4.1 Radiation Crosslinking of Polymer Materials

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Summary

It was found that some polyfunctional monomers (PFM) like triallyl isocyanurate (TAIC) and trimethallyl isocyanurate (TMAIC) when incorporated at low concentrations, are effective for promotion of crosslinking of biodegradable polymers such as polycaprolactone (PCL), poly(butylene succinate-co-adipate) (PBS) and poly(lactic acid) (PLA). PFM are kneaded with biodegradable polymers at molten condition before irradiation. Radiation crosslinking of PBS and PCL with 1% TAIC gave gel fractions of 80% at 20kGy. This crosslinking is effective to improve deformation of biodegradable polymers at high temperature. The irradiated materials retained their biodegradability even after crosslinking when subjected to soil burial test.

Irradiation at molten state (melting temperature, 340°C) led to crosslinking structures for polytetrafluoroethylene (PTFE). Crosslinked PTFE forms transparent films with high abrasion property and high radiation resistance. High-density polyethylene (HDPE) has a higher gel fraction in irradiation at molten state than irradiation at ordinary temperature. Crosslinked HDPE has been applied as knee joints in order to have high abrasion. Radiation crosslinked polycarbosilane (PCS) fiber gives high heat resistant silicon carbide (SiC) after firing. EB irradiation of PCS is effective to improve strength of product and to inhibit flow during carbonization. SiC, being resistant to high temperature will be applied in turbine and body of rockets.

1. Introduction

Practical applications for radiation processing of polymeric materials have been evolving since the introduction of this technology nearly fifty years ago. Radiation technical is a very convenient tool for the improvement or modification of polymer materials through crosslinking, grafting or degradation. Among them, radiation crosslinking is a key technology in the field of radiation processing. Crosslinking of plastic materials was the earliest development in industry, and the use of this technical is widely practiced today [1-2].

Radiation can induce crosslink structures in polymeric materials at various phases such as solid, molten and solution states. EB irradiation crosslinking can be used to produce polymeric material possessing heat-shrinkable property, resistance to abrasion, heat resistance for industrial products. Some polymers such as polyethylene, polypropylene and poly(vinyl chloride) and PLA were already widely used to improve the resistance to abrasion and process ability of car tires and heat resistance of insulation wire by radiation crosslinking. In order to produce some functional polymeric materials possessing heat-shrinkable property, resistance to abrasion, heat resistance for industrial application, recently, several research works were proposed to introduce crosslinking structures for degradation type polymers, such as PTFE,
biodegradable aliphatic polyester and polysaccharides. In this article, EB radiation crosslinking of biodegradable aliphatic polyester, PTFE, and PCS and their application are reported.

2. Materials and Irradiation

PCL and PBS with average molecular weights $2.19\times10^5$ and $2.96\times10^5$, respectively, were used in this work. Two different PFM such as TAIC and TMAIC, were used as additive to prepare the mixed samples at 150°C by a labo platomill model mixer. The sheet form mixed sample was irradiated by EB irradiation.

PTFE sheet with 0.5mm thickness was used for this work. The sheet was set in an irradiation vessel with heating device, and heated up to 340°C in Ar gas atmosphere and kept the temperature within ±3°C. The sample was irradiated by EB irradiation.

PCS fiber with φ20μm was used for EB irradiation at Ar or H$_2$ atmosphere for crosslinking. Figure 1 showed these chemical structures.

3. Preparation of biodegradable materials based on PCL, PBS

PCL and PBS are known to be crosslinkable polymer. When the polymer is exposed to irradiation, the molecular weight of the polymer increases and forms an insoluble fraction called gel fraction. This process affects the mechanical, physical, and chemical properties of the polymer, thereby changing the quality of the original material.

Figure 2 and Figure 3 showed the gel contents of the irradiated PCL / PBS with different amounts of TAMIC. TAMIC yield a higher gel content in radiation crosslinking of PCL due to TAMIC has additional allylic hydrogens as α-methyl groups. In addition, TAMIC has a cyclic unit that can achieve greater three-dimensional network by irradiation. It can be seen that irradiated PCL containing 0.5%, and 1% TMAIC form higher gel content than that of PCL containing 3% TMAIC at the same irradiation doses. Similar behavior was found for irradiated PBS containing TMAIC at dose of 10 and 20kGy. The optimum gel fraction was formed in the presence of 1%TAMIC at dose of 50kGy for both PCL and PBS.

In this study, it was found that high gel fraction largely improves heat stability of PCL, PBS, while biodegradability evaluated by soil burial test of the crosslinked polymers is slightly retarded, however they are effectively destroyed with a slightly smaller rate. The effect of PFM on biodegradability was shown in Figure 4. It can be seen that weight loss of irradiated PBS containing 1% TAMIC (83% gel) slightly diminishes compared to irradiated pure PBS (26% gel) and unirradiated PBS (without gel). Therefore, after radiation crosslinking the polymer samples still keep biodegradable capacity [3-4].

4. Radiation crosslinking of PTFE at molten state

PTFE is widely applied for the materials for daily use and for industrial
equipment due to its heat resistant, high electrical insulation, and high stability to any chemical solvent. However, PTFE is a typical polymer to degrade by radiation under-goes through chain scission. The mechanical properties and molecular weight are decreasing with a small dose. In this report, a new technology was introduced to make PTFE crosslinking. It was found that the PTFE could be crosslinking by irradiation in a special condition, the molten state (heating up to 340°C in oxygen-free atmosphere) [5-8]. Figure 5 showed the relationship between mechanical properties and irradiation temperature for PTFE irradiated with 100kGy under oxygen-free atmosphere. The elongation at break and tensile strength decreased with increasing temperature until 300°C, but the change drastically around the melting temperature of 327°C. The peaks in Figure 5 were about 340°C. The elongation at break is rather higher than that of non-irradiated PTFE. Above 350°C, both of them decreased sharply. The changes and the behavior in the molten state strongly suggest the network formation by the radiation induced crosslinking in PTFE.

Furthermore, DSC analyses revealed that in the crosslinked PTFE, the temperature of crystals decreased with dose and also the heat of crystallization (∆H) decreased. It means that by the radiation induced crosslinking at molten state, PTFE could not form the crystals by cooling from the molten state. Therefore, PTFE sheet of white color changes to transparency by decreasing the crystallinity as seen in Figure 6. In addition, crosslinked PTFE also possesses good resistance to abrasion and high radiation resistance. Figure 7 showed the abrasion factor of crosslinked PTFE.

5. Radiation crosslinking of PCS for reducing oxygen content

PCS fiber as a precursor for ceramic fiber of silicon carbide (SiC) was usually cured to maintain the integrity of the fiber during pyrolysis to convert it to a ceramic at high temperature. However, the thermal oxidation treatment brought oxygen content in the ceramic fiber, and this should result decomposition at high temperature (>1573K). In order to reduce the oxygen content in the fiber and improve the heat resistance of the SiC fiber, a new technology using EB irradiation for curing treatment was introduced in this report [8]. Figure 8. showed the synthesis process of EB cured SiC fiber.

In this new technology, PCS fiber was irradiated in He or Ar gas atmosphere to crosslink it. The degree of crosslinking as monitored by measuring the variation of the gel formation with the adsorbed dose as shown in Fig 9. A SiC fiber with very low oxygen content was successfully synthesis by EB irradiation. The heat resistance can be improved up to 1973 K. This process was already developed to industrial plant (Hi-Nicalon). It was also found that the mechanical property of the SiC fiber was improved by this EB irradiation compared to thermal oxidation (Fig.10). Finally, radiation curing for the precursor fiber can be carried out at lower temperatures, and control of the curing is much easier than with the thermal oxidation process. SiC, being resistant to high temperature will be applied in turbine and body of rockets.
References

Fig. 1. Structure of polymer materials.

Fig. 2. Radiation crosslinking of PCL in presence of PFM.
Fig. 3. Radiation crosslinking of PBS in presence of PFM.

Fig. 4. Biodegradability of radiation crosslinked PBS with TMAIC in soil.
Fig. 5. Relationship between mechanical properties and irradiation temperature for PTFE irradiated at 100kGy under oxygen-free atmosphere.

Optical Property of Crosslinked PTFE

Fig. 6. Optical property of crosslinked PTFE.
Abrasion Factor of Crosslinked PTFE

![Graph showing abrasion factor of crosslinked PTFE](image)

Fig. 7. Abrasion factor of crosslinked PTFE.

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**Fig. 8. Synthesis process of EB cured SiC fiber.**

1. Polycarbosilane (PCS)
2. Melt Spinning → PCS fiber
3. Curing → Thermal oxidation
   - EB irradiation in He
4. Cured PCS
5. Firing → in Ar at 1500°C
6. SiC fiber
Fig. 9. Gel fraction of irradiated PCS fiber after heat treatment at 500°C.

Fig. 10. Mechanical property of radiation crosslinked SiC fiber.