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## 論文の内容の要旨

Most of the plastics produced in the world are petroleum-based ones. Since they are used for thermal recycle after processing, petroleum resources are being consumed at an ever-increasing rate. Against this backdrop, the use of biomass plastics, which are abundant in resources and are renewable, as an alternative to petroleum-based plastics, is progressing. Existing plastics have excellent mechanical properties and durability compared to biomass-based plastics. Therefore biomass-based plastics have not been substituted because of their lack of stability, which is inherent for biomass-based materials in general. In order to eliminate these disadvantages and make significant progress in substitution, a great deal of research has been conducted in the plastics industry. For example, cellulose, known as the most abundant resource on the earth, is modified to provide, good mechanical properties and high heat resistance. In particular esterification and etherification provided commercially success materials. In addition, poly(lactic acid) (PLA) has been developed from biomass-based materials, which is currently one of the most famous biomass-based plastics.

In this study, a great effort has been paid for cellulose acetate (CA), one of the most popular cellulose derivatives, to provide thermos-processability by addition of a plasticizer. Moreover, considering the impact on the environment, citrate ester, which is also known as a biomass-based materials, was employed. Before rheological measurements, various citrate esters were blended with CA and their compatibility was evaluated. Among the citric acid esters employed, triethyl citrate (TEC), which has the shortest alkyl chain, showed excellent miscibility with CA. 40 wt.% TEC can be added to CA without bleed-out. The temperature dependence of the dynamic tensile modulus indicated that TEC had no ability to dissolve CA crystals. However, melt extrusion was possible at 205 °C, and the obtained products showed smooth surface without unstable flow even at high shear rates. The uniaxial elongational viscosity was measured and strain hardening was detected. This is because crystals remained in the sample at the measured temperature, which acted as a pseudo-branch point. It indicates the plasticized CA with, TEC exhibits good melt-processability.

Another type of cellulose esters was also used to modify the rheological properties of PLA in this study. PLA has attracted particular attention among biomass-based plastics. It is produced by fermentation and synthesis of starch and has advantages such as biodegradability and lower CO<sub>2</sub> emissions during production and combustion compared to commodity plastics. However, it has disadvantages such as slow crystallization, low melt elasticity, and limited molding and processing methods due to the lack of long-chain branching in its structure. Therefore, its substitution from conventional plastics has not progressed significantly. I attempted to modify PLA to solve these disadvantages by

blending CAP, a commercially available cellulose derivative. For miscible systems, strain-hardening can be imparted by blending a long-chain branched polymer. Although PLA/CAP is an incompatible system, the temperature dependence of the dynamic tensile modulus showed that the glass transition temperature ( $T_g$ ) of PLA shifted to higher temperatures with increasing the CAP content. It suggested that some of the CAP chains are dissolved into the amorphous region of PLA. Moreover, the frequency dependence of oscillatory shear moduli at various temperature revealed that CAP showed thermos-rheological complexity. This could be attributed to the crystallinity of CAP; a similar phenomenon was observed for PLA/CAP. As a result, the viscosity increased greatly at low temperature because some of the CAP chains were dissolved in PLA. During uniaxial elongational flow, PLA does not show strain-hardening in transient viscosity. However, by blending CAP, strain hardening was observed. During elongational flow, CAP dispersion was found to be undeformed. The result indicated that strain-hardening was provided by the dissolved CAP chains in PLA, which have pseudo-branch points due to the presence of crystals. Extrusion processability was found to be good for the blends. Therefore, CAP, which is derived from biomass, is an appropriate modifier to improve the processability of PLA.

Keywords: Cellulose derived, Biomass-based plasticizer, Elongational viscosity, Rheological properties

## 論文審査の結果の要旨

本論文は、セルロース誘導体を用いたバイオプラスチックのレオロジー改質に関する内容であり、具体的には、(1) 熱可塑性を示さないセルロース・アセテート (CA) にバイオマスベースの可塑剤であるクエン酸トリエチル (TEC) を添加して熱可塑性を付与する研究と、(2) セルロース・アセテート・プロピオネート (CAP) によりポリ乳酸 (PLA) の流動特性を制御する研究から構成されている。

まず、CA と TEC の系では、バイオマス可塑剤である TEC が CA に優れた混和性を示し、その濃度が 40 重量%に至ってもブリードアウトするなどの現象が観測されないことを明らかにした。さらに、TEC が 40 重量%添加された試料は良好な熱可塑性を示し、熔融押出加工が可能となる。これまでの CA では不可能であった成形加工方法であり、汎用性が高い。また、TEC の添加は CA の結晶性を大きく阻害しない。その結果、成形温度で系は長鎖分岐高分子のレオロジー特性を示し、伸長粘度のひずみ硬化性が顕在化する。このレオロジー特性により、フィルム成形時の厚みムラや幅方向の収縮が大幅に抑えられることが明らかになった。

PLA と CAP の系では、これまで両ポリマーは非相溶系であると報告されていたが、低分子量の CAP を用いることで、その一部が PLA に分子レベルで溶解することを初めて明らかにした。また、CAP にはわずかな結晶が成形加工温度でも存在し、PLA 中に溶解した CAP は長鎖分岐高分子としてのレオロジー特性を示す。その結果、PLA では観測されない伸長粘度のひずみ硬化性を示すことになる。もちろん、熔融押出加工性の向上が期待される。このように、熔融成形の加工温度域で結晶性を示す高分子を成形加工改質剤として利用する報告はこれまでに行われたことがなく、新規な知見である。この知見は他のポリマーへの応用も期待できる。

以上、石油由来の樹脂の使用量削減が求められる中、CA の熱可塑性や PLA の成形加工改質に関する関心は高く、本論文の内容は社会的ニーズに応える研究成果である。

また、本論文は、セルロース系樹脂の結晶を利用したレオロジー特性の改質について研究したものであり、学術的に貢献するところも大きい。よって博士 (マテリアルサイエンス) の学位論文として十分価値あるものと認めた。