SYNTHESIS AND CHARACTERIZATION OF POLYURETHANE-STARCH COMPOSITES FOR ENHANCED IMPACT RESISTANCE

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Summary

Polyurethane (PU) has emerged as a prominent polymer in various industries, owing to its versatile applications and desirable properties. This research aims to enhance the impact resistance quality of PU by incorporating starch as a sustain-able additive, which will contribute to the development of more durable and reliable polyurethane materials for multiple industries. Starch, a plentiful natural resource, offers advantages of affordability, biodegradability, widespread availability, and environmental friendliness, which makes it an optimal additive choice for this research. The synthesis process involves the combination of starch with two polyols, namely glycerol and castor oil. Afterwards, the polymerization process begins with the introduction of toluene diisocyanate (TDI) and addition of dibutyltin dilaurate (DBTL) as a catalyst. Various proportions of glycerol to castor oil were evaluated during the synthesis process to generate a series of polyurethane samples, aiming to identify the optimal ratio that provides the highest impact resistance. Subsequently, the impact resistance capability of polyurethanes (Pus) was further explored by introducing varying quantities of castor oil into the synthesis process. After the preparation of all the PU samples, the two most promising formulations, one with starch and one without starch, were selected for further analysis using Fourier Transform Infrared Spectroscopy (FTIR). Achieved results showed that starch addition improves impact resistance, as indicated by the presence of hydroxyl (OH) groups. The successful completion of the reaction confirms starch's effectiveness as an eco-friendly and cost-effective additive for enhancing impact resistance in polyurethane.

Keywords: impact resistant polymers, polyurethane, starch, toluene diisocyanate, Fourier Transform Infrared Spectroscopy

Аннотация

1 Introduction

Polyurethanes (Pus) are a class of highly versatile materials known for their unique mechanical, physical, biological, and chemical properties. According to the 2012 production statistics from the United States, Pus are widely utilized in various industrial sectors due to their exceptional mechanical properties and durability. Notably, the building and transportation sectors prominently employ Pus. These materials have found extensive applications in the development of diverse products within these sectors. [1]

The primary objective of this experiment was to improve the impact resistance characteristics of polyurethane (PU) by introducing starch as a sustainable additive. This research study is of significant importance due to several compelling reasons: Firstly, safety considerations are crucial in many PU applications, such as automotive parts, sporting equipment, and protective gear. These products are designed to withstand impacts, and by improving the impact resistance of PU, we can effectively reduce the risk of injury to users. Durability is another significant aspect to consider. PU products that experience repeated impacts may undergo wear and tear, resulting in reduced lifespan and increased maintenance costs. Additionally, certain PU applications require a high level of impact resistance to fulfill their intended functions effectively. By improving the impact resistance

and durability, we can ensure that these products perform optimally and meet the desired functionality requirements while also achieving a decrease in replacement expenses. [2]

The selection of starch as the additive instead of other materials like cellulose, lignin, or chitin, which possess superior mechanical and thermal properties is based on several compelling reasons: Starch presents itself as a suitable additive due to its affordability, abundance, renewability, biodegradability, widespread availability, and environmentally friendly nature. It is a natural raw resource, making it an excellent substitute for developing sustainable polyurethane formulations. When incorporated into PU, starch enhances its strength, thermal stability, and flexibility by facilitating the formation of intermolecular hydrogen bonds between the polymer chains through cross-linking mechanisms. [3]

While other materials may have the potential to improve the impact resistance of polyurethane, their environmental impact and cost considerations may not be as favorable as those associated with starch. Therefore, utilizing starch as an additive offers an eco-friendly and cost-effective solution to enhance the impact resistance of polyurethane.

2 Preparation of Polyurethane Samples

Utilized Materials and Equipment

The synthesis of polyurethane commences with the mixing process of two polyols, namely glycerol and castor oil, utilizing a magnetic stirrer. During the preliminary trials, ethylene glycol was employed instead of glycerol; however, the resulting samples exhibited excessive rigidity and a lack of flexibility. Consequently, glycerol was selected as the preferred option and incorporated in the subsequent sessions. To ensure a comprehensive evaluation, the starch-mixed variation is crucial for all polyurethane formulations, and therefore, corn starch is occasionally introduced after the polyols as part of the experimental procedure. While the solution was continuously stirring, the polymer chain reaction was initiated by the introduction of toluene diisocyanate (TDI), followed by the addition of dibutyltin dilaurate (DBTL) as a catalyst after a short mixing period. The reaction can naturally take a significant amount of time to complete, but the inclusion of DBTL accelerates the reaction, reducing the curing time of the polymer to overnight. Since the reaction is exothermic, it generates heat, which can serve as an indicator of the initiation of the reaction. Stirring should be halted as soon as a slight temperature rise is detected, as further mixing can compromise the structure, a critical factor influencing the impact-resistant quality of the polymer. [4]

Due to the potential hazards associated with TDI, safety precautions and the use of appropriate equipment were implemented. These precautions included wearing masks throughout the entire session, as well as lab coats and safety eyewear to ensure adequate protection. A range of tools was utilized, such as a pipette for precise allocation of small quantities, scales with an accuracy of four significant figures for precise measurements, and a magnetic heater and stirrer to achieve an efficient mixing.

Calculation method

The calculation of raw material quantities in the study was performed using the Parts by Weight (PBW) method. The first step started with the determination of the equivalent weights of isocyanate and polyols utilized in the reactions by using appropriate formulas.

$$Isocyanate\ equivalent\ weight = 4200 \div NCO\ value \quad (1)$$

$$Polyol\ equivalent\ weight = 56100 \div OH\ value \quad (2)$$

Subsequently, the total weight of toluene diisocyanate (TDI) was calculated using the following formula:

$$Total\ weight\ of\ TDI\ required = index * TDI\ equivalent\ weight * \{(pbw\ of\ polyol\ A/equivalent\ weight\ of\ polyol\ A) + (pbw\ of\ polyol\ B/equivalent\ weight\ of\ polyol\ B)\} \quad (3)$$

This calculation takes into account the weight percentages of the polyols. By incorporating an excess amount of raw materials to ensure the success of the reaction, different proportions of the raw materials were explored, and the resulting samples were thoroughly investigated. [5]

Procedure

The experimental procedure began by determining the optimal proportion of the reacting polyols. Initial calculations were conducted based on ratios of 1:2, 1:3, and 1:4, with a fixed amount of 7.5 g of castor oil for each ratio (see Table 1). Polyurethanes were prepared using the 1:2 and 1:3 ratios, both with and without starch. Through careful observation, it became evident that the samples with a 1:2 ratio exhibited superior results compared to the 1:3 ratio. To further investigate, a modified 1:3 sample was prepared using 10 g of castor oil, however, the results indicated that higher proportions not only increased the material's softness but also diminished its impact resistance when starch was utilized as an additive under these conditions. Consequently, the assumption was revised, and the ratio was changed from 1:4 to 1:1 to confirm whether the 1:2 ratio could indeed be considered the optimal configuration. Upon examination, it was observed that the sample without starch exhibited a sticky consistency and evident lack of impact resistance, while the sample with starch showed improvement but still fell short in comparison to the 1:2 ratio. Hence, the results conclusively demonstrated that the 1:2 ratio yielded the most balanced outcome among the aforementioned ratios, with the other ratios exhibiting unstable structures.

Table 1. Amount of Used Materials for each proportion.

Used Materials	Proportions (Glycerol:Castor Oil) [g]		
	1:1	1:2	1:3
Glycerol	0.74	0.37	0.25
Castor Oil	7.50	7.50	7.50
TDI	6.64	4.98	4.43
Starch	0.41 / -	0.39 / -	0.38 / -

Next, the focus shifted towards determining the optimal quantity of castor oil for the 1:2 proportion. Samples were prepared using a range of 7.5, 10, 12, and 15 g of castor oil, both with and without starch (see **Table 2**

Table **2**) Throughout the experimental procedure, a consistent trend emerged, indicating that an increase in the quantity of castor oil resulted in a decrease in impact resistance while simultaneously observing an increase in flexibility and softness. At higher amounts of castor oil, the precipitation of starch occurred, leading to the formation of undissolved starch particles and the generation of bubbles in the solution. Attempts were made to address this issue by heating the solution during the mixing process; however, these attempts proved ineffective in resolving the problem. It became apparent that alternative approaches such as degassing and modifying the proportion or type of starch might be necessary to overcome this issue, thereby opening up promising pathways for further research aimed at enhancing the impact resistance property.

Table 2. Chemical Composition for 1:2 Samples with Varying Castor Oil Amounts.

Optimum proportion	Castor Oil [g]			
1:2	7.5	10	12	15
Glycerol	0.37	0.49	0.59	0.74
TDI	4.98	6.64	7.97	9.96
Starch	0.39 / -	0.52 / -	0.63 / -	0.79 / -

3 Testing and Final Results

Characterization Methods for Polyurethane Properties

Polyurethane properties are accurately assessed through various testing methods. In this study, four primary techniques were employed: Dynamic Mechanical Analysis (DMA), Differential

Scanning Calorimetry (DSC), Tensile Test, and Fourier Transform Infrared Spectroscopy (FTIR). DMA is utilized to measure the viscoelastic properties of polyurethane, including storage modulus, loss modulus, and damping coefficient. This technique provides valuable insights into the material's mechanical behavior under dynamic loading conditions. DSC enables the evaluation of thermal properties, such as the glass transition temperature, melting temperature, and crystallization temperature of polyurethane. It allows for the determination of important thermal characteristics that affect the material's performance. The Tensile Test, a mechanical testing method, was employed to determine the tensile strength, elongation at break, and modulus of the polyurethane samples. This test involves subjecting the samples to a controlled tensile force and measuring the resulting deformation, providing essential information about the material's mechanical properties. [6] Finally, FTIR analysis was conducted to identify the chemical composition of polyurethane by analyzing its absorption of infrared radiation. This technique allows for the identification of specific functional groups and provides insights into the molecular structure and composition of the material. These four characterization methods collectively contribute to a comprehensive understanding of the properties of polyurethane, enabling researchers to evaluate its mechanical, thermal, and chemical attributes. [7]

Overview of Fourier Transform Infrared Spectroscopy (FTIR) Technique

Fourier Transform Infrared Spectroscopy (FTIR) is a widely used technique in the field of infrared spectroscopy. It operates based on the principle of infrared radiation absorption. When infrared radiation passes through a sample, a portion of the radiation is absorbed, while the remaining radiation is recorded. The resulting spectra, which are unique to different molecules, allow for the identification and distinction of the chemical composition of the material.

The absorption of radiation at specific wavelengths selectively modifies the vibrational energy in the covalent bonds of molecules. The induced vibration can be either stretching or bending, depending on the atoms involved in the bond. Different bonds and functional groups exhibit absorption at distinct frequencies, leading to unique transmittance patterns among molecules. The obtained spectrum from FTIR is graphically represented with wavenumber (cm^–1) on the X-axis and transmittance on the Y-axis. Wavenumber, as the inverse of wavelength, corresponds to the vibrational energy of the molecular bonds. [8]

FTIR is the preferred method of infrared spectroscopy for several reasons. It does not destroy the sample, offering non-destructive analysis. Moreover, FTIR is faster compared to older techniques, and it provides higher sensitivity and precision. In this study, the Bruker Alpha FTIR instrument was employed for testing purposes.

Analysis of the Test Results

The obtained results comprise of two samples at 1:2 ratio: one incorporating polyurethane with 7.5 g starch and the other without starch (see Fig. 1). Both samples were sent to Institute of Petrochemical Processes for FTIR testing. Based on the results (see Fig. 2 and Figure 1), it is evident that the second sample, which lacks starch, demonstrates a higher concentration of hydroxyl (OH) groups in comparison to the first sample. These OH groups significantly contribute to the improvement in impact resistance, aligning with the intended objective. This enhancement can be attributed to the presence of starch as an additive. Overall, the results indicate the successful completion of the reaction.

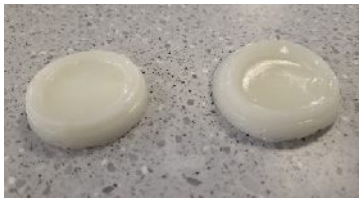

Figure 1. ***1:2 Proportion Samples with 7.5 g Castor Oil***
(Left) With Starch
(Right) Without Starch

However, it is important to note that this experiment is not conclusive, and further investigations are warranted. Additional samples will be prepared, incorporating varying ratios and even different components, in order to develop more suitable polyurethane materials. Subsequently, all four testing

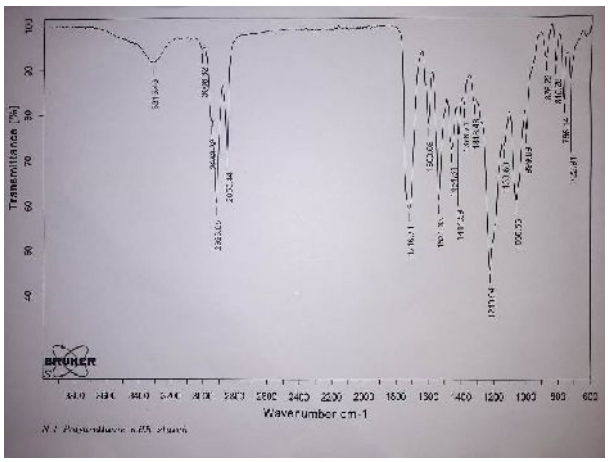

Figure 2. ***FTIR results for sample with starch***

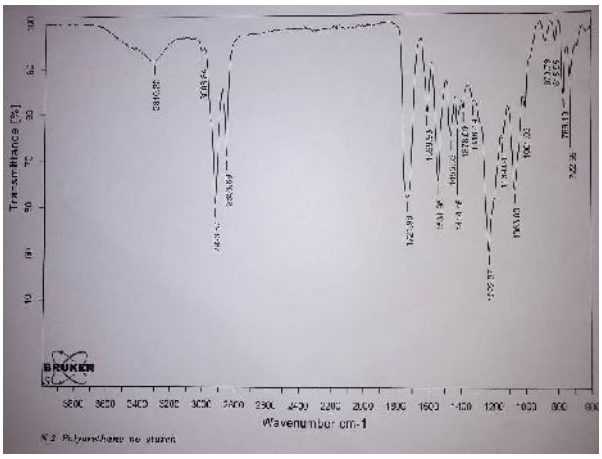

Figure 1. ***FTIR results for sample with no starch***

methods mentioned earlier will be employed to comprehensively assess these samples. The outcomes of these experiments will be meticulously compiled and documented in a scientific paper in near future.

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