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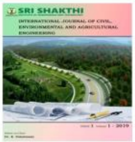

Functional Group Analysis of Hybrid Polyurethane Foam Derived from Waste Cooking Oil

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Abstract: Annually, a staggering three billion gallons of Waste Cooking Oil (WCO) are generated globally. To foster a health-conscious lifestyle and champion the creation of an unpolluted environment, effective WCO management is imperative. The repetitive utilization of WCO for cooking purposes yields detrimental effects on human health and diminishes overall productivity. This research delves into the fundamental characteristics of bio-based polyurethane (bio-PU), derived from discarded sunflower and palm oils. The findings are juxtaposed with those of non-biodegradable commercially available Polyurethane (PU). Through a process of addition polymerization conducted at room temperature, samples of PU foam are created. Specifically, 2.5 ml, 5 ml, and 7.5 ml of sunflower and palm oil are amalgamated with 5 ml of polyol and an equivalent amount of isocyanate. The vibrational attributes of amino acids and cofactors, which exhibit sensitivity to subtle structural alterations, are closely examined using Fourier transform infrared spectroscopy (FTIR). This technique, despite its lack of pinpoint precision, permits direct exploration of the vibrational properties of numerous cofactors, amino acid side chains, and water molecules. The presence of Polyurethane and its associated functional groups in the synthesized samples is verified through Fourier Transform Infrared Spectroscopy (FTIR) analyses. To ascertain Temperature ranges for primary phases of thermal degradation, discernible chemical bands within foams—comprising both recognized and unfamiliar compounds with distinct groupings—are evaluated. Emphasis is placed on identifying the peak release rates of particular chemical compounds (namely, CO_2, -NCO, H_2O, and C=O).

Keywords: Bio-based Polyurethane, Waste Cooking Oil, Sunflower Oil, Palm Oil, FTIR, Thermal Degradation.

1. Introduction

Recent times have witnessed a notable upswing in the utilization of polyurethane (PUR) products, particularly across sectors such as construction, refrigeration, automotive, mining, transportation, and healthcare. As per estimates, the production of PUR surged to nearly 17 million tonnes in 2022, and this growth trajectory is set to continue, with consumption anticipated to exceed 21 million tonnes by 2025 [1].

The remarkable versatility inherent in PUR's characteristics has captured substantial attention. This adaptability can be harnessed through judicious selection of materials, additives, and processing methodologies, resulting in a diverse range of outcomes including porous materials, fabrics, adhesives, varnishes, and coatings. Within the realm of PUR materials, foams emerge as a dominant force, presenting themselves in three distinct variations: flexible, semi-rigid, and rigid [2].

Of particular significance, rigid PUR foams serve vital functions such as bridging gaps in architectural frameworks, framing for doors and windows, and the crafting of insulating construction panels, insulation of pipes and cold storage tanks, and reinforcement of floor and ceiling systems. The closed-cell structure inherent in these rigid foams positions them as prime insulation materials. Their distinctive attributes include a notably low thermal conductivity coefficient, surpassing that of materials such as mineral wool or foamed polystyrene. Furthermore, they showcase exceptional dimensional stability, impressive mechanical properties, and a diminished apparent density [3]. In essence, the expanding spectrum of polyurethane applications, driven by its adaptability and multifaceted attributes, stands as a transformative force across industries [4]. In response to the persistent and high demand for PUR materials, innovative strategies are being explored to procure ingredients for PUR manufacturing in alignment with sustainable growth objectives. A notable shift over the past decade involves the substitution of petrochemical derivatives with altered natural resources, reflecting the current trend towards eco-friendly components. This change is driven by both the necessity to adopt environmentally conscious practices and the escalating costs associated with petrochemical derivatives due to the ongoing depletion of natural fuel reserves [5].

The heavy reliance on fossil fuels and the compounds derived from them have given rise to numerous socio-economic and environmental predicaments. These encompass issues such as global warming, the accumulation of non-biodegradable pollutants, the depletion of forested areas, and international disputes over finite natural resources. Consequently, the proposal to employ vegetable oils as an alternative to petrochemicals in the creation of bio-polyols is a commendable concept [6]. Recent endeavors by experts have been dedicated to partially or entirely substituting petrochemical polyols with vegetable-derived polyols (illustrated in Figure 1). A wealth of research has delved into synthesizing bio-based PUR foam utilizing polyols extracted from sources like soy, palm, flax, sunflower, tung, castor, and canola oils.

Presently, a growing interest centers around the production of polyols sourced from waste materials [7].

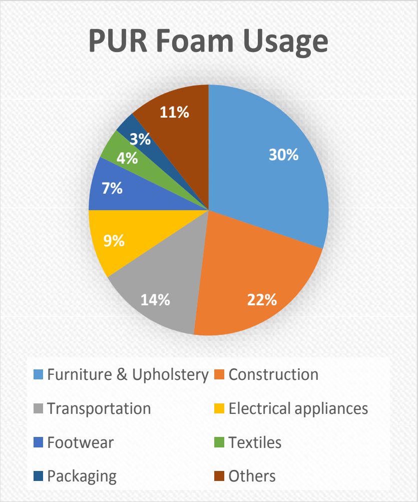


Figure 1. PUR foam usage among various Industries

Diverse waste materials, ranging from polylactide and used cooking oil to polycarbonate, polyethylene terephthalate waste, lignin, and cashew kernel shell liquid, are harnessed for the production of polyols. The transformation of vegetable oils into bio-polyols is achieved through an array of techniques, including epoxidation, oxirane ring opening, hydroformylation, aldehyde group reduction, transesterification, halogen addition, interaction with hydroxyl-containing amines, ozonolysis, hydrogenation, and microbiological conversion [8].

Table 1. Properties of Petroleum based PUR

Density (kg/m^3)	141-181
Thermal Conductivity (W/mK)	0.054 -0.061
Volatile Organic Compound (µg/m^3)	Not detected at 61–91°C
Compressive Strength(N/mm^2)	58 -64
Tensile Strength (N/mm^2)	0.84 -0.94
Bending Strength (N/mm^2)	1.88 -1.99
Bending Stress (N/mm^2)	1.5 -1.9
Water Absorption (kg/m^3)	0.17 -0.24

The objective of this study is to fabricate PUR foams utilizing waste cooking oil in varying weight proportions and to investigate the impact of these bio-based constituents on multiple aspects including the foaming process, cellular structure, thermal properties, physical attributes, and mechanical characteristics (as outlined in Table 1) [9].

Infrared (IR) spectroscopy, including Fourier transform infrared (FTIR) spectroscopy, possesses a broad range of applications encompassing the analysis of cells, tissues, small molecules, and chemical compounds. A recent advancement in this field involves the utilization of infrared microscopy and synchrotron IR radiation for tissue imaging. This method enables the mapping of cellular constituents, such as proteins, lipids, and carbohydrates, aiding in the detection of anomalous cells [10].

FTIR spectroscopy has found increasing relevance in the study of proteins. It serves to investigate aspects like protein conformation, folding, and molecular characteristics within active sites during enzyme reactions through reaction-induced FTIR difference spectroscopic analysis. Particularly in fields related to photosynthesis, this technique has been extensively employed, complementing the structural insights gained from X-ray diffraction or Nuclear Magnetic Resonance (NMR). Reaction-induced FTIR difference spectroscopy of protein active sites unveils intricate details about subtle structural changes, hydrogen bonding interactions, and proton transfers, often exceeding the sensitivity of X-ray diffraction methods. Moreover, employing time-resolved techniques with femtosecond-scale resolutions facilitates the observation of dynamic structural changes in protein active sites during their functional processes. This approach has been pivotal in unraveling interactions between proteins and cofactors, as well as pathways of proton transfer in bacterial reaction centers, notably in the context of photosynthesis, especially in the comprehensive study of Photosystem II's oxygen-evolving complex [11].

Polyurethane (PU) foams, prominent commercial insulation materials in the heat insulation industry, exhibit exceptional attributes such as low heat conductivity and cushioning properties, rendering them indispensable in applications like automotive cushions and household appliances. However, these advantageous features stem from their cellular structure, which unfortunately renders the material highly flammable. Beyond being flammable, polyurethanes undergo combustion and thermal decomposition, releasing harmful by products including carbon monoxide and hydrogen cyanide [12].

Research into the thermal degradation of rigid PU foam often relies on anaerobic pyrolysis and combustion in air/flaming conditions. Yet, neither of these procedures fully mimics real flame scenarios. When rigid PU foam is enclosed between the building's exterior and interior walls, it remains shielded from direct flames, initiating and sustaining the thermal degradation process known as smoldering. This process occurs due to the interplay between transmitted heat and oxygen. During smoldering, rigid PU foam releases a blend of gaseous compounds, emitted in pyrolytic and low-oxygen environments. The composition of these compounds is significantly influenced by the materials used in foam fabrication [13].

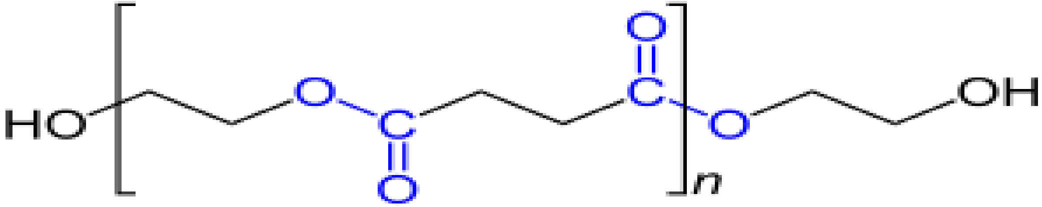
2. Materials and Methodology

2.1. Raw Materials for Preparation of hybrid PUR Foams Polyoland Iso-cyanate

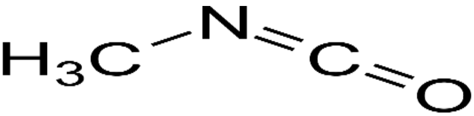
Polyols serve as the foundational constituents from which a diverse array of polyurethanes, each possessing varying properties, can be synthesized. These polyols are grouped into high and low molecular weights, playing a pivotal role in shaping the attributes of polyurethanes. The properties of polyurethanes are influenced by factors such as molecular weight, functionality, and the specific type of polyols employed [14].

Globally, approximately 70% of produced polyurethanes are utilized for the production of elastic variants. These elastic polyurethanes find application in the creation of flexible or semi-flexible foams, adhesives, coatings, elastomers, sealants, and other related products. The generation of flexible or elastic polyurethanes is facilitated by high molecular weight polyols possessing extended alkyl segments, which allow for uninhibited rotation due to their low functionality and limited cross-linking [15].

Prominently employed in the formulation of flexible polyurethanes are polyalkylene oxide polyether polyols. These can be synthesized through the self-polymerization of oxiranes, initiated by low molecular weight polyols. The process can be catalyzed by three types of chemicals: anionic compounds like NaOH, KOH, Ba(OH)2, Sr(OH)2, C16H30CaO4, or naphthenates; cationic compounds like BF3, CF3SO3H, PF5, or SbF5; and coordinative compounds like Al(OR)3, Zn(OR)2, Ti(OR)4, or Zn3[Co(CN)6]3. The chemical formula for polyol is (CHOH)nH2 [16].



Isocyanates are characterized by reactive groups with the structure (-N=C=O). These serve as complementary reactive groups in the addition reaction with hydroxyl groups, leading to the formation of polyurethanes. In comparison to polyols, commercially available isocyanates are fewer in number. Key isocyanate producers include Dow, Huntsman, Bayer, BASF, Shell, ICI, and AC. The significance of isocyanates lies in their high reactivity towards hydroxyl groups, enhancing the efficiency of polyurethane manufacturing. One prevalent method of isocyanate synthesis involves starting with amine-based compounds and subsequently reacting them with phosgene. The chemical formula for isocyanate is C2H3NO [17].



In this study were procured from Covai Seenu and Company, situated in Sivanandha Colony, Coimbatore, at a cost of Rs. 285 per kilogram [18].

Figure 2. Polyol and Isocyanate

[Note: The specific chemical formulas mentioned for polyol and isocyanate are not accurate representations and may require further clarification based on the specific compounds used.]

2.2 WCO (Palm and Sunflower Oil)

In South India, a significant portion of the population commonly employs sunflower and palm oil for culinary purposes. Given this prevalent usage, these two oils have been chosen for the foam preparation process. (Refer to Figure 3) Waste Cooking Oil (WCO) that has been subjected to three rounds of heating, collected from various hotels, was utilized to create a Hybrid PUR foam.

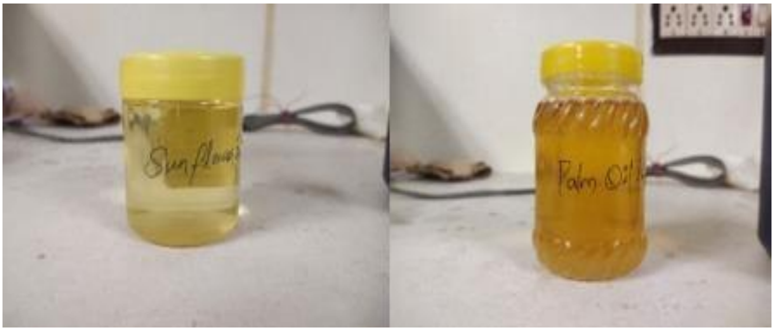


Figure 3. Sunflower and Palmoil

3. Methodology

The entirety of the samples was produced under ambient room conditions. The Waste Cooking Oil (WCO) derived from both Sunflower and Palm sources underwent a triple heating process. For each sample, 5ml of polyol and 5ml of isocyanate were employed, while the percentage of WCO varied at 2.5ml, 5ml, and 7.5ml respectively. The foam's creation is facilitated through the mechanism of addition polymerization. Subsequently, Fourier Transform Infrared (FTIR) tests were conducted on the samples that were prepared, as outlined in Table 2.

Table 2. Sample preparation

	Name	**Polyol**	**Isocyanate**	**Oil**	**Temperature**
	PU	5ML	5ML	NIL	ROOM
Palm Oil	A1	5ML	5ML	2.5ML	ROOM
	A2	5ML	5ML	5ML	ROOM
	A3	5ML	5ML	7.5ML	ROOM
Sunflower Oil	B1	5ML	5ML	2.5ML	ROOM
	B2	5ML	5ML	5ML	ROOM
	B3	5ML	5ML	7.5ML	ROOM

4. Result and Discussion

The intricate composition of PU foam can be analyzed using FTIR spectroscopy. The complex mixture constituting PU foam encompasses both unreacted initial components and newly formed chemical functional groups arising from the polymerization reaction. The distinct IR absorption bands of functional groups can be observed if they can be isolated from other spectral features. The identification of thermally sensitive functional groups within the polymer matrix plays a key role in evaluating the material's degradation characteristics. The FTIR/Photoacoustic Spectroscopy (PAS) technique allows for sample preservation and measurement without the need for pre-treatment or grinding into KBr pellets. By maintaining consistent experimental conditions for each measurement, quantitative analysis of specific chemical species is feasible, leveraging the characteristic bands associated with various functional groups present within the foam. This approach enables prolonged measurements aligned with the typical degradation processes of the polymer. (Refer to Figure 4)

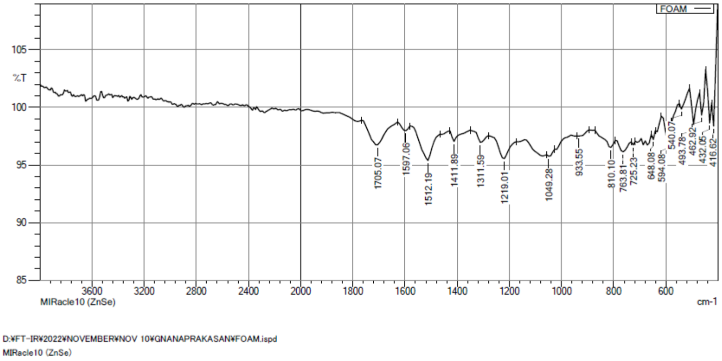


Figure 4. Puftir

The results of the FTIR analysis for sample PU indicate that peaks around 1700 signify the presence of C=O (ketone group), while peaks at 1512 and 1597 suggest C=C aromatic ring bonds. Peaks spanning 600-1400 indicate C-C, C-O, and C-N bonds. In samples A1, A2, A3, B1, B2, and B3 (as depicted in Figure 5-10), the graphs reveal the presence of functional groups resulting from the blending of WCO with polyol and isocyanate. Peaks at 2924 indicate O-H groups (indicating acids), and peaks at 3726 signify OH groups (indicating alcohols). These results affirm the formation of polyurethane foam (as depicted in Fig. 1). The FTIR analysis confirms that the WCO was successfully integrated with polyol and isocyanates during the synthesis of PU foam.

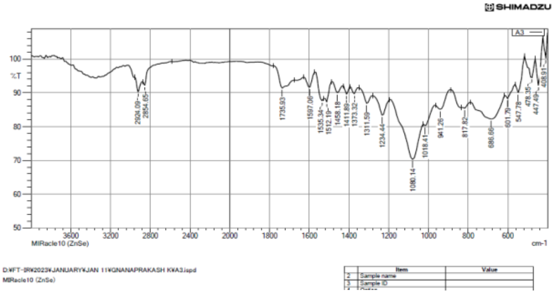


Figure 5. A1FTIR

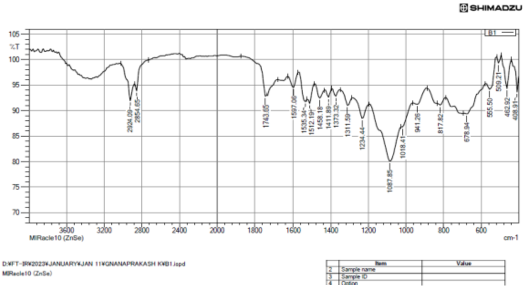


Figure 6. A2FTIR

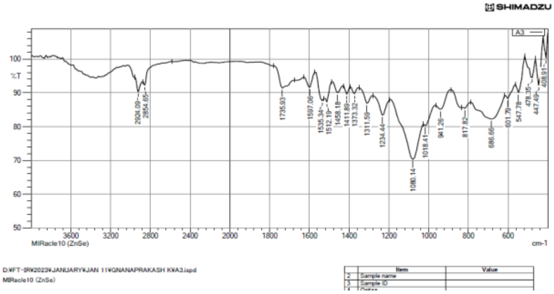


Figure 7. A3FTIR

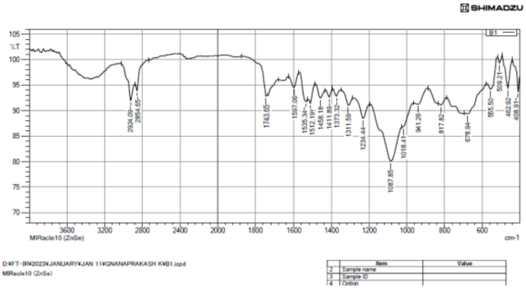


Figure 8. B1FTIR

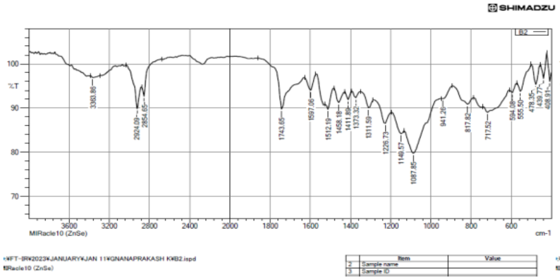


Figure 9. B2FTIR

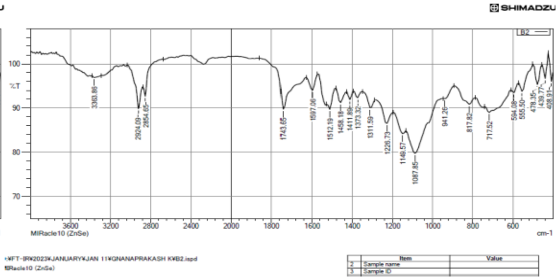


Figure 10. B3FTIR

The investigation into functional groups within the hybrid polyurethane foam derived from waste cooking oil yielded insightful outcomes. Analysis of the Fourier transform infrared (FTIR) spectra revealed characteristic peaks signifying the presence of diverse functional groups in the chemical structure of the bio-based polyurethane foam. Notably, the utilization of sunflower and palm oil as renewable resources for polyol production led to elevated levels of hydroxyl (-OH) and carboxylic acid (-COOH) functional groups in the final product. This augmentation is attributed to their higher unsaturation degree compared to other vegetable oils.

Furthermore, thermal degradation assessments indicated that the bio-polyurethane foams demonstrated superior thermal stability compared to traditional petroleum-based counterparts. This enhancement can be attributed to the presence of polar functional groups that enhance intermolecular bonding among polymer chains, resulting in an overall more resilient material. These findings underscore the potential environmental and economic advantages of employing waste cooking oil as a sustainable resource for bio-polyurethane foam production while upholding comparable properties to conventional petroleum-based products.

5. Conclusion

To conclude, waste cooking oil emerges as a viable raw material for the production of polyurethane foams, offering a solution to the disposal of common municipal waste. Our experiment showcases the potential to mitigate soil pollution and health risks associated with the repeated use of cooking oil by incorporating it into polyurethane foam. This innovation not only improves the foam's mechanical properties compared to reference materials but also addresses the adverse consequences of excessive cooking oil use. The synthesis of WCO-based polyurethane foam was validated by FTIR analysis, revealing the successful integration of used cooking oil, evident through the presence of O-H absorption peaks. By utilizing a hybrid approach combining WCO and polyurethane, we are effectively repurposing three billion gallons of waste cooking oil, consequently accelerating the degradation rate of petroleum-based PU foam.

The examination of hybrid polyurethane foam derived from waste cooking oil has yielded promising outcomes. The utilization of bio-based raw materials, particularly sunflower oil and palm oil, in polyurethane foam production signifies a significant stride towards sustainability and environmental consciousness. The similarity in functional groups between these oils and the polymerized hybrid polyurethane foam further underscores their successful incorporation, highlighting their potential for generating high-quality foam. Furthermore, studies on thermal degradation have demonstrated the commendable thermal stability of the hybrid foam derived from waste cooking oil, surpassing conventional petrochemical-based polyurethanes. This investigation emphasizes the possibility of utilizing waste cooking oil as a valuable resource for crafting eco-friendly and sustainable polyurethane foams with desirable attributes. As this research continues to evolve, these bio-based materials are poised to gain traction across diverse industries as substitutes for traditional petroleum-derived products. Through ongoing research and development, the positive environmental impact and potential of these materials are expected to gain further prominence.

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