The 9 th Research Grant Application in 2023
International Polyurethane Technology Foundation

/ / 2023

To: International Polyurethane Technology Foundation

Recommender
Organization:
Address:
Tel:
Title/Name: (Sign or Seal)

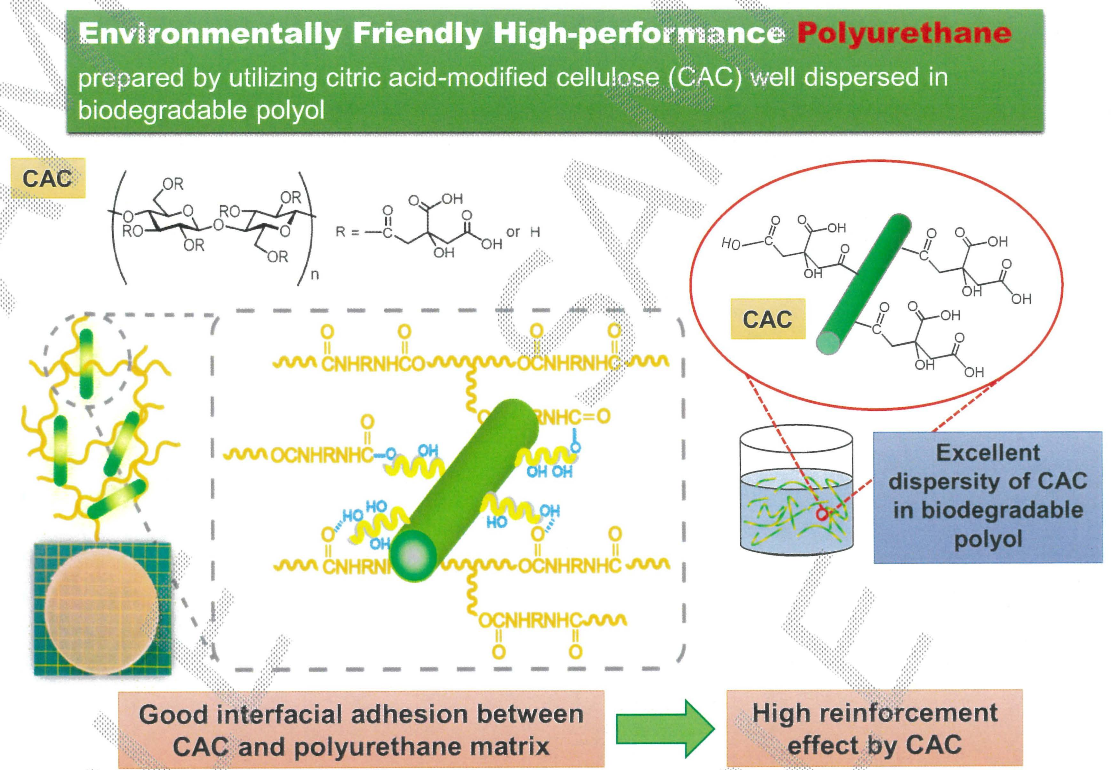
I recommend the following organization/person as a candidate who will be provided with a research grant of International Polyurethane Technology Foundation.

Representative researcher		
Name and Date of Birth Organization (University or Research institute), Department and Title of researcher Organization address TEL and FAX No. Email address		
Major collaborate researchers		
Name	Organization, Department and Title of researcher	Address
Research Title In Japanese クエン酸変性セルロースを用いる高性能生分解性ポリウレタン複合材料の開発 In English Development of high-performance biodegradable polyurethane composites using citrate modified cellulose		

Research Objectives (Please provide background, objectives, goals, etc. on one page)

Cellulose and its derivatives are renewable, environmentally friendly, naturally abundant, biodegradable, and have excellent mechanical properties that make them promising fillers for polymeric materials. Polyurethane (PU) is widely used in many areas such as foams, elastomers, coatings, and adhesives, but because it is derived from non-renewable petroleum resources and is non-biodegradable, there is a strong need to use sustainable materials and to make PU biodegradable due to the recent increase in environmental protection awareness. In this study, we aim to develop environmentally friendly high-performance PU by utilizing cellulose, a typical biomass resource, as a filler and investigating polyurethane reinforcement with biodegradable polyols. We have found that secondary modified cellulose based on citrate modified cellulose disperses well in poly(propylene glycol) and is useful for high performance PU. This modified cellulose acts as a reactive filler and forms a good interfacial adhesion between the cellulose and the PU matrix, which allows the composite to be strengthened. In this study, we utilize this knowledge to create high-performance biodegradable PU by selecting aliphatic polyester polyols to impart biodegradability to PU and developing cellulose fillers that are highly dispersed in polyester polyols. Since the key is to form good interfacial adhesion between cellulose and polyurethane matrix, (1) development of highly dispersed modified cellulose filler in polyester polyol and (2) synthesis and characterization of biodegradable PU reinforced with cellulose filler will be investigated. In the filler development, the amount of citric acid introduced, fiber diameter, and dispersibility in polyester polyol will be evaluated. In the synthesis of cellulose filler-reinforced biodegradable PU, the correlation between structure and physical properties will be investigated using polyol addition ratio, filler addition amount, presence and amount of catalyst (tin-based), and reaction temperature and time as parameters. Based on the above, we will establish a material design that improves the interfacial affinity between the PU matrix and the cellulose filler to create an interface with controllable physicochemical properties in the development of high-performance biodegradable polyurethane composite materials. The cellulose filler forms potential physical and chemical cross-linking points in the PU matrix, which is expected to improve the performance of biodegradable PU. We believe that this research is significant as a fundamental study for the creation and social implementation of PUs that contribute to decarbonization and the construction of a recycling-oriented society.

Abstract (Please post the graphic abstract in this frame)



Research objectives (Please fill 1 page of the background, objectives and target. If the limit of page is exceeded, the application will not be selected.)

The plastics industry has played a central role in the chemical industry, supporting the packaging industry and other manufacturing industries and contributing significantly to the development of the Japanese economy. On the other hand, **many plastics do not biodegrade in the natural environment**, which is a major social issue of concern, including global warming and the depletion of oil resources. **Cellulose and its derivatives have attracted significant attention because they are renewable, environmentally friendly, naturally abundant, biodegradable, and have excellent mechanical properties**. Furthermore, their structure is composed of numerous β-glucoses polymerized on a linear chain by glycosidic bonds, and they are highly crystalline due to intermolecular hydrogen bonds, resulting in high strength. These characteristics are expected to be utilized as fillers for polymeric materials.

PU is a multi-block copolymer composed of polyol oligomers and diisocyanate, and the combination of polyol and diisocyanate determines various mechanical properties. Therefore, PU is widely used in many fields such as foams, elastomers, coatings, and adhesives. Most of the PUs currently available on the market are derived from non-renewable petroleum resources and are non-biodegradable. However, with the growing awareness of environmental protection in recent years, **there is a strong demand for the use of sustainable materials and biodegradability for PUs**. However, the recent increase in awareness of environmental protection has led to a strong demand for the use of sustainable materials and biodegradability in PU. In this study, we aim to **develop an environmentally friendly high-performance PU by using cellulose, a typical biomass resource, as a filler to reinforce polyurethane with biodegradable polyols**. Cellulose is generally poorly dispersible in PU, and could not be applied to foam molding applications such as heat insulators and sponges. On the other hand, we have found that secondary modified cellulose based on **citrate-modified cellulose** (**CAC**, Fig. 1) disperses well in poly(propylene glycol) and is useful for improving PU performance (Fig. 2) [1] The modified cellulose acts as a reactive filler and forms **a good interfacial adhesion between CAC and the PU matrix**, which can make the composite material stronger. In this study, we utilize this knowledge to create high-performance biodegradable PU by selecting polyester polyols (poly(ε-caprolactone) (PCL) and poly(butylene adipate) (PBA)) to impart biodegradability to PU and developing cellulose fillers that are highly dispersible in polyester polyols. The cellulose filler forms potential physical and chemical cross-linking points in the PU matrix , which is expected to improve the performance of biodegradable PU. We believe that this research is significant as basic research for the creation and social implementation of PUs that contribute to decarbonization and the construction of a recycling-oriented society.

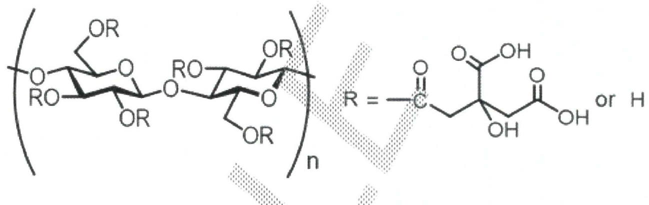


Fig. 1: Chemical structure of CAC

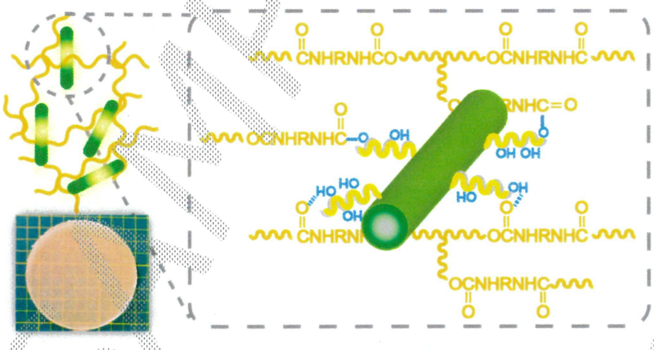


Fig. 2: Schematic of cross-linked structure by oligomers grafted from the surface of cellulose fibers

Reference (Please fill in if there are special notes regarding reference materials and preparation status related to this research)

[1] X. Cui *et al.*, *Compos. Sci. Technol.*, **2021**, *202*, 108595

Outline of the research plan (Please fill in documents, figures, graphs, etc. within one page. If the limit of page is exceeded, the application will not be selected.)

In order to develop high performance biodegradable polyurethane composites, the **key is to form a good interfacial adhesion between cellulose and polyurethane matrix**. In this study, we investigate (1) the development of highly dispersed polyester polyol modified cellulose fillers and (2) the synthesis and characterization of biodegradable PU reinforced with cellulose fillers.

(1) Development of highly dispersed polyester polyol modified cellulose filler

We have already established a technology to control the amount of carboxylic acid on the surface of CAC and the cellulose diameter by understanding the material such as grinders (Fig. 3). We have also developed a secondary modified cellulose with a large number of highly reactive hydroxyl groups by grafting glycidol and other substances from the carboxylic acid on the CAC surface. In this study, we will utilize these findings to develop cellulose fillers dispersed in polyester polyols (PCL and PBA). The dispersibility in polyester polyol will be evaluated using the amount of citric acid introduced, fiber diameter, and, if necessary, glycidol grafting as parameters. Fiber diameter was reduced to 500 nm by grinder treatment (Fig. 4, CACNF), which is expected to improve dispersibility in polyol. These findings will be correlated with the results of study item (2) and fed back to filler development.

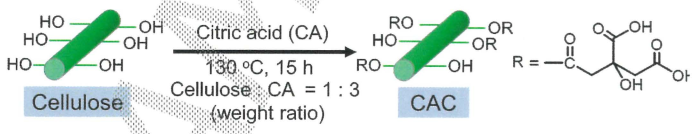


Fig. 3: Scheme for synthesis of CAC

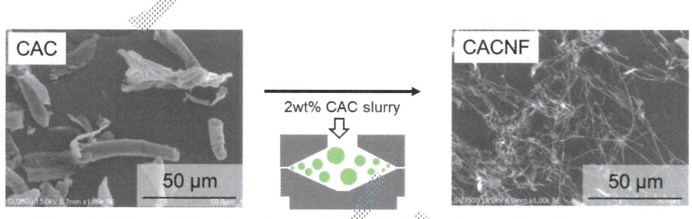


Fig. 4: Nanofiberization of CAC by micronization process

(2) Synthesis and characterization of biodegradable PU reinforced with cellulose filler

Cellulose filler reinforced biodegradable PU is synthesized by adding diisocyanate to PCL or PBA dispersed with modified cellulose prepared in (1). Toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), and hexamethylene diisocyanate (HDI), which are typical industrial products, are used as diisocyanates. Mainly TDI is used, and samples are prepared by varying the polyol addition ratio, filler addition amount, presence and amount of catalyst (tin-based), and reaction temperature and time. The samples are formed into film shapes, and their mechanical strength is evaluated by tensile testing, and their thermal properties and heat resistance are also examined by DSC and TG/DTA. The effect of filler addition is evaluated by dynamic viscoelasticity, and filler dispersion in PU is evaluated by SEM. These are comprehensively evaluated to optimize the composition and synthesis conditions of biodegradable PU composites. Next, the enzymatic (lipase) degradability of the PU film is evaluated as a preliminary assessment of biodegradability. The effect of diisocyanate structure on degradability will be investigated based on the difference between aromatic (TDI, MDI) and aliphatic (HDI) diisocyanates. Next, biodegradable PU foams will be prepared by water addition. Referring to the results of film production, the reaction conditions, especially the foaming conditions, will be screened based on the amount of water added, etc. As a preliminary study, we have found that the addition of CAC improves tensile strength in PCL/HDI systems, and we will use that result as a basis. In addition, morphology observation confirms the improvement of the interface structure between cellulose fibers and PU matrix. In particular, this is assumed to be based on the interaction between the carboxylic acid groups on the CAC surface and the polyester polyol, which will also be verified in this study. Based on these observations, **a material design that improves the interfacial affinity between the PU matrix and the cellulose filler will be established to create an interface with controllable physicochemical properties for the development of high-performance biodegradable polyurethane composites.**

Required amount of research expenses

Fiscal 2023	Item	Budget (US$)
Research Expense	Facilities and equipment	
	Supplies	
	Raw Material	
	Transportation and accommodation	
	Others	
	Total	
Contents of equipment (Please describe the equipment and its specifications)		

Results of research activity and current activity status
(You can add one more page if necessary)

Representative applicant for research grant
Organization:
Name:

1. Results of past research activities
Prizes awarded by scientific societies and associations
(Prize name and date of award)

2. Current research activities
(1) Research reports (Journal name (year of publication), volume and page)
Note: Write in reverse chronological order

(2) Oral presentation (Name of Society, the venue and date of presentation)
Note: It excludes presentations by commercial organizations other than academic societies

(2) Membership organization name
(Ex. Kanto branch secretary, Japan Rubber Association)