

## Radiation Copolymerization of Styrene Monomer onto Tapioca and Natural Rubber

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**Abstract.** To overcome the problem of plastics waste, research activities of radiation copolymerisation of styrene monomer onto tapioca and natural rubber have been done. Tapioca gel, natural rubber latex, styrene monomer, and emulsifier were mixed in the blender, and irradiated. Gamma radiation from Cobalt<sup>60</sup> source was used as inisiator on copolymerisation. The irradiated copolymer emulsion was dried in the oven, and made a sample film using hydraulic and cold press machine. The effect of radiation, composition, recycle process on the hardness, tensile strength, tear resistant, water content, dissolution on acetone, and degradability of copolymers were evaluated. The results show that the irradiated tapioca-polystyrene-natural rubber copolymer was thermoplastic bio-degradable. After buried in the soil for two months and 10 days, the copolymer was completely degraded. The composition and radiation were affected on the physical properties of copolymer. The maximum of tensile strength of copolymer was 12.4 MPa, tear strength was 66.9 kg/cm, and hardness was 96.4 Shore A, at 10 kGy of irradiation dose.

**Keywords:** Copolymer; tapioca; polystyrene; natural rubber; irradiation

### Introduction

Natural rubber is a polymer of isoprene that was originally derived from a milky colloidal suspension, or latex, which has poor mechanical properties and chemical solvent resistance. These inherent drawbacks of natural rubber have limited its application in industry. To extend its application, various methods were developed in order to modify its properties.

According to George F. B. [1], modification of natural rubber has been performed in different ways. One of the processes to modify natural rubber is graft copolymerization. Small amounts of latex were put into emulsion polymerization of vinyl monomer to produce adhesives for producing particle board from coconut fiber, radiation shielding material, electrical gloves, improvement of mechanical properties of natural rubber, and degradable thermoplastic [2-8].

According to Charlessby [9], polystyrene is a thermoplastic polymer with high dimensional stability, high impact, low shrinkage, and chemical non-organic resistance. Styrene monomer

was used in this experiment to enhance thermoplasticity, impact strength and toughness of natural rubber. While, tapioca is biodegradable natural polymer will be degraded after contact with microorganism such as *aspergillus niger* and *penicillium pinophilum*, it is also has high temperature resistance, and relatively cheap [10, 11]. Tapioca was used in this experiment to improve biodegradability, and Gamma ray from Cobalt-60 source was used as copolymerization initiator.

The main purpose in this study is to obtain degradable thermoplastic alternative. The effect of composition, radiation and film forming condition on physical properties and degradation of copolymer were evaluated.

## **Experimental**

### *Materials*

Styrene monomer was used technical grade, tapioca powder was used commercially available, natural rubber latex was ASTM quality obtained from PTP XI Nusantara, Indonesia and Tween 20 used as emulsifier.

### *Preparation of tapioca-polystyrene-natural rubber copolymer*

Tapioca gel and natural rubber latex was used in this experimental, the tapioca gel mixed with monomer styrene, natural rubber latex, and emulsifier. The emulsion resulted was then irradiated with gamma ray from Cobalt-60 source. The irradiated emulsion was dried in the oven. The dried copolymer resulted was blended using laboplastomil and made films using hot and cold press machine. The mechanical properties and degradability of copolymer film was then evaluated.

### *Mechanical properties test*

The mechanical properties such as tensile strength was evaluated using Strogaph-R1 tensile tester machine according to ASTM D 412 with 500 mm/min speed.

### *Soil burial degradability*

The tapioca-polystyrene-natural rubber copolymer film to be tested was in dried condition and constant weight. The sample films were buried completely into soil outdoors and left it. The pH of soil was about 7. The tested samples were removed at intervals time. The degradability of sample film was indicated from weight loss of sample and calculated gravimetrically.

## Results and Discussion

### *Radiation copolymerization*

Graft copolymerization of styrene monomer on tapioca gel and natural rubber latex was prepared by emulsion polymerization using tween 20 as emulsifier and Gamma ray from Cobalt-60 source as initiator respectively. To confirm the occurrence of polystyrene graft tapioca and natural rubber, the product was identified by FTIR.

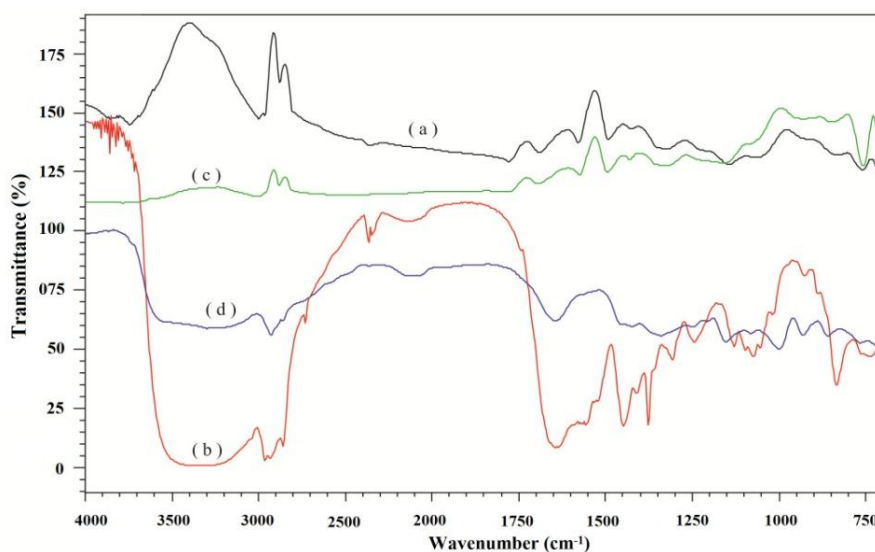
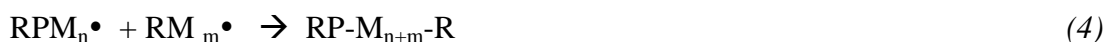


Figure 1. The FTIR spectrum of, tapioca-polystyrene-natural rubber copolymer, natural rubber, polystyrene, and tapioca.

Fig. 1 illustrated the FTIR spectra of tapioca-polystyrene-natural rubber copolymer (black line), natural rubber (red line), polystyrene (green line) and tapioca (blue line). FTIR assignment of tapioca, natural rubber and polystyrene had been reported by many researchers [12,13,14]. The characteristic absorption bands of  $R_2C=CHR$  of isoprene was confirmed at  $839\text{ cm}^{-1}$ . The peaks at  $3095$  and  $2939\text{ cm}^{-1}$  was assigned to the aromatic C-H stretching ring of polystyrene. The signal at  $1440$  and  $1364\text{ cm}^{-1}$  were attributed to the aliphatic C-H stretching in natural rubber. The peak of grafted natural rubber, which was appeared at  $1600\text{ cm}^{-1}$  was C=C stretching of the benzene ring of styrene. This confirmed the existence of grafting polystyrene onto the natural rubber backbone. The characteristic absorption band of O-H stretching of tapioca was confirmed at  $3000\text{--}3600\text{ cm}^{-1}$ . The peak at  $2933$  and  $2881\text{ cm}^{-1}$  was assigned to C-H stretching of  $\text{CH}_2$ , and peak at  $1190\text{--}950\text{ cm}^{-1}$  was assigned to C-O stretching. For starch-graft-PS copolymers, the characteristic peaks were:  $3020\text{--}3080$  (C-H vibrations of the aromatic ring),  $2000\text{--}1660$  (C-C vibrations in the

benzene ring), 1490, 76 and 700  $\text{cm}^{-1}$  (C–H stretching of the aromatic ring), originally from the polystyrene, and 3000–3600 (O–H stretching), 2880–2920 (C–H stretching), 1645 (O–H first overtone) and 1190–950  $\text{cm}^{-1}$  (C–O stretching), originally from the starch.

The chemical bonding of the grafted copolymer is related with reaction mechanism of graft copolymerization, where the free radical reaction was involved [8]. The first stage of free radical reaction was interaction of  $\gamma$ -ray with water to form free radical ( $\text{R}\cdot$ ). At the second stage, the free radical formed was then initiate free radical reaction with monomer (M) and polymer (P) to form new free radical of monomer ( $\text{M}\cdot$ ) and polymer ( $\text{P}\cdot$ ). While at the third stage, propagation of free radical formed by reaction of new free radical with monomer ( $\text{RM}_{n+1}\cdot$ ) and polymer ( $\text{RP}_{n+1}\cdot$ ). At the last stage of free radical reaction, recombination between free radicals occurred to form homopolymer ( $\text{R-M}_{n+m}\text{-R}$ ), and grafted copolymer ( $\text{RP-M}_{n+m}\text{-R}$ ). Schematically the reaction mechanism of the graft copolymerization of monomer onto polymer illustrated as follow,



### *Effect composition*

The data experimental of the effect of composition of tapioca, polystyrene and natural rubber on tensile strength of tapioca-polystyrene-natural rubber copolymer illustrated in Table 1. Where the copolymerization irradiation dose was conducted at 5 kGy, and the irradiated copolymer was blended using laboplastomill for 20 min at 170°C with 60 rpm speed, and the sample film molded at 170°C for 1.5 minutes and pressed by 17.5 MPa. According to Table 1, the tapioca content was affected on tensile strength of tapioca-polystyrene-natural rubber copolymer.

Table 1. Tensile strength of tapioca-polystyrene-natural rubber copolymer in different composition of tapioca (T), polystyrene (Pst) and natural rubber (NR).

Composition T/Pst/NR	Tensile strength, MPa
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133/200/100	7.5
100/200/100	8.9
65.5/200/100	9.5

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The tensile strength of tapioca-polystyrene-natural rubber copolymer was increased with decreasing of tapioca content, from 7.5 MPa tensile strength for composition of tapioca-polystyrene-natural rubber copolymer = 133/200/100 to 8.9 MPa for composition of tapioca-polystyrene-natural rubber copolymer = 100/200/100, and become 9.5 MPa for composition of tapioca-polystyrene-natural rubber copolymer = 65.5/200/100.

Increasing of tensile strength of tapioca-polystyrene-natural rubber copolymer strong relation with copolymer molecular alteration.

#### *Effect of $\gamma$ -irradiation*

The effect of  $\gamma$ -irradiation on tensile strength of tapioca-polystyrene-natural rubber copolymer containing of 25% tapioca, 50% polystyrene and 25% natural rubber illustrated in Fig. 1. According to this figure, the tensile strength of tapioca-polystyrene-natural rubber copolymer increased with increasing irradiation dose, from 2.9 MPa at irradiation dose 2.5 kGy, to 8.9 MPa at irradiation dose 5.0 kGy, and become 12.4 MPa at irradiation dose 10 kGy.

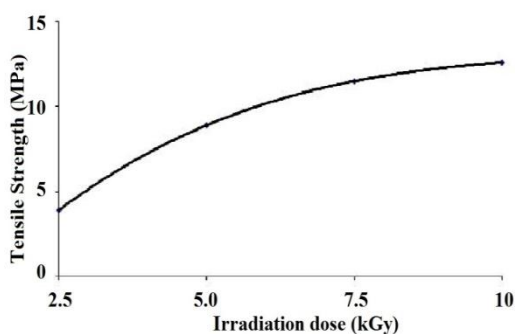


Figure 2. Effect of  $\gamma$ -ray irradiation on tensile strength of tapioca-polystyrene-natural rubber copolymer.

According to Glazer J. [15], the increasing tensile strength of tapioca-polystyrene-natural rubber copolymer strong relation with chemical bonding of copolymer molecule, its mean with increasing irradiation dose, the chemical bonding of tapioca-polystyrene-natural rubber copolymer were increased.

#### *Effect of film forming condition*

The effect of temperature and pressure of film forming on tensile strength of tapioca-polystyrene-natural rubber copolymer illustrated in Fig. 3 and Fig. 4.

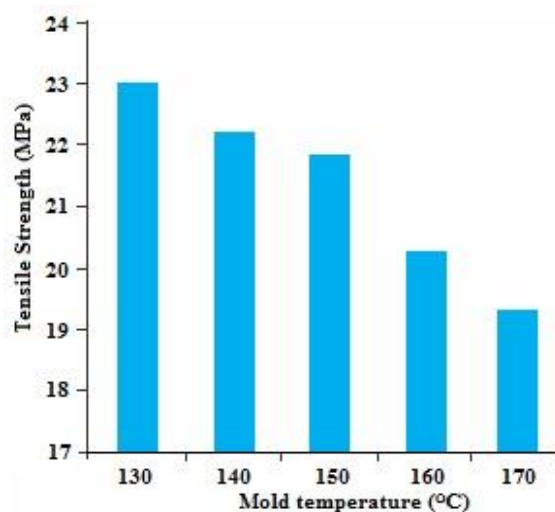


Figure 3. The effect of temperature of molding on tensile strength of tapioca- polystyrene-natural rubber copolymer.

According to figure 3, the appropriate film forming condition was at temperature 130°C and pressure 20 MPa respectively. With increasing molding temperature above 130°C, the tensile strength of tapioca-polystyrene-natural rubber copolymer was decreased from 23.0 MPa at molding temperature 130°C to minimal level 19.3 MPa and at molding temperature 170°C. The decreasing tensile strength of tapioca-polystyrene-natural rubber copolymer because of in higher temperature, breaking of the inter-chain bond occurred [9].

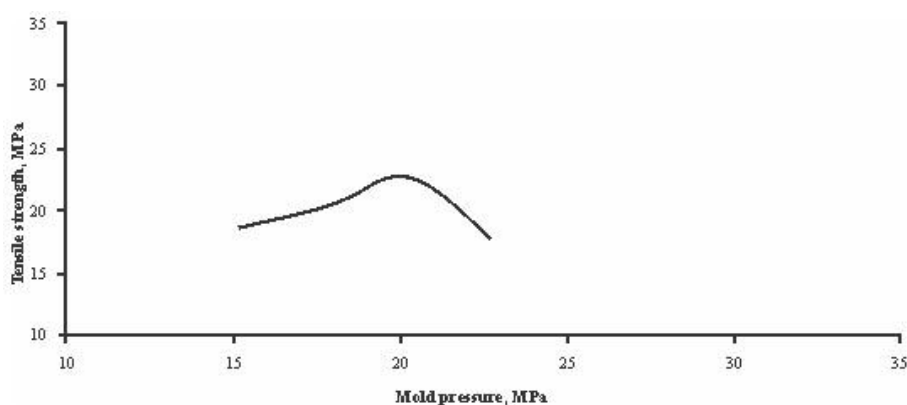


Figure 4. Effect of pressure of molding on tensile strength of tapioca-polystyrene-natural rubber copolymer.

According to Fig. 4, with increasing of molding pressure above 15 MPa, tensile strength of tapioca-polystyrene-natural rubber copolymer increased from 19.3 MPa at pressure of

molding 15.0 MPa to maximum level 23.0 MPa at pressure of molding 20.0 MPa, then decreased to 18.4 MPa at pressure of molding 22.5 MPa. The increasing tensile strength of tapioca-polystyrene-natural rubber copolymer also is due to increasing in molecular crosslink density in the copolymer, while decreasing tensile strength of the tapioca-polystyrene-natural rubber copolymer due to excess the crosslinked molecule number and the copolymer become brittle [15].

#### *Soil burial degradability*

The experimental results of soil burial degradability of tapioca-polystyrene-natural rubber copolymer in different duration time illustrated in Fig. 5. According to this table, with increasing of soil buried duration time, the weight loss of tapioca-polystyrene-natural rubber copolymer was increased from 2.9% at 21 d duration time, become 24.7 % at 35 d duration time, then 48,0% at 48 d duration time, and 91.3 % at 60 d duration time, finally up to 100% at 70 d duration time.

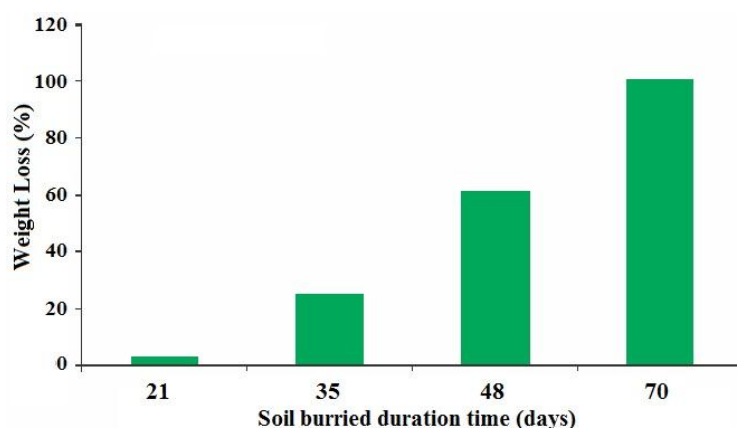


Figure 5. The effect of soil burial on weight loss of tapioca-polystyrene-natural rubber copolymer.

According to Suda and Surdia [10,11], the *aspergilluz niger* and *penicillium phinophilum* micro organism was enhanced degradation of tapioca-polystyrene-natural rubber copolymer by attacked to cleave the copolymer chain, thus yielding fragments to further degradation in environment because of their low molecular weight, beside that it was also rubber copolymer was eaten by termites.

## **Conclusions**

According to experiment data, the tapioca-polystyrene-natural rubber copolymer is biodegradable thermoplastic. Reducing tapioca content and increasing irradiation dose was enhanced the tensile strength of tapioca-polystyrene-natural rubber copolymer. The

temperature 130°C and pressure 20.0 MPa. The tapioca-polystyrene-natural rubber copolymer was degraded completely after soil buried for about 70 d.

## Acknowledgements

The author would like to acknowledge Mr. Armanu, Mr. Bonang, Mr. Edi Mulyana and Mr. Cahyono for helping on irradiation of samples. Special acknowledge also to bureau of Cooperation Legal and Public Relation of National Nuclear Energy Agency for propose this invention to Patent of Indonesia

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