

## EFFECT OF SILICA OBTAINED FROM RICE HUSK ON THE STRUCTURAL AND THERMAL PROPERTIES OF POLYLACTIC ACID/POLYETHYLENE GLYCOL FILMS

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### Abstract

Most of the plastic materials used in the packaging industry are petroleum-based. These plastics do not decompose in soil for many years and they lead to increase CO<sub>2</sub> in the atmosphere. Biodegradable polymers derived from renewable resources such as polylactic acid (PLA) are considered as promising alternatives to petroleum-based polymers. Although PLA has attracted attention due to having properties such as biodegradable, environment friendly, and biocompatible, it cannot be used in many applications due to its poor gas barrier properties, low thermal stability, high brittleness, and cost. In this study, in the first step silica was obtained from the rice husk. The obtained silica (5,10 and 20%) were added to PLA solutions containing 20% polyethylene glycol (PEG) and the composite films were prepared using solvent casting method. The thermal and structural properties of the composite films were determined by Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscope (SEM), Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and Water Absorption Capacity Test. According to results of analysis, the addition of silica to the PLA-PEG films improved the thermal stability and increased the water absorption capacities of films.

**Keywords:** Polylactic acid, Rice husk, Silica, Biodegradable polymer, Composite material

## PİRİNÇ KABUĞUNDAN ELDE EDİLEN SİLİKANIN POLİLAKTİK ASİT/POLİETİLEN GLİKOL FİLMLEİNİN YAPISAL VE TERMAL ÖZELLİKLERİNE ETKİSİ

### Özet

Ambalaj sektöründe kullanılan plastik malzemelerin çoğu petrol kökenlidir. Bu tür malzemeler doğada uzun yıllar çözünmeyip atmosferdeki CO<sub>2</sub>'in artmasına neden olur. Yenilenebilir kaynaklardan elde edilen polilaktik asit (PLA) benzeri biyobozunur polimerler petrol kökenli polimerlere alternatif olarak görülmektedir. PLA çevre dostu, biyobozunur ve biyoyumlu olması gibi birçok avantaja sahip olmasına rağmen düşük gaz bariyer özellikleri, termal dayanımı, kırılgan ve maliyetli olması birçok uygulamada kullanımını sınırlamaktadır. Bu çalışmada ilk olarak atık olarak görülen pirinç kabuğundan silika elde edilmiştir. Farklı katkı yüzdelerinde (%5, 10 ve 20) silika %20 polietilen glikol (PEG) içeren PLA çözeltilerine eklenmiş ve kompozit filmler çözücü döküm yöntemi ile hazırlanmıştır. Filmlerin termal ve yapısal özellikleri Fourier Dönüşümlü İnfrared Spektroskopisi (FT-IR), Taramalı Elektron Mikroskopu (SEM), Termogravimetrik Analiz (TGA), Diferansiyel Taramalı Kalorimetre (DSC) ve Su Absorpsiyon Kapasitesi Testi ile belirlenmiştir. Analiz sonuçlarına göre, silikanın PLA-PEG filmlerinin termal dayanımını iyileştirdiği ve su tutma kapasitelerini artırdığı görülmüştür.

**Anahtar Kelimeler:** Polilaktik asit, Pirinç kabuğu, Silika, Biyobozunur polimer, Kompozit malzeme

### Cite

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### 1. Introduction

Most of the plastic materials used in the packaging industry are petroleum-based. These plastics such as polyethylene (PE), polystyrene (PS) and, polyethylene terephthalate (PET) do not decompose in soil for many years. They lead to increase environmental pollution and

CO<sub>2</sub> in the atmosphere. There have been various approaches to eliminate environmental pollution caused by plastics. Today, the best approach is seen as using biodegradable polymers [1].

Among the biodegradable polymers, polylactic acid (PLA) has attracted attention due to having properties such as biodegradable, environmental-friendly,

biocompatible, easily processable, transparent, high modulus and strength. Although PLA has these advantages, it cannot be used in many applications due to its poor gas barrier properties, low thermal stability, fragile and cost [2,3]. The physical, thermal or mechanical properties of PLA can be improved by several methods, such as adding of plasticizers [4-6], using reinforcements [7-10] or polymer blends [11-13]. Natural fillers as reinforcements to PLA have advantages such as low cost, renewability and biodegradability. Therefore, biodegradable polymer composites reinforced with natural fillers appear to be an alternative material to petroleum-based materials.

Rice husk is an agricultural waste obtained by rice production process. It is cheap, biodegradable and has been abundance in the world. In developed countries, such products are not seen as waste but as a new source. Therefore, such materials can be used for environmental protection and the design of new materials. Ash content of rice husk mainly consists of silica (approximately 94% of silica) [14]. Since rice husk is a renewable, biodegradable, low cost, easily available resource, it is seen as a good alternative to conventional reinforcements such as carbon black, commercial silica and clay to reduce the cost of production and improve the properties of biodegradable polymer materials [15]. In this study, PLAPEG-silica composites were prepared using silica obtained from waste rice husk and structural and thermal properties of composite films were investigated in detail.

## 2. Material and Methods

### 2.1. Material and Preparation Techniques

PLA2003D (1.24 g/cm<sup>3</sup>, 125,780 g/mole) was purchased from NatureWorks. PEG600 (1.13 g/cm<sup>3</sup>, 570-630 g/mole) by Merck, Chloroform (1.49 g/cm<sup>3</sup>) and Hydrochloric acid (1.18 g/cm<sup>3</sup>) by Sigma-Aldrich were supplied. Rice husk was procured from Bafra, Samsun.

Silica was prepared from rice husk based on a procedure reported previously [15]. The rice husks were purified with pure water. 10 g of rice husks in 0.4 M 100 ml HCl solution was boiled at 105 °C for 45 minutes and they were washed with water to remove acid and then dried in an oven (110 °C) for 4 hours. Additionally, rice husks were burned at 600 °C in the muffle furnace and silica was obtained after 6 hours. The obtained silica was ground in a coffee grinder and sieved to a particle size of less than 45 μm. Figure 1 shows the rice husk and obtained rice husk ash in the study.



(a) (b)

Figure 1. (a) Rice husk; (b) Rice husk ash.

In this study, PLAPEG-silica films with 5, 10 and 20 weight percent (wt.%) compositions (from now onward referred to as PLAPEG5, PLAPEG10 and PLAPEG20, respectively) were prepared using solvent casting method. Before film preparation, PLA granules were dried at 60 °C for 24 h. 5 wt. % of PLA solution in chloroform was prepared with the help of magnetic stirrer. PEG (20 wt.%) was dissolved into PLA solutions. The desired amount of silica (5, 10 and 20 wt.%) was added to polymer blend. The mixture was stirred in magnetic and ultrasonic stirrer for 1 day and cast onto petri dish. It was allowed to dry in an oven at 40 °C for 3 days. The method is briefly summarized in the Figure 2. The thermal and structural properties of the prepared composite films were determined by SEM (Scanning Electron Microscope), FT-IR (Fourier Transform Infrared Spectroscopy), TGA (Thermogravimetric Analysis). Water absorption capacity of films were also investigated.

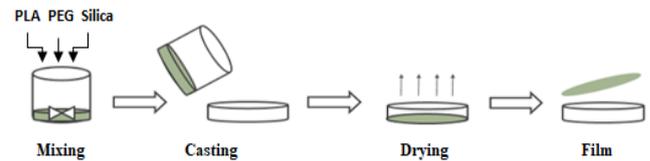


Figure 2. Solvent casting method.

### 2.2. Characterization

Fourier Transform Infrared Spectrometer (FT-IR/ATR, Perkin Elmer-2000FTIR) was used to investigate interaction between polymer matrix and reinforcement. For analysis, 5-10 mg of samples placed in the appliance. The spectra of films were recorded between in the wavenumber range of 650-4000 cm<sup>-1</sup>.

Thermal behaviour of the samples was determined by using TGA (TA, SDTQ600). Approximately 5-10 mg of sample was placed in the sample cup and kept at a heating rate of 10 °C/min under N<sub>2</sub> flow of 50 ml/min from room temperature to 600 °C.

DSC analysis (TA, DSCQ2000) of the samples were determined under heating speed of 10 °C/min in the range of 25-200 °C. The samples were first heated from room temperature to 200 °C under a heating rate of 10 °C/min, cooled to 25 °C at the same heating rate and then reheated to 200 °C.

Thermal properties of the films such as crystallization temperature (T<sub>c</sub>), melting point temperature (T<sub>m</sub>), crystallization enthalpy (ΔH<sub>c</sub>) and melting enthalpy (ΔH<sub>m</sub>) were determined by DSC analysis. The degree of crystallinity (%X<sub>c</sub>) was calculated using the following equation.

$$\%X_c = \frac{\Delta H_m}{f \times \Delta H_m^0} \times 100 \quad (1)$$

ΔH<sub>m</sub> = Melting enthalpy (J/g)

$\Delta H_m^0$  = Theoretical melting enthalpy of 100% crystalline PLA (93.7 J/g) [16]

f = Weight fraction of PLA

Surface characterization of polymer composite films and silica were determined by Scanning Electron Microscopy (SEM, Jeol, JSM-7001F). Approximately 5 mg of samples were coated with gold and palladium before SEM analysis.

To determine the water absorption capacity of the sample, the film samples were cut to 10mm×10mm dimensions and dried (105 °C) until constant weight ( $W_0$ ). The sample was kept in the closed containers containing pure water in a shaking water bath at 30 °C for 24 hours. At the end of the period, the sample was dried with a cloth and weighed ( $W_1$ ). The water absorption capacity of the film was determined by using the mass difference in the sample. Measurements were completed by taking at least 3 samples for each film.

$$\% \text{Water Absorption Capacity} = \frac{W_1 - W_0}{W_0} \times 100 \quad (2)$$

### 3. Results and Discussion

#### 3.1. Analysis Result of Silica

The functional groups in silica obtained from rice husk were determined by FT-IR. As seen in Figure 3, stretching and bending vibration of Si-O-Si is determined at the wavenumber of 1047 and 798  $\text{cm}^{-1}$ [17].

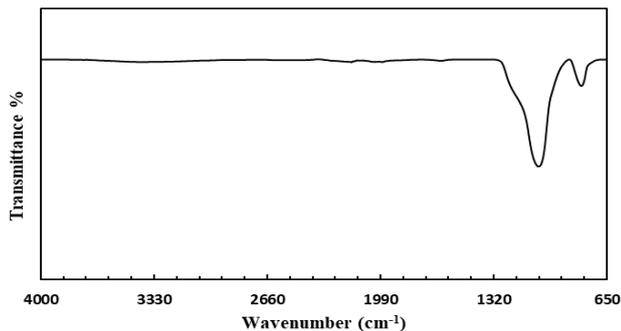


Figure 3. FT-IR spectra of silica obtained from rice husk.

SEM images of silica are given in Figure 4. It is seen that structure has an irregular shape and tends to aggregate [18]. The particle size of silica is found to be less than 45  $\mu\text{m}$ . The elements in the structure were determined by Energy Dispersive Spectroscopy (EDS) analysis and it was found that silica contains 62.85 oxygen and 37.15 silicon (wt.%). The results of the analysis are shown in Table 1.

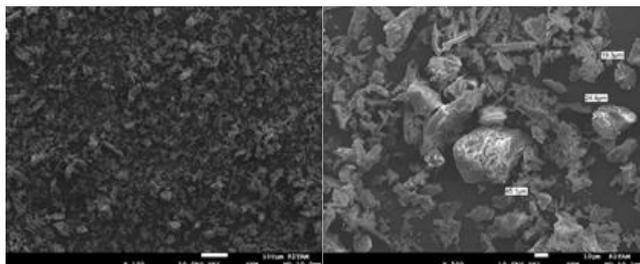


Figure 4. SEM images of silica obtained from rice husk.

Table 1. SEM-EDS results of silica obtained from rice husk.

Element	%
O	62.85
Si	37.15
Total	100

#### 3.2. Analysis Result of Composite Films

As depicted in Figure 5, the silicon-derived peak at 800  $\text{cm}^{-1}$  is apparent. It was determined that the spectra of the films including silica have peaks similar to the peaks in the spectrum of the PLAPEG film. This shows that the structure contains the same groups that no new bond formation occurs and there is no strong chemical interaction.

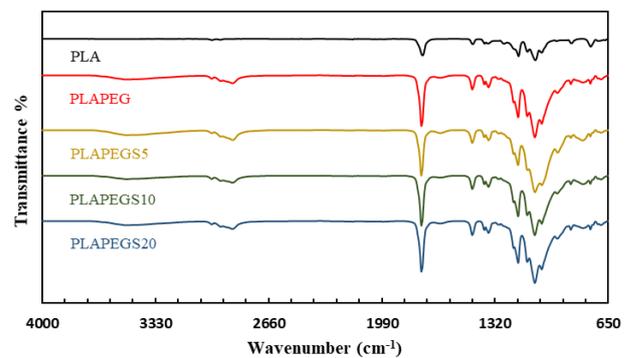


Figure 5. FT-IR spectra of composite films.

TGA results of composite films are given in Figure 6 and Table 2. When the values of pure PLA are considered, it is seen that PLA is completely degraded at the end of 600 °C and has the best thermal stability. Decomposition of PLA occurred between 275 °C and 380 °C. The use of PEG increases the mobility of the polymer chains and improves the flexibility of PLA. According to curves, PEG leads to decrease thermal stability of PLA [16, 19]. With the addition of PEG, the thermal decomposition temperature decreased from 280 °C to 224 °C and the temperature at which 50% mass loss occurred decreased from 351 °C to 298 °C. The final decomposition temperature of PLA increased from 378 °C to 415 °C in the presence of PEG [15].

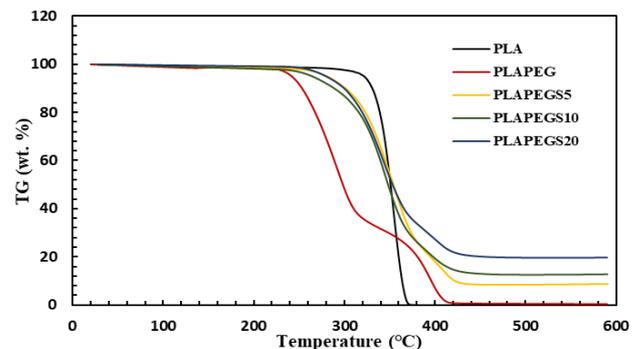


Figure 6. TGA curves of films.

Table 2. TGA results of composite films.

Samples	T <sub>d</sub> (°C)	T <sub>%5</sub> (°C)	T <sub>%10</sub> (°C)	T <sub>%50</sub> (°C)	T <sub>f</sub> (°C)
PLA	280	322	331	351	378
PLAPEG	224	242	253	298	415
PLAPEG5	228	281	301	354	456
PLAPEG10	229	279	300	353	465
PLAPEG20	235	264	289	348	472

By using of silica, it became difficult to remove volatile components from the structure and the thermal decomposition temperature began shifted to higher temperatures. The thermal stability of all composites is higher than PLAPEG film [17]. The results showed that silica could improve the thermal degradation temperature of PLA-PEG blend.

DSC analysis results of the films are shown in Table 3. T<sub>m</sub> and T<sub>c</sub> values of pure PLA were determined as 149.48 °C and 123.56 °C, respectively. When the plasticizer is added to the PLA, the interaction between the molecular chains decreases and the free volume of the PLA increases. This effect can be determined by the decrease in the T<sub>g</sub> and T<sub>c</sub> of the polymer. The T<sub>m</sub> and T<sub>c</sub> of the PLAPEG film were 147.14 °C and 75.33 °C, respectively. The results show that the polymers are compatible and miscible with each other. This attribution was supported by SEM images of the films. A decrease of approximately 2-3 °C in the melting point indicates that PEG does not affect the melting point of PLA. %X<sub>c</sub> of PLAPEG film increased from 17.38% to 34.47% with the addition of PEG in accordance with the literature [16]. This result shows that plasticizer increases chain movement of PLA and gains flexibility to PLA [20].

Table 3. DSC results of composite films.

Samples	T <sub>c</sub> (°C)	ΔH <sub>c</sub> (J/g)	T <sub>m</sub> (°C)	ΔH <sub>m</sub> (J/g)	X <sub>c</sub> (%)
PLA	123.56	16.75	149.48	16.27	17.38
PLAPEG	75.33	16.04	147.14	25.81	34.47
PLAPEG5	72.58	14.84	146.58	25.41	35.72
PLAPEG10	79.19	18.55	147.18	19.39	28.77
PLAPEG20	84.83	16.15	146.87	16.55	27.63

The fact that the crystallization temperature value of composite films is lower than pure PLA is interpreted as the silica increases the crystallization rate of the polymer. The fillers act as a nucleating agent for crystallization and causes decrease in the crystallization temperature [21]. When 5% of silica was added to the PEG-including films, the T<sub>c</sub> value of the films decreased from 75.33 to 72.58 °C, respectively. The decreasing %X<sub>c</sub> value of the film containing 10% and 20% silica may be due to the voids in the structure with increasing filler amounts [10]. Crystals are more easily formed by the nucleation effect of particles when the amounts of filler are low. As the amount of filler increases, the

crystallization behaviour of PLA may decreases due to aggregation [22].

SEM analysis was performed to determine the morphological structure of polymer films. As seen from Figure 7, the pure PLA which forms the matrix in composite films has a smooth and homogeneous surface. This smooth structure shows the fragility of PLA [20]. In the SEM image of the PLAPEG film, a homogeneous structure is formed and the mixture has a smooth surface. It is seen that the polymers in the mixture are compatible with each other [23].

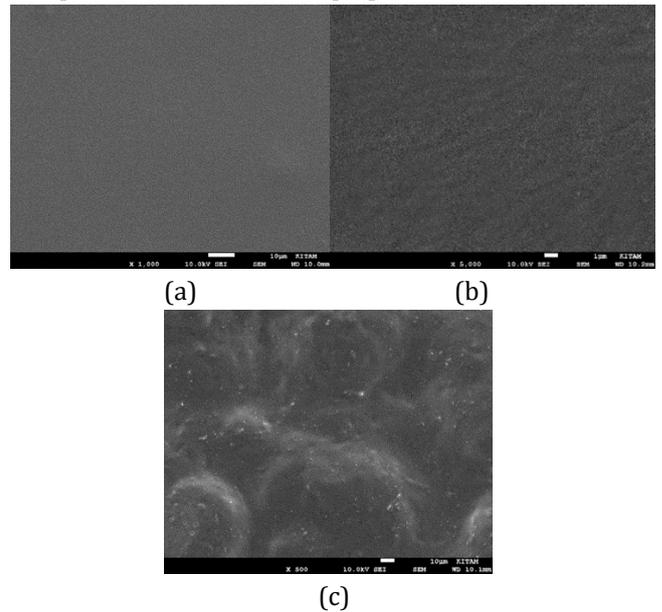


Figure 7. SEM images of composite films a) neat PLA b) PLAPEG c) PLAPEG20.

The distribution of fillers in the polymer matrix effects the physical properties of the material. The strong interaction between matrix and silica improves the thermal, mechanical and structural properties of the material [24].

In the SEM image of the silica-doped film, gaps and irregular cracks occur in the structure resulting from weak adhesion forces and stress between the matrix and the reinforcing element [20]. It is thought that the cavities on the surface are caused by chloroform which is withdraw from the structure. The silica particles in the structure were identified as white dots. Due to the small particle size of the fillers, they were embedded in the matrix and distributed homogeneously. The particles were far away from each other and there were no remarkable aggregates.

Water acts as a plasticizer in many materials. It leads to size change and reduces the mechanical properties. Hydrophilic additives swell when combined with water. Thus, composite films absorb more water and improve the biodegradability behaviour of the material [25].

Figure 8 shows the water absorption capacities of the composite films with different silica content. PLA is a hydrophobic polymer. In this study, water absorption capacity of PLA was determined as 0% as given in the literature [26]. Considering the amount of water

absorbed by the films, the water absorption capacity increased due to the hygroscopic nature of the fillers. As the filler content increased from 10% to 20%, water absorption capacities of silica-containing film increased from 9% to 21%. These results showed that 1 gram of film containing 10% silica and 20% silica can absorb 0.09 ml and 0.21 ml of water, respectively.

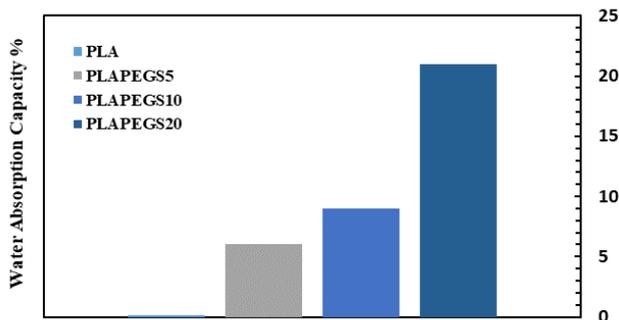


Figure 8. Water absorption capacities of films.

#### 4. Conclusion

The aim of this study was to improve the thermal and structural properties of pure PLA. In order to obtain flexible PLA, a polymer mixture was formed with PEG. The degree of crystallinity of the PLAPEG film increased from 17.38% to 34.47%. This shows that PLA has increased chain movement and gained flexibility in the presence of PEG. It has been seen that the water absorption capacity of PLA film increased with the addition of silica. The rate of degradation of biodegradable polymers in a suitable compost environment depends on the water absorption ability. PLA can be completely degraded in 2 years on average. Silica-doped PLA can be degraded in a shorter time in comparison with neat PLA. Silica also improved the thermal stability of the films which was reduced by plasticizing effect. All composites were found to have better thermal stability than PLAPEG film.

#### 5. Acknowledgment

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