

Effect of Rice Straw on the Mechanical and Biodegradability Properties of the Poly (Polyethylene-G-Acrylic Acid)

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<p>Received: March 25, 2025 Peer-reviewed: March 28, 2025 Accepted: April 21, 2025</p>	<p>ABSTRACT A polyethylene/acrylic copolymer was synthesized using a grafting technique with benzoyl peroxide as a catalyst and xylene as a solvent. Acrylic acid (AA) was grafted onto polyethylene (PE) in a 1:5 ratio. The resulting grafted copolymer, characterized by FTIR, was blended with rice straw at varying percentages of 3%, 5%, and 7% to produce biodegradable films. The properties of these films in water were evaluated through analyses of viscosity, tensile strength, elongation at break, water contact angle, and solubility. Incorporating rice straw enhanced the grafted copolymer's biodegradability, resulting in increased viscosity, tensile strength, and elongation at break of the films, while reducing the water contact angle and solubility. However, incorporating 7% rice straw in the grafted copolymer-based on PE (1.0%) and AA (5.0%) resulted in increases in viscosity, tensile strength, and elongation at break by 29.5%, 46.1%, and 9.6%, respectively, while reducing the contact angle and biodegradability solubility time at 45°C by 25.8%.</p>
	<p>Keywords: Polyethylene, acrylic acid, rice straw, biodegradable, mechanical, sustainability.</p>
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Introduction

Synthetic polymers, such as polyethylene and polypropylene, have become widely used as packing materials due to their advantageous physico-mechanical properties and cost-effectiveness [1]. However, polyethylene and polypropylene, non-biodegradable polymers contribute to the growing challenge of plastic waste management, with their quantities increasing each year [[2], [3], [4]]. Recent

studies highlight the importance of pinpointing plastic waste sources and differentiating polymers by structural traits, including their crystalline and amorphous forms [5]. Such distinctions are vital for understanding how these materials affect aquatic ecosystems and organisms [6]. Beyond being highly toxic, the key chemicals used in manufacturing plastic bags, such as polyethylene, polypropylene, benzene and vinyl chloride, are known carcinogens [[6], [7]]. These, along with gaseous and liquid

hydrocarbons, not only pose serious health risks but also contribute significantly to environmental degradation. Numerous methods, including blending, derivation, and graft copolymerization, have been extensively studied to improve the characteristics of synthetic polymers using starch; this is attributed to its complete biodegradability [[8], [9], [10]]. Modified polyethylene using grafting polymerization with starch in the presence of benzoyl peroxide as a catalyst and xylene as a solvent. The ratio between PE and starch was 1: 5 w/w%. The grafted copolymer was combined with rice straw, wheat straw, and calcium carbonate (CaCO_3) as a filler to produce biodegradable films. Starch, calcium carbonate (CaCO_3), and rice and wheat straws enhanced the biodegradability of the grafted copolymer. The inclusion of CaCO_3 , alongside rice and wheat straws, increased the viscosity and tensile properties [11]. Rice straw fiber-reinforced high-density polyethylene (HDPE) composites were developed to explore how rice straw fiber morphology and varying concentrations of maleic anhydride polyethylene (MAPE) influence their mechanical and thermal properties. The result showed that higher aspect ratio rice straw fibers were utilized to enhance tensile strength, while lower aspect ratio fibers were applied to improve the flexural strength of the composites. An increase in rice straw fiber content from 20 to 40 wt% within the HDPE matrix slightly boosted flexural strength; however, impact strength dropped significantly due to the fiber's stiffness. The addition of MAPE to the system improved tensile, flexural, and impact strength for composites containing 20 wt% rice straw fiber, although it led to a marginal reduction in tensile elongation at break [12]. This study investigates the modification of polyethylene via graft polymerization, using acrylic acid as the grafting monomer and benzoyl peroxide as the catalytic initiator. The modified polymer is subsequently blended with rice straw to enhance its mechanical properties.

Materials and Methods

Low density polyethylene (PE), xylene, benzoyl peroxide, and acrylic acid (AA) were purchased from Sigma-Aldrich Company (USA). Rice straw was gathered from the fields and allowed air to dry. The dried straw was subsequently cut into pieces measuring 2–5 mm in length and milled into a fine powder.

Synthesis of polyethylene-g-acrylic acid P(PE-g-AA)

Graft polymerization was conducted in a three-necked flask equipped with a mechanical stirrer under a nitrogen atmosphere. Polyethylene (1.0 g) was dissolved in xylene (50 g) by stirring in a water bath maintained at 80°C. Once dissolved, benzoyl peroxide (0.1 g) was introduced as a catalytic initiator. After 5 minutes, acrylic acid (5 g) was added as the grafting monomer. The reaction mixture was maintained at 80°C for 3 hours under constant stirring in a nitrogen environment. The resulting product was precipitated using 2-propanol, air-dried at room temperature, and subsequently oven-dried at 60°C to achieve a constant weight.

Film formation

For the first film, polyethylene-g-acrylic acid P(PE-g-AA) was incorporated into glycerol at 50°C and stirred for 30 minutes until achieving homogeneity. The resulting material was cast onto a levelled surface and designated as PEA. For the second film, the fully grafted copolymer was dissolved in glycerol, followed by the addition of rice straw in varying proportions (3, 5, and 7 w/w%). The mixture was then milled for 40 minutes, cast onto a leveled surface, and labeled as PEAS. All films were left to dry at room temperature for 10 days before being stored in a desiccator at ambient conditions for subsequent characterization and analysis.

Measurements

FTIR absorbance spectra were acquired using a Bruker Tensor 37 FTIR spectrometer, with spectral data collected in the range of 4000–400 cm^{-1} . The viscosity (η) of the dispersions was measured with a Brookfield viscometer (Model LVTDV-II) at a shear rate of 100 s^{-1} and a temperature of 25°C. The contact angle between water droplets and the sample surface was determined using a CAHN DCA-322 contact angle analyzer at 25°C, operating at a velocity of 100 $\mu\text{m/s}$. A microsyringe was used to deposit water droplets onto the sample surface, and contact angles were measured via monitor observation, with three measurements taken at different locations on the film. Mechanical properties, including tensile strength and elongation at break, were evaluated following ASTM D882-91 [13] standards using an MTS 10/M tensile testing machine at a crosshead speed of 50 mm/min. A minimum of three readings was averaged, with a 1-kN load cell employed during the testing process. Thermogravimetric analysis (TGA) was performed using METTLER TOLEDO's TGA/SDTA851e system

with aluminum-cripped pans under a nitrogen flow of 20 mL/min. The analysis covered a temperature range of 100–500°C at a heating rate of 10°C/min, allowing for the determination of degradation temperature and thermal stability.

Results and discussion of FTIR analysis

Figure 1 presents the FTIR spectra of polyethylene (PE), highlighting key characteristic peaks. The peaks observed at 2914 cm^{-1} and 2847 cm^{-1} correspond to the asymmetric stretching vibrations of CH_2 groups. Additionally, the peak at 1463 cm^{-1} indicates bending deformation, while the peak at 719 cm^{-1} is attributed to rocking deformation [14]. Figure 2 illustrates the FTIR absorbance spectra of PE-g-AA, revealing new characteristic peaks. A peak at 2848 cm^{-1} corresponds to C-H stretching, while peaks at 1370 cm^{-1} and 738 cm^{-1} are attributed to the C-H vibrations of ethylene groups. Additionally, a peak at 1179 cm^{-1} signifies C-O-C stretching, 1462 cm^{-1}

related to CH_2 scissor, 980 cm^{-1} to CH_2 twist, 809 cm^{-1} to CH bend and the presence of a peak at 1722 cm^{-1} indicates the carbonyl group, which confirms the successful grafting of polyethylene with acrylic acid (AA) [[15], [16], [17]].

Viscosity

Table 1 demonstrates the viscosity enhancement of the P(PE-g-AA) when blended with rice straw. For instance, incorporating 3% rice straw into P(PE-g-AA) increased its viscosity from 475 mPa·s to 560 mPa·s. With a further increase in rice straw content to 5%, the mixture's viscosity rose to 573 mPa·s, while 7% rice straw achieved the highest viscosity of 615 mPa·s. This viscosity increase can be attributed to the more polar nature and larger surface area of rice straw, which significantly improves the interaction and viscosity relative to the grafted copolymer [[18], [19]]. Consistent with the findings previously reported by the authors [11], the viscosity of polyethylene/starch films increases with the incorporation of rice straw

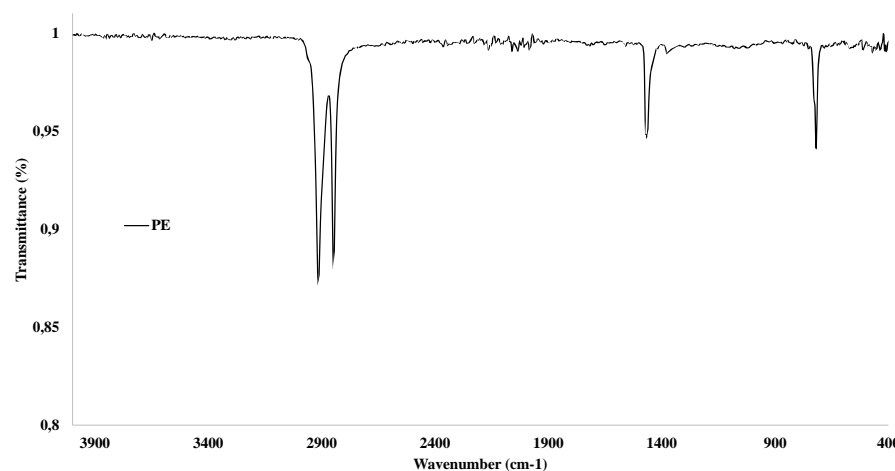


Figure 1 - FTIR spectra of polyethylene (PE)

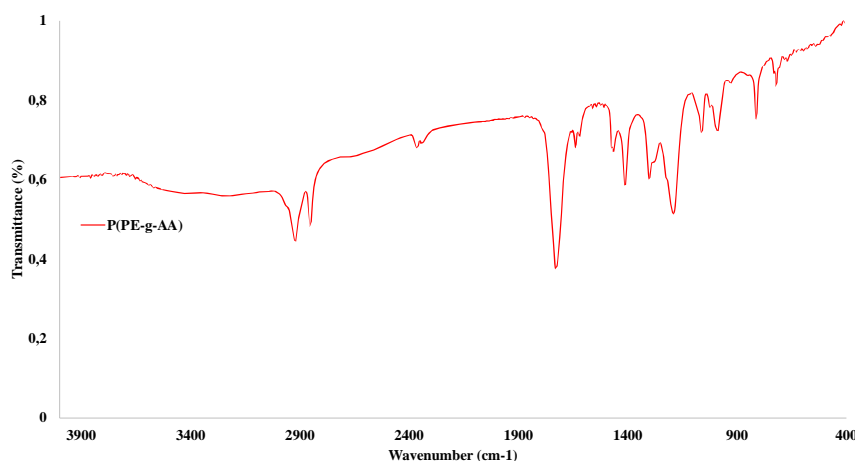


Figure 2 - FTIR spectra of the P(PE-g-AA)

Table 1 - Viscosity values for the P(PE-g-AA) and its mixture with glycerol, rice straw

Samples	Composition	Viscosity (mPa-s)
PEA	P(PE-g-AA), glycerol	475
PEAS1	P(PE-g-AA), glycerol, and rice straw 3%	560
PEAS2	P(PE-g-AA), glycerol, and rice straw 5%	573
PEAS3	P(PE-g-AA), glycerol, and rice straw 7%	615

Table 2 - Water contact angles of P(PE-g-AA) and the grafted copolymer mixed with rice straw

Sample Number	Contact angle (deg)
PEA	102
PEAS1	98
PEAS2	95
PEAS3	89

Table 3 - Mechanical properties of P(PE-g-AA) and the grafted copolymer mixed with rice straw

Samples	Tensile strength (MPa)	Elongation (%)
PEA	25.2	114
PEAS1	27.6	119
PEAS2	32.5	122
PEAS3	36.8	125

Water contact angle

The water contact angle serves as a critical parameter for assessing the hydrophilicity of dried polymer films. As shown in Table 2, incorporating rice straw into P(PE-g-AA) resulted in a progressive decrease in the water contact angle, with the addition of rice straw yielding the lowest values. Specifically, the integration of 3% rice straw reduced the water contact angle of the grafted copolymer by 3.6%, while 5% rice straw further decreased it by 6.8%. The addition of 7% rice straw exhibited the greatest impact, enhancing hydrophilicity by 12.7%. The hydrophilicity of these polymers is influenced by various factors, including the type of polymer matrix, additives, ingredients, fillers and rice straw utilized [[20], [21]]. The same behavior was observed by Irmukhametova et al. [8], who reported on the biodegradability of polymer blends composed of polyvinyl alcohol, starch, and chitosan, enhanced by the addition of rice straw.

Mechanical properties

The influence of rice straw on tensile strength and elongation at break is illustrated in Table 3. Incorporating rice straw into the grafted copolymer resulted in an increase in tensile strength from 25.2 MPa to 27.6 MPa, a change attributed to the higher

SiO₂ content in the rice straw, as in the study reported in Ref. [[3], [4], [22], [23]]. Further enhancement in tensile strength, from 27.6 MPa to 36.8 MPa, was observed with a rice straw concentration increase from 3% to 7%. The highest tensile strength of 36.8 MPa was achieved at 7% rice straw. Additionally, the elongation at break improved significantly, rising from 4.3% to 9.6% with the addition of rice straw to the grafted copolymer.

Biodegradability properties of P(PE-g-AA) films

The effect of rice straw on the swelling behavior of grafted copolymer films, as influenced by time and temperature, is presented in Figure 3. Swelling time was observed to decrease with increasing temperatures from 30°C to 45°C. Additionally, incorporating rice straw into the grafted copolymer reduced swelling time compared to the grafted PEA copolymer. Swelling time further decreased with higher rice straw content in the grafted copolymer. For instance, at 45°C, the swelling time decreased by 5.8% with 3% rice straw, 15% with 5% rice straw, and 25.8% with 7% rice straw. This reduction in swelling time is attributed to the role of rice straw in enhancing the water solubility of the blend films.

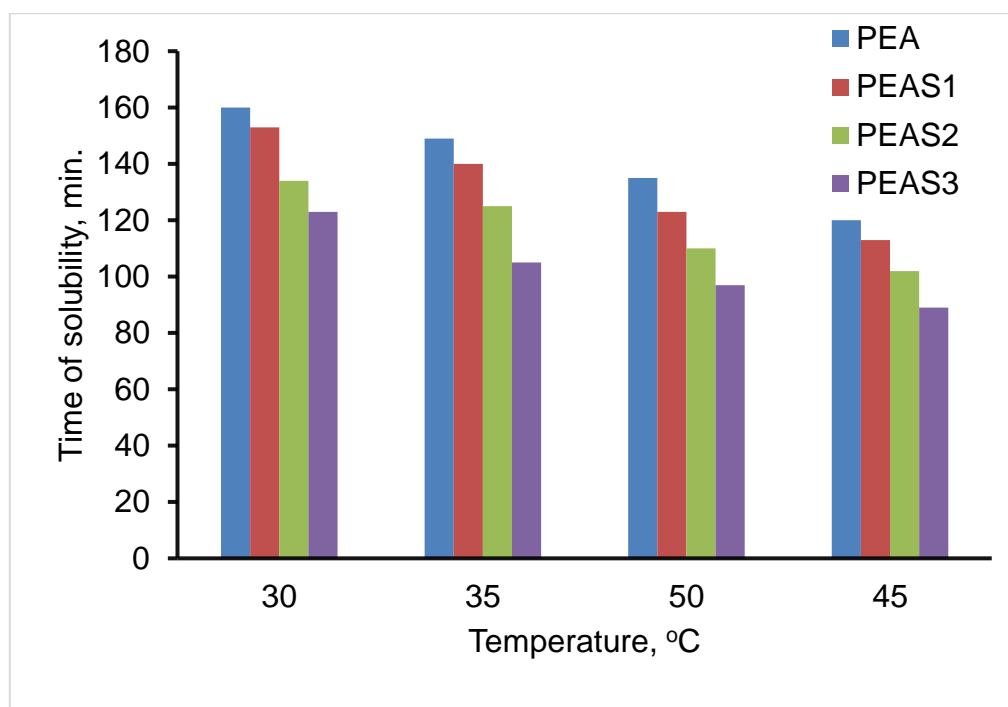


Figure 3 - The effect of water on the biodegradability of films

Conclusions

A polyethylene (PE)-based copolymer grafted with acrylic acid (AA) in a 1:5 ratio was synthesized using a grafting polymerization technique. Rice straw was incorporated into the grafted copolymer at varying concentrations (3%, 5%, and 7%) to enhance its biodegradability. The findings demonstrated that the addition of rice straw improved both the mechanical properties and biodegradability of the copolymer. The grafted copolymer containing 5% rice straw exhibited the best mechanical performance and a shorter swelling time compared to the grafted copolymer without rice straw. We explored the potential of utilizing the prepared grafted films, incorporating 5% rice straw (based on grafted polymer weight), for packaging applications. Furthermore, we evaluated alternative approaches to developing eco-friendly packaging

films, alongside the essential role of petroleum in polymer production.

CRedit author statement: G. Yeligbayeva: Writing-original draft; Zh. Orazalin, A. Abdassalam: Writing review; K. Omirzakova: Methodology; N. Milissova and Eny Kusirini: Formal analysis.

All authors have read and agreed to the published version of the manuscript.

Acknowledgments. The work was financially supported by the Ministry of Science and Education of the Republic of Kazakhstan, competition for grant funding for scientific and technical projects 2023–2025. Project No. (AP19676789), entitled “Production of biodegradable plastic bags based on ethylene and cornstarch, Republic of Kazakhstan”.

Conflicts of interest. Authors declare no conflict of interest, financial or otherwise.

Cite this article as: Yeligbayeva G, Orazalin ZhK, Abdassalam A, Alfergani, Omirzakova KK, Milissova NB, Eny Kusirini. Effect of Rice Straw on the Mechanical and Biodegradability Properties of the Poly (Polyethylene-G-Acrylic Acid). Kompleksnoe Ispolzovanie Mineralnogo Syra = Complex Use of Mineral Resources. 2026; 338(3):51-58. <https://doi.org/10.31643/2026/6445.28>

Күріш сабанының полиэтилен-г-акрил қышқылының механикалық және биологиялық ыдырайтын қасиеттеріне әсері

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<p>Мақала келді: 25 наурыз 2025 Сараптамадан өтті: 28 наурыз 2025 Қабылданды: 21 сәуір 2025</p>	<p>ТҮЙІНДЕМЕ Полиэтилен/акрил сополимері катализатор ретінде бензоил пероксиді және еріткіш ретінде ксилолмен егу әдісін қолдану арқылы синтезделді. Акрил қышқылы (AA) 1:5 қатынасында полиэтиленге (ПЭ) егілді. FTIR арқылы сипатталатын егілу арқылы алынған сополимер биологиялық ыдырайтын қабықшаларды алу үшін әртүрлі 3%, 5% және 7% арақатынаста күріш сабанымен араластырылды. Бұл қабықтардың судағы қасиеттері тұтқырлық, созылу беріктігі, үзілу кезіндегі ұзару, сумен жанасу бұрышы және ерігіштік талдаулары арқылы бағаланды. Күріш сабанын қосу арқылы егілген сополимердің биологиялық ыдырағыштығы артты, нәтижесінде тұтқырлық, созылу беріктігі және пленкалардың үзілуі кезінде созылу артады, сонымен бірге сумен жанасу бұрышы мен ерігіштігі төмендеді. Дегенмен, ПЭ (1,0%) және AA (5,0%) негізіндегі егілген сополимерге 7% күріш сабанын қосу тұтқырлықты, созылу беріктігін және үзілу кезіндегі ұзаруды тиісінше 29,5%, 46,1% және 9,6% арттыруға әкелді, бұл сәйкес жанасу бұрышы мен биоградация уақытын 45°C-да 54 25,8%-ға төмендетеді.</p>
	<p>Түйін сөздер: Полиэтилен, акрил қышқылы, күріш сабаны, биологиялық ыдырайтын, механикалық.</p>
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Влияние рисовой соломы на механические и биоразлагаемые свойства полиэтилен-г-акриловой кислоты

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<p>Поступила: 25 марта 2025 Рецензирование: 28 марта 2025 Принята в печать: 21 апреля 2025</p>	<p>Аннотация Полиэтилен/акриловый сополимер был синтезирован с использованием техники прививки с бензоилпероксидом в качестве катализатора и ксиленом в качестве растворителя. Акриловая кислота (АК) была привита к полиэтилену (ПЭ) в соотношении 1:5. Полученный привитой сополимер, охарактеризованный FTIR, был смешан с рисовой соломой в различных соотношениях 3%, 5% и 7% для получения биоразлагаемых пленок. Свойства этих пленок в воде были оценены с помощью анализа вязкости, прочности на разрыв, удлинения при разрыве, угла контакта с водой и растворимости. Включение рисовой соломы повысило биоразлагаемость привитого сополимера, что привело к повышению вязкости, прочности на разрыв и удлинения при разрыве пленок, при этом уменьшив угол контакта с водой и растворимость. Однако включение 7% рисовой соломы в привитой сополимер на основе ПЭ (1,0%) и АА (5,0%) привело к увеличению вязкости, прочности на разрыв и удлинения при разрыве на 29,5%, 46,1% и 9,6% соответственно, при одновременном снижении угла контакта и времени растворимости при биоразлагаемости при 45°C на 25,8%.</p>
	<p>Ключевые слова: Полиэтилен, акриловая кислота, рисовая солома, биоразлагаемый, механический.</p>
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