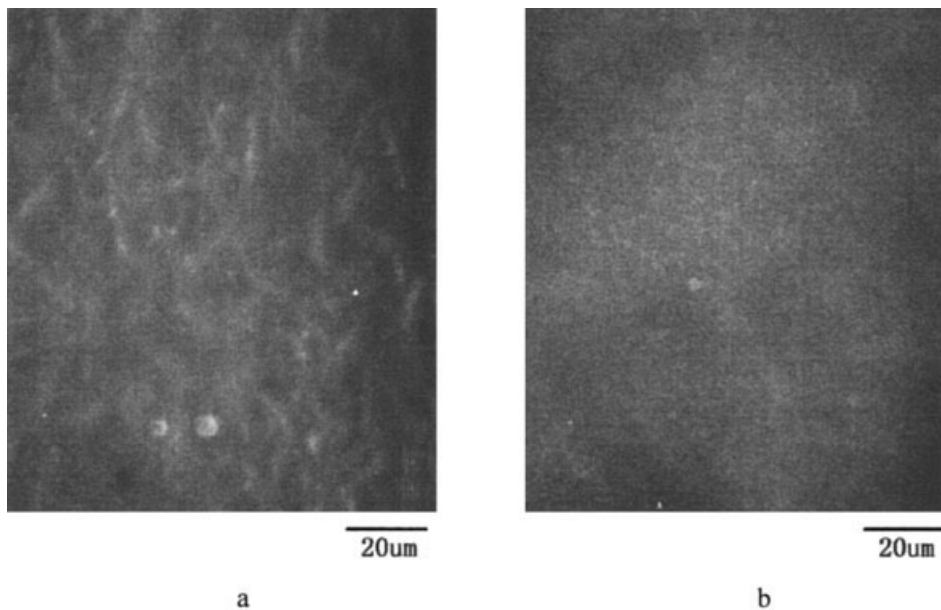The contact angle measurement was used for studying the hydrophilicity of chitosan-g-BuA films. The con-

**Figure 3** SEMs. (a) SEM of chitosan film and (b) SEM of chitosan-g-PBuA film (grafting percentage 273.06%).

tact angle values of water were measured by a JY-82 contact angle finder.

## Impact strength

The impact strength of grafted films were measured using a QCJ impact machine at room temperature.

## Coating seed germination studies

The solution of graft copolymer was poured into a glass bottle containing 50 g wheat seeds. The mixture was stirred for 5 min. The coating seeds were then spread and left a predetermined time for solidify. The coating seed germination studies were performed by measuring germination percentage following the GBT 3543.7-1995 norm of the People's Republic of China. The results of measurements were studied together with a control (no treatment).

## RESULTS AND DISCUSSION

### Characterization of the chitosan-g-PBuA

Figure 1 shows IR spectra of BuA, untreated chitosan, and chitosan-g-PBuA. Compared with pure chitosan, the IR spectrum of chitosan-g-PBuA has an additional peak at $1740 \text{ cm}^{-1}$ due to the ester carbonyl group of PBuA.
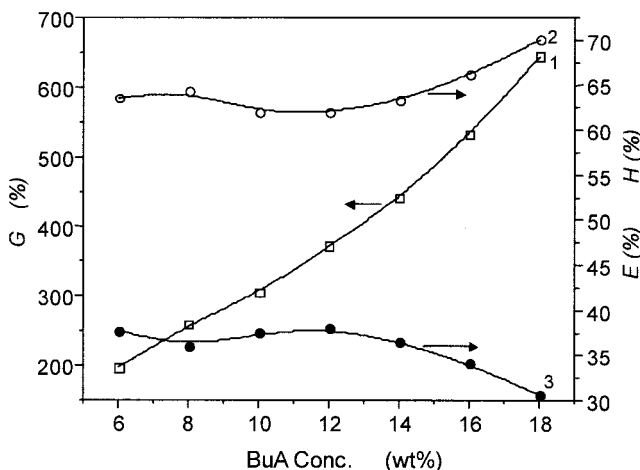


**Figure 4** Effect of BuA concentration. Dose rate: 66.32 Gy/min; dose: 6000 Gy; $T=30°C$. (1) Grafting percentage, (2) grafting efficiency, and (3) homopolymer percentage.
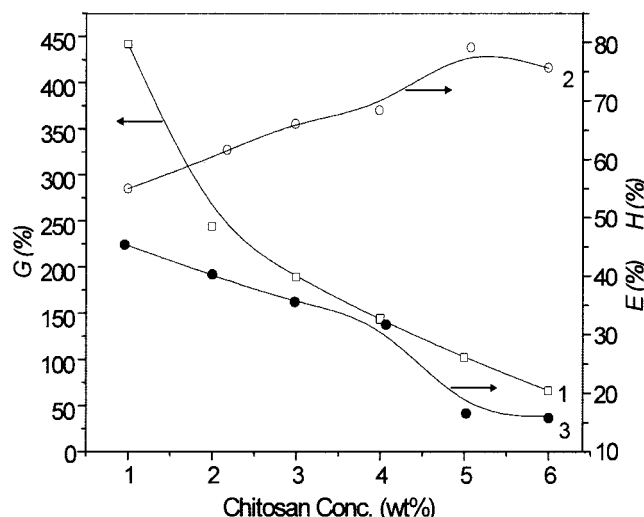


**Figure 5** Effect of chitosan concentration. Dose rate: 66.32 Gy/min; dose: 6000 Gy; $T= 30°C$. (1) Grafting percentage, (2) grafting efficiency, (3) homopolymer percentage.
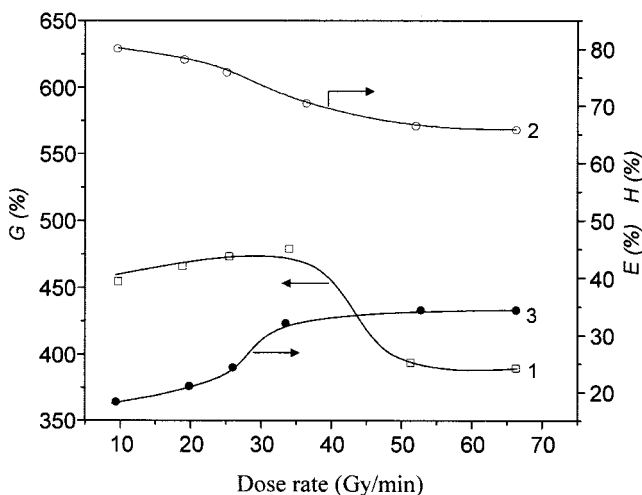
Diffractograms of pure chitosan and chitosan-g-PBuA are presented in Figure 2. The diffractograms of pure chitosan samples shows the characteristic peak at $2\theta=11°$ and $20°$. Note that the peak $2\theta=11°$ disappeared and the peak $2\theta=20°$ decreased sharply in chitosan-g-PBuA. A decrease in crystallinity may be due to introduction of bulky pendant chains of grafted PBuA in chitosan matrix.

The scanning electron micrographs of pure chitosan and chitosan-g-PBuA film are shown in Figure 3. Compared with pure chitosan film, there is a significant increment of smoothing on the surface of chitosan-g-PBuA film. This may be due to the conglutination of PBuA grafting chains, which have a high pliancy and plasticity, and they cover the surface of grafted film at a high grafting percentage.
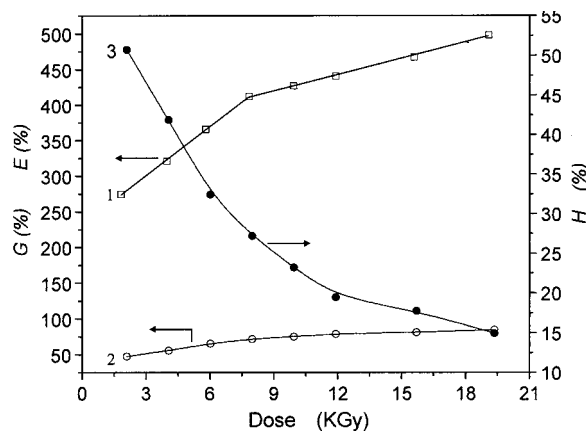
### Influence of reaction conditions on graft parameters

#### Effect of monomer concentration

The effect of monomer concentration on graft copolymerization of BuA onto chitosan is depicted in Figure 4. With an increase in monomer concentration, $G\%$ increases continuously, which is a very general trend in grafting reaction. When below 12% (monomer concentration), $E\%$ and $H\%$ have no significant change, whereas above 12% (monomer concentration) $E\%$ gets a substantial rise and $H\%$ declines. This may be explained as follows: with an increase in monomer concentration, the amount of grafting chains rise; when the concentration of monomer is higher, the radicals generated by the irradiation of γ-ray on grafting chains continuously initiate graft of monomer. Therefore, $E\%$ increases and $H\%$ decreases correspondingly.
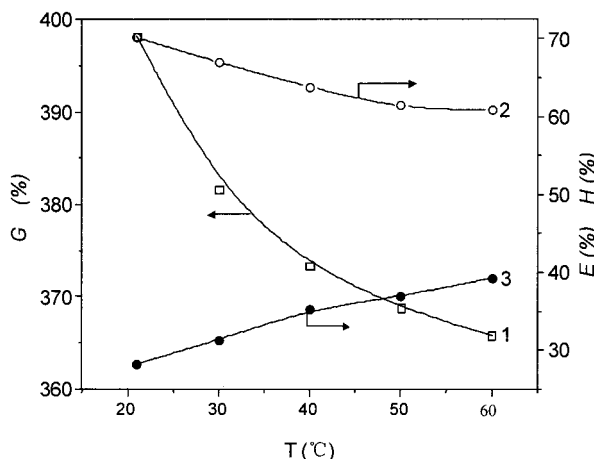
**Figure 7** Effect of radiation dose. Chitosan: 14.3 wt %; BuA: 85.7 wt %; dose rate: 65.41 Gy/min; $T$= 30°C. (1) Grafting percentage, (2) grafting efficiency, (3) homopolymer percentage.

#### Effect of chitosan concentration

Figure 5 shows the relation between graft parameters and chitosan concentration. The decrease of $G\%$ may be due to the decreasing relative amount of macroradicals and the increasing viscosity of system that reduces the migration of BuA molecules to macroradicals. Despite the relative amount decreases, the absolute amount of macroradicals is increased which results in the decrease of monomer radicals. Accordingly, $E\%$ increases and $H\%$ decreases.

#### Effect of dose rate and total dose

The intensity dependence of graft parameter was investigated for the irradiation dose rate range, 10–70 Gy/min. The result are depicted in Figure 6. It is found that $G\%$ has no significant change in the rang of

**Figure 6** Effect of radiation dose. Chitosan: 14.3 wt %; BuA: 85.7 wt %; dose: 6000 Gy; $T$= 30°C. (1) Grafting percentage, (2) grafting efficiency, and (3) homopolymer percentage.

**Figure 8** Effect of reaction temperature. Chitosan: 14.3 wt %; BuA: 85.7 wt %; dose rate: 63.68 Gy/min; dose: 6000 Gy. (1) grafting percentage, (2) grafting efficiency, (3) homopolymer percentage.

**TABLE I**
**Water Absorption of Samples**

| Sample grafting percentage (%) | 264.43 | 319.81 | 372.62 | 439.54 | 550.36 |
|---|---|---|---|---|---|
| Water absorption (%) | 40.89 | 33.05 | 24.67 | 16.02 | 10.24 |

lower dose rates, 10–35 Gy/min. This is expected behavior for irradiating grafted systems. At dose rates higher than 35 Gy/min, $G\%$ decreases sharply and finally tends to level off with a further increase in the dose rate. This could possibly be due to the increasing rate of homopolymerization. The number of free radical species increases with dose rate. During the graft copolymerization process, monomer molecules will continuously diffuse into the polymer matrix at a constant rate, irrespective of irradiation dose rate. Under such conditions, the greater availability free radicals at a higher dose rate will increase the rate of homopolymerization. As a result, the relative rate of grafting reaction will decrease significantly at higher dose rates.

The decrease of $E\%$ and the increase of $H\%$ may also be due to the homopolymerization of monomers. However, with the increase of dose rate, the amount of free radicals increases and the termination reaction of radicals speed up. Therefore, beyond 35 Gy/min (dose rate) there is marked decrease in the homopolymerizion rate and tends to level off.

The influence of dose on the graft parameters of chitosan-g-PBuA is investigated and shown in Figure 7. It can be seen that $E\%$ increases slowly with increasing irradiation dose, which may be due to the increasing concentration of free radicals formed in the polymer substrate. The figure shows that $H\%$ is decreased continuously with the increase of dose. This may be due to the fact that homopolymer is grafted onto the chitosan under the irradiation of $\gamma$-ray.

The figure also exhibits an increase in $G\%$ with the increase in dose of irradiation up to 8 kGy; beyond this, there is a marked decrease in the rate of grafting. During the initial stages of grafting, the reaction is controlled by grafting kinetics, and hence the grafting rate decided by the amount of free radicals formed in the polymer substrate. Thereafter, with the increase of irradiation dose, the rate of generating radicals exceeds the rate of monomer diffusing to substrate. As a result, grafting reaction is controlled by diffusion, which results in the decrease of grafting rate.

Effect of temperature

When the other conditions are invariable, the effect of reaction temperature on graft parameters is shown in

Figure 8. It is obvious that $E\%$ and $G\%$ decrease with the increase of reaction temperature, and $H\%$ increases correspondingly. This is attributed to the fact that the termination reaction and homopolymerization speed up and the degrading rate of chitosan increases under a higher temperature.

Water absorption and hydrophilicity studies

The poor water-resisting properties of chitosan were due to its high water absorption power and hydrophilicity. The graft of poly(BuA) onto chitosan will modify the hydrophilic properties of the copolymer.

Table I shows the water absorption percentage for chitosan-g-PBuA films. It shows a decreasing trend of water absorption percentage with the level of BuA grafting onto chitosan. The crosslinking of BuA molecules in the polymer network and the hydrophobicity of BuA may be responsible for the decrease of water absorption percentage.

The values of contact angles ($\theta$) of chitosan and its grafted films are showed in Table II. With the increase of grafting percentage, $\theta$ increases continuously. The increase of $\theta$ means the decrease of hydrophilicity. The hydrophilic nature of chitosan is due to the presence of free amino groups on the C-2 carbon. During the grafting process, a substantial number of free amino groups are blocked by the growing chains of PBuA. At a high graft ratio, the surface of films were covered by the grafting chains of PBuA, which are hydrophobic. These changes may be responsible for the decreasing hydrophilicity of grafted films.

**Impact strength**

The effect of chitosan-g-BuA ratio on the impact strength of grafted films is depicted in Figure 9. Since pure chitosan film is very brittle, we did not measure its impact strength. It can be observed that the impact strength increases significantly with the increase of BuA content. PBuA grafts introduce toughness in the structure of the copolymer, which enhances the impact strength of grafted films.

**Coating seed germination studies**

Avirulence is one of the most important properties that are required of seed coating. The material used as

**TABLE II**
**Contact Angles ($\theta$) of Chitosan and Its Grafted Films**

| Sample grafting percentage (%) | Chitosan | 273.06 | 319.81 | 372.62 | 439.14 |
|---|---|---|---|---|---|
| Contact angle ($\theta$) | 54.42° | 93.00° | 95.17° | 100.33° | 106.67° |

seed coating cannot inhibit the germination of seed. In this study, we investigated the effect of the BuA to chitosan ratio on the germination percentage of coating seeds. The analysis of variance is shows in Table III. In the range 0.5–1 (BuA/chitosan), there are no significant differences in germination percentage between the treated seeds and the control. When the ratio of BuA to chitosan is up to 2, the germination percentage of coating seeds were decreased. This may be due to the increasing hydrophobicity of seed coating, which inhibits the supply of water for seeds.

## CONCLUSION

PBuA was grafted onto chitosan in acetic acid aqueous solution by the γ-ray irradiation polymerization. The proof of grafting was obtain from FTIR spectrum, X-ray diffraction, and SEM tests.

Increasing grafting percentage was observed when the monomer concentration and total dose were increased or when the chitosan concentration and reac-
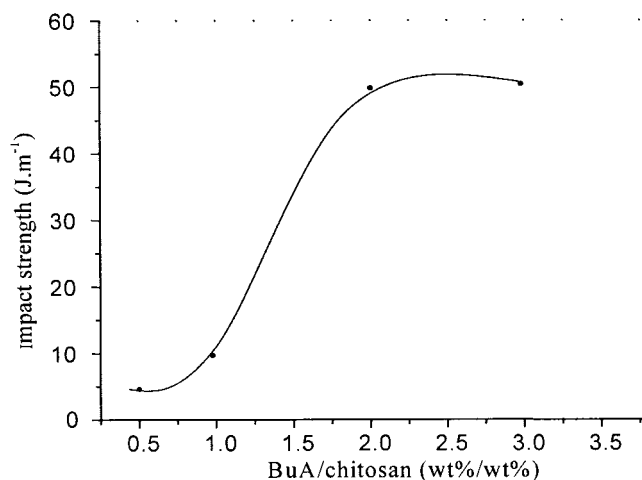
**Figure 9**  Effect of BuA-to-chitosan ratio on the impact strength of grafted films.

**TABLE III**
**Effect of BuA-to-Chitosan Ratio on the Germination Percentage of Coating Seeds**

|  | BuA/chitosan (wt %/wt %) | Germination percentage (%) | | | | |
|---|---|---|---|---|---|---|
|  |  | 1 | 2 | 3 | 4 | Average |
| Grafted sample |  |  |  |  |  |  |
| 1 | 0.5 | 95 | 93 | 97 | 99 | 96 |
| 2 | 1 | 94 | 96 | 97 | 93 | 95 |
| 3 | 2 | 92 | 90 | 90 | 93 | 91.25 |
| Control |  | 95 | 98 | 97 | 94 | 96 |

tion temperature were decreased. Under lower dose rates, the grafting percentage has no significant change, whereas, above 35 Gy/min (dose rate) the grafting percentage gets a sharp decrease.

Compared with pure chitosan film, the chitosan-g-PBuA films have enhanced hydrophobic and impact strength for their practical use. The coating seed germination experiences brought out that below 2 (weight ratio of BuA-to-chitosan), there is no significant decrease in the germination percentage of coating seeds. The chitosan-g-PBuA films can be expected to have broad application for seed coating.

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