

## ผลของการฉายรังสีแกมมาต่อสมบัติเชิงกลของพอลิเมอร์ผสม ระหว่างพอลิเอทิลีนความหนาแน่นต่ำและแป้งมันสำปะหลัง

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### บทคัดย่อ

นำพอลิเอทิลีนความหนาแน่นต่ำมาผสมกับแป้งมันสำปะหลัง โดยผสมแป้งในอัตราส่วน 10 20 และ 30 เปอร์เซ็นต์โดยน้ำหนัก จากนั้นนำพอลิเมอร์ผสมที่ได้ไปขึ้นรูปให้เป็นแผ่น ด้วยเครื่องหล่อพิมพ์แบบอัดความดัน และนำแผ่นพลาสติกที่ได้มาตัดให้เป็นตัวอย่างที่มีรูปทรงคล้ายกระดูก นำตัวอย่างไปฉายรังสีแกมมาในอากาศ ด้วยปริมาณรังสี 10 20 50 และ 100 กิโลเกรย์ จากนั้นจึงศึกษาสมบัติเชิงกลของตัวอย่างที่ไม่ผ่านการฉายรังสี และตัวอย่างที่ผ่านการฉายรังสี ด้วยเครื่องทดสอบคุณสมบัติเชิงกลของพอลิเมอร์ ผลการทดลองแสดงให้เห็นว่าความแข็งแรงของพอลิเมอร์ผสมเพิ่มขึ้นตามปริมาณรังสี แต่ในขณะเดียวกัน กลับลดลงตามความเข้มข้นของแป้ง

คำสำคัญ: แกมมา รังสี พอลิเอทิลีน แป้ง พอลิเมอร์ผสม สมบัติเชิงกล

### Effects of Gamma Irradiation

### on Mechanical Properties of LDPE/Cassava Starch Blends

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### Abstract

Low density polyethylene (LDPE) was blended with cassava starch. The starch content was varied from 10, 20 to 30%. The blends were compression molded to form plastic sheets. The sheets were cut into dog bone-shaped specimens. The samples were gamma irradiated in air with the total dose of 10, 20, 50 and 100 kGy. The mechanical properties of both the unirradiated and irradiated samples were characterized using a Universal Testing Machine. The results demonstrated that tensile strength of the LDPE/Starch blends increased with dose, while it simultaneously decreased with starch content.

**Keywords:** Gamma, Radiation, LDPE, Starch, Blend, Tensile

## Introduction

Polyethylene (PE) is one of the most extensively produced and utilized synthetic polymers worldwide, from food packaging materials to medical products, simply due to various advantages, from economical price to convenient processing. As a result, PE has globally become the major component of plastic waste. Resistant to microbial attack, PE and many other synthetic polymers are non-biodegradable<sup>1</sup>. This issue has become one of the most crucial environmental problems. Alternatively, many natural polymers, such as starch and cellulose, can be easily degraded in natural environments. Biodegradable and renewable, these natural polymers are gaining public interest as a promising alternative to replace synthetic polymers. They are not good candidates for plastic commodities, due to a number of reasons, from processing difficulty to poor mechanical properties. Nonetheless, the use of natural polymer as filler in plastics can be and have been done to impart biodegradability to synthetic polymers, at low cost and in abundance<sup>2-8</sup>.

One viable method to develop new polymers that can be processed without difficulty and can be easily decomposed in a natural environment is to blend synthetic with natural polymer. However, this blending will give merely physical blends, without chemical reactions between molecules of natural and synthetic polymers. This can result in an immiscible blend if the two polymers mixed are not compatible. The objective of this research is to use radiation as a mean to induce cross-linking between the molecules of natural and synthetic polymers.

Radiation is one of the most convenient methods applied to improve final properties of various polymers<sup>9</sup>. During irradiation, the energy transferred to polymer chains can induce alterations in chemical and molecular structure. The two major effects are cross-linking and degradation, which can occur simultaneously. Depending on the chemical structure, the ratio between these two reactions will determine whether a polymer is more likely to cross-link or degrade, upon irradiation. Generally, cross-linking tends to improve various properties, such as mechanical and thermal properties. Cost-effective and efficient, radiation processing can induce cross-linking without any initiators and can be done at ambient temperature. This research aims to apply the aforementioned advantages that radiation can offer to LDPE/cassava starch blends to induce cross-linking between LDPE and starch molecules.

## Experiments

### Materials

Starch (Cassava starch) was supplied by Siam Quality Starch Co., Ltd. Low density polyethylene (LDPE) was contributed by Thai Polyethylene Co., Ltd.

### Preparation of LDPE/Starch blends

LDPE and cassava starch (10%, 20% and 30% by weight) were thoroughly mixed using a two roll mill. The temperature was set at 160°C and 150°C for front roll and back roll, respectively. The blends were then compression molded at 170°C into smooth, square plastic sheets. The sheets were cut into dog bone-shaped specimens, as shown in Figure 1.

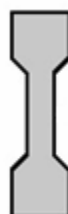


Figure 1: Dog bone-shaped or dumbbell-shaped sample.

### Sample irradiation

The polymer blends were irradiated in a gamma radiation chamber (Gammacell 220 Excel, MDS Nordion, Canada) at the total dose of 10, 20, 50 and 100 kGy. Irradiation was carried out in air at ambient temperature.

### Characterization

The samples were characterized by Fourier transform infrared spectrometer (FTIR Tensor27, Bruker) and thermal gravimetric analyzer (TGA/SDTA851°, Mettler Toledo) to confirm the presence of starch in the blends. The mechanical properties of the unirradiated and irradiated polymer blends were characterized by a universal testing machine (AG-G Series, Shimadzu). Initial grip separation was set at 10 mm.

## Results and discussion

### FTIR

The FTIR spectra of LDPE, Cassava starch, and LDPE/Starch blend were taken and are comparatively shown in Figure 2, while the structures of LDPE and starch are illustrated in Figure 3. Additionally, a detailed numerical listing of some key functional groups of LDPE, starch, LDPE/Starch blend, along with their IR absorption frequencies, are summarized in Table 1. The FTIR spectra clearly confirm the presence of starch molecules in LDPE/Starch blends.

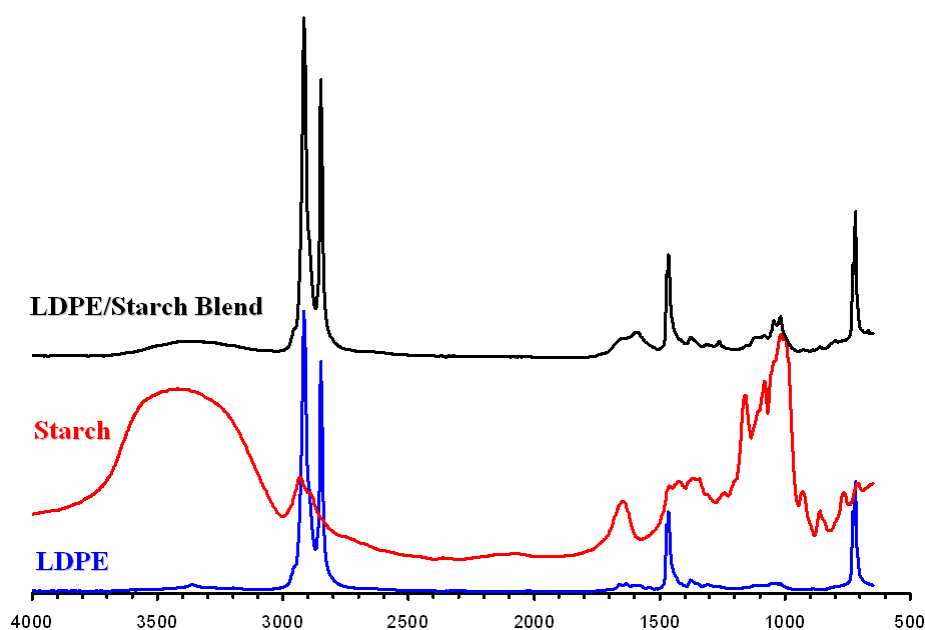


Figure 2: FTIR spectra of LDPE, starch, and LDPE/Starch blend.

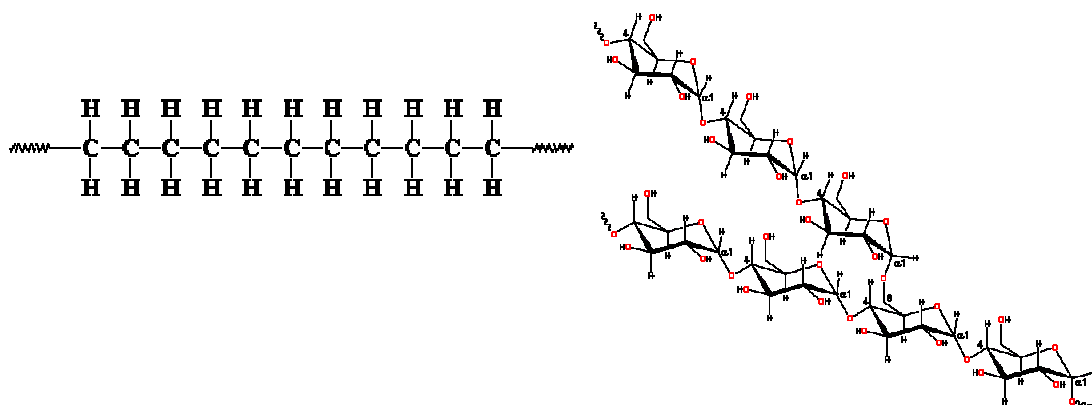


Figure 3: Chemical structures of LDPE (left) and starch (right).

Table 1: A list of key functional groups with their IR absorption frequencies.

LDPE		Starch		LDPE/Starch Blend	
Frequency	Assignment	Frequency	Assignment	Frequency	Assignment
		3600-3200	O-H Stretch	3600-3200	O-H Stretch
		2923	C-H Stretch		
2916	C-H Stretch			2916	C-H Stretch
2848	C-H Stretch			2848	C-H Stretch
1461	CH <sub>2</sub>	1458	CH <sub>2</sub>	1460	CH <sub>2</sub>
		1157	-CR <sub>2</sub> -OH	1157	-CR <sub>2</sub> -OH
		1080	-CRH-OH-	1080	-CRH-OH-
		1012	C-O Stretch	1012	C-O Stretch
		925	Cyclic C-O-C	925	Cyclic C-O-C
719	CH <sub>2</sub> Rocking			719	CH <sub>2</sub> Rocking
		705	C-OH Def	705	C-OH Def

## TGA

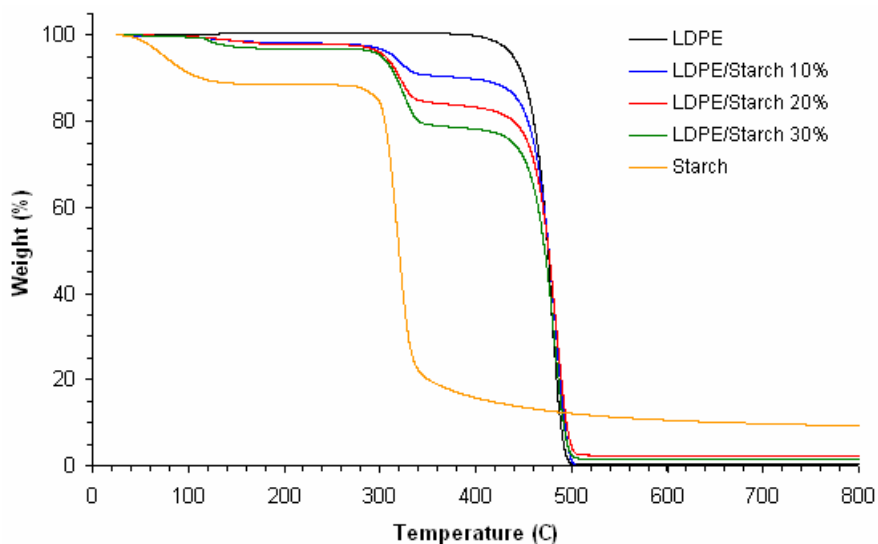


Figure 4: TGA thermograms of LDPE, starch and LDPE/Starch blends.

TGA thermograms of LDPE, starch and LDPE/Starch blends with different starch content are shown in Figure 4. LDPE showed a one-stage weight loss process, with highest maximum rate of weight loss centered at approximately 470°C, and completely decomposed after

500°C, leaving no char yield. The thermogram of starch displayed a two-stage weight loss process. The first process started very early and slowly continued until 160°C, indicating the evaporation of approximately 12% moisture content in starch. The second weight loss process began at about 270°C and reached its maximum rate of weight loss at roughly 320°C. Unlike LDPE, starch did not entirely degrade. The amount of char left at 800°C is nearly 10%. For all LDPE/Starch blends, a three-stage weight loss process was observed. The first two processes demonstrated the similar pattern as seen in starch's thermogram, while the last one replicated the pattern observed in thermogram of LDPE, thus confirming the presence of starch in the polymer blends. Between 300 – 500°C, the three thermograms illustrated obvious differences in terms of weight loss percentage, obviously showing different starch content in the three polymer blends.

#### Effect of radiation dose on mechanical properties

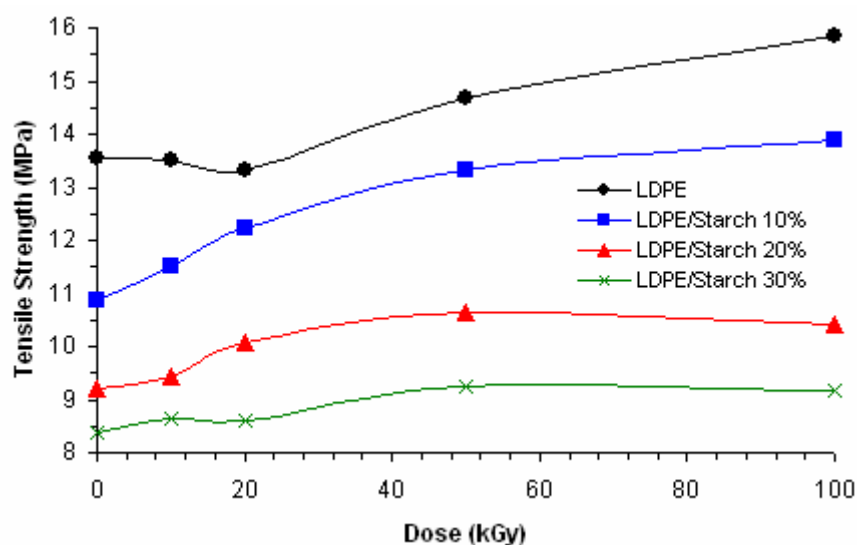


Figure 5: Tensile strength of LDPE and LDPE/Starch blends.

Mechanical properties of unirradiated and irradiated LDPE and LDPE/Starch blends were analyzed. Figure 5 shows tensile strength of LDPE and the blends as a function of dose and starch content. For LDPE, there is no significant change at low dose. However, at high dose, an obvious increase in tensile strength clearly indicates that radiation does improve the tensile strength of LDPE. It is a well established fact that the tensile strength of a polymer is profoundly dependent on its molecular weight, i.e. tensile strength increases with molecular weight. It is also well

known that, upon irradiation, PE molecular chains are more likely to cross-link. And as a result of that, high molecular weight networks are formed. This clearly explains why the tensile strength of LDPE samples increases with dose. Radiation has similar effects on the tensile strength of LDPE/Starch blends. That is, for all three polymer blends with different starch content, the tensile strength also improves with increasing radiation dose. Nevertheless, the effects seem to level off as dose and starch content increase. For the blend with 10% starch content, the tensile strength was still improving from 50 to 100 kGy. On the other hand, for the blend containing 20% and 30% starch, the tensile strength at 100 kGy was comparable to that at 50 kGy.

### **Effect of starch content on mechanical properties**

From Figure 5, it is obvious that tensile strength of LDPE/Starch blends decreases with starch content. This is understandable from the fact that, in terms of chemical structure, as seen in Figure 3, PE is hydrophobic, whereas starch is hydrophilic. Consequently, these two polymers are incompatible. In this case, the content of LDPE is much higher than that of starch. Thus, starch behaves as a filler in LDPE matrix. The presence of incompatible filler, therefore, weakens the mechanical properties of LDPE. Moreover, when subjected to ionizing radiation, starch itself tends to degrade rather than cross-link. These radiation-induced chain scission reactions lessen the molecular weight of the starch molecules, leading further to a decline in tensile strength of the blends. Nonetheless, at low starch content and high dose, i.e. 10% starch content at 50 and 100 kGy, the tensile strength of the LDPE/Starch blends was comparable to those of pure LDPE at low dose. This result implies that the decline in mechanical properties of LDPE/Starch blends due to starch incorporation can be compensated by the mechanical properties improvement due to cross-linking induced by radiation. This is highly interesting, since the presence of starch can be beneficial to the biodegradability of the LDPE/Starch blends. However, the effects that radiation and the presence of starch have on the biodegradability of the LDPE/Starch blends need to be further studied, and are now under investigation.

## Conclusions

In the present study, the effect that radiation has upon mechanical properties of LDPE/Starch blends was studied. The results showed that radiation enhanced the tensile strength of LDPE, while the presence of starch weakened it. However, the tensile loss due to the existence of starch in the blends can be counterbalanced by the tensile strength increase due to radiation-induced cross-linking between LDPE molecules or between starch and LDPE molecules.

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