

CHAPTER 5

CONCLUSION AND SUGGESTION

In this thesis, we prepared starch-g-polystyrene copolymers by a simultaneous irradiation technique from a ^{60}Co source at a fixed dose rate of 2.5×10^{-3} kGy/sec to various total doses (2-16 kGy). The graft copolymers were characterized in terms of the homopolymer content, grafting efficiency, grafting ratio, conversion and percent add-on. The graft copolymers (prepared by the total dose of 10 kGy) were mixed as part of the styrene-based polymer for the study of degradation of starch filled polystyrene plastic. The results are summarized as follows:

Cassava starch-g-polystyrene graft copolymers were synthesized and confirmed by the FTIR spectrophotometry. After radiation copolymerization of styrene onto cassava starch, one can observe the C-H stretching peak of aromatic ring at 3024 cm^{-1} , the C=C stretching peak at 1601 cm^{-1} and the absorption peak of cassava starch at $3300\text{-}3500\text{ cm}^{-1}$, $2850\text{-}2920\text{ cm}^{-1}$, and $960\text{-}1190\text{ cm}^{-1}$. It indicates that styrene was grafted on the starch backbone.

By increasing the quantities of total dose, at a fixed dose rate of 2.5×10^{-3} kGy/sec, we found that the grafting efficiency is the highest at the total dose of 10 kGy (62.6%) and decreased with increasing the total doses higher than 10 kGy. This suggests that the decreasing of grafting efficiency is due to the formation of small fragments of OH^\cdot and e_{aq}^- to form the homopolymer of styrene at the expense of grafting. Likewise, the lowest homopolymer formed occurred at the total dose of 10 kGy and the homopolymer content increased when the total dose was higher than 10 kGy.

Adding nitric acid in the reaction solution before irradiation increased the percent grafting efficiency and decreased the percent homopolymer content. In the acid media, the presence of H^+ ions can increase $G(\text{H}^\cdot)$ value which increases the number of hydrogen radicals (H^\cdot) in the system. The hydrogen radicals in the system can lead to

the increased number of grafting sites followed by increasing grafting probability. Thus the grafting efficiency is increased and the homopolymer is decreased accordingly. The conversion of monomer is decreased, because the amount of acid might be too concentrate and the starch might be hydrolyzed before it can be grafted with styrene when the granular cassava starch is used to make the graft copolymerization.

The cassava starch graft polystyrene used in the present work has 62.6% grafting efficiency, 35.6% grafting ratio and 25.2% add-on. The graft copolymer and starch are introduced into the polystyrene plastic, which contain 800-1200 ppm of lubricant of zinc stearate. At the same starch content, it was found that tensile strength and elongation at break decreased with increasing graft copolymer content (PS-S5-G10 < PS-S5-G5). For the PS-G15 sheets, the tensile strength and elongation at break are lower than those of PS-S15 sheets (PS-G15 < PS-S15). The results may indicate that incorporation of starch and starch-g-polystyrene in the presence of Epolene wax could possibly not be very well misible with polystyrene plastic. The amount of zinc stearate and soya oil did not affect significantly the mechanical properties of the plastic sheets, but their presence were essential to promote autooxidation.

The degradation behavior was followed by monitoring tensile strength and elongation at break, the extent of degradation by carbonyl index, Shore A hardness, molecular weights and distribution, thermal property of the plastic during outdoor exposure, soil burial test, gamma radiation, and UV irradiation. From Table 5.1, it was found that physical properties of PS sheet were gradually decreased with the outdoor exposure test. The behavior of PS-G15/36 sheet differed from that of the PS sheet, physical properties decreased rapidly with exposure time, so did gamma and UV irradiations. The PS and composite PS sheets took a longer time to degrade by soil burial test. Biodegradability resistance of PS and composite PS sheets to *Bacillus coagulans* 352, the SEM micrographs of the composite PS sheets reveal the destroyed area of starch that is the starting point of degradation. The experiments show that there was some significant effect between the plastic samples in solid and liquid media. In solid media, the side of plastic contacted with the media become yellowish while the other side remained unchanged. In liquid media, both sides of the plastics are yellowish.

Table 5.1 Properties of PS and PS-G15/36 sheets at various degradation testing

Test Method	Properties					
	Tensile Strength (MPa)	Carbonyl Index	Shore A Hardness	Mw	Ea (kJ.mol ⁻¹)	SEM Observation
Indoor Exposure ^a PS PS-G15/36	43, -, 43 20, -, 19.8	-	-	-	-	-
Outdoor Exposure ^b PS PS-G15/36	43, 36.2, 30.8 20, 2.1, 0	0.41, 0.51, 0.63 0.27, 0.78, 0.98	-	484040, 425695, 398238 395008, 362744, 277292	201.3, -, 166.3 97.8, -, 92.7	-
UV Irradiation ^c PS PS-G15/36	-	0.41, 0.41, 0.44 0.27, 0.32, 0.39	40.2, 36, 36 39.5, 34, 32	484040, 407692, 403652 395008, 346086, 304196	201.3, -, 239.0 97.8, -, 104.8	-
Gamma Irradiation ^d PS PS-G15/36	43, 44.6, 38.2 20, 22.1, 7.4	0.41, 0.56, 0.61 0.27, 0.29, 0.68	40.2, 40.5, 38.2 39.5, 40, 35.2	484040, 435568, 425319 395008, 377263, 328835	201.3, -, 204.6 97.8, -, 109.6	-
Soil Burial Test ^e PS PS-G15/36	43, 39.2, 33.9 20, 6.5, 3.3	-	-	-	-	not change has many holes
Resistance to <i>Bacillus coagulans</i> 352 PS PS-G15/36	-	-	-	-	-	not change has many holes

^{a, b, e} at control, 3-month, and 6-month exposure time

^c at control, 10-hour, and 21-hour UV Irradiation

^d at control, 100 kGy, and 300 kGy Gamma Irradiation

This work shows that the use of starch-g-polystyrene graft copolymers as part of the styrene based polymer for induced degradation of polystyrene plastic was the significant attribute to increase the degradation of polystyrene plastic. The rapid disintegration of the plastic in the environments was probably due to the initial biodegradation of starch to provide greater surface areas and many holes in the matrix for oxidative breakdown of the polymer, followed by the microbial digestion of the degradation products.

Suggestions

At present, there are more advancements in the use of degradable plastics, but at the same time the steadily increasing proportion of plastic wastes cause major problems of handling and disposal of domestic and industrial wastes. Ideally, the starch-PS composites should have desirable physical and mechanical properties during its service life but are easy to degrade under a specific treatment. Thus this work contributes somewhat a solution of plastic waste problem by incorporation of starch-g-polystyrene graft copolymers into polystyrene plastics. When these plastics are exposed to UV irradiation or soil burial, deterioration of the plastic could be started but time consuming. However plastic degradation should be studied further in the aspects of:

In this research, the γ -irradiator configuration allows the use of total doses can be investigated at a fixed dose rate. Intensive research work elsewhere indicated that an optimum dose rate enhanced significantly a grafting reaction of this type. Modifications of the gamma source to study the effect of dose rate on the grafting performance of styrene onto cassava starch are essential. Cassava starch grafted polystyrenes with the higher grafted starch, in another word many levels of grafted starch should be mixes to replace the virgin starch so as to study the degradation behavior.

The effect of polyfunctional comonomers and inorganic salts for enhancing the grafting of styrene onto cassava starch such as trimethylolpropane triacrylate (TMPTA), trimethylolpropane trimethylacrylate (TMPTMA), and lithium perchlorate, should be made in order to introduce bulkiness to polystyrene. More free volumes within the polymer chains can accommodate more starch or its derivation to enhance

degradation. Both starch/starch grafts and acrylate containing monomers are degradable because they all contain either the hydroxyl, ester, which are susceptible to degradable.

The effect of other types of prooxidants containing other salts or complex salts of metals such as manganese, ferrous, cobalt, chromium, nickel and copper should be tried.

The effect of moisture and microorganisms on lifespan of starch- or grafted starch-PS plastics, in a wrapped or unwrapped condition should be performed to observed changes in physical and chemical properties during storage. The ideal degradable plastic would protect its contents during storage and degrade quickly in an environment after disposal. Resistance to moisture would be essential in achieving a product stability during storage.

A combined degradation (method) obtained from this research can be designed. Outdoor exposure of the plastics should be performed first and soil burial test of the plastics is carried out subsequently. Changes in physical and chemical properties of the plastics before and after each test should be followed to conclude the significant effect.

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