

論文 / 著書情報
Article / Book Information

題目(和文)	PMMA / PVDF ブレンドにおける新奇微細構造の可視化とその形成メカニズムに関する研究
Title(English)	
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学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

(博士課程)
Doctoral Program

論文要旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	応用化学 応用化学	系 コース	申請学位 (専攻分野)： Academic Degree Requested	博士 Doctor of	(工学)
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要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words)

This doctoral thesis is entitled “A study on visualization of novel fine structures in PMMA/PVDF blends and their formation mechanisms” and is composed of six chapters.

In Chapter 1 entitled “Introduction,” the significance of polymer materials for a sustainable society in the future is first mentioned. Next, the importance of polymer composites for multifunctionality and high performance is explained. Then, the followings are further described: the key function of these polymer materials is thermal melting property, and the effectiveness of using “miscible amorphous/crystalline polymer blends” to control this property; the polymethyl methacrylate (PMMA)/ polyvinylidene fluoride (PVDF) blends are representative of these polymer blends.

In Chapter 2 entitled “Various properties of miscible polymer blends and PVDF, and their characterization methods,” the specific properties of miscible polymer blends are mentioned at first. Specifically, the melting point depression of crystalline polymers in miscible amorphous/crystalline polymer blends and the interaction between PMMA and PVDF are explained in detail with methods of its characterization. In addition, the polymerization process, and physical properties of PVDF, which dominantly change the physical properties of PMMA/PVDF blends, are described. Finally, two methods of characterization for polymer materials that feature in this study, electron microscopy and atomic force microscopy (AFM), are explained in detail.

In Chapter 3 entitled “Visualization of novel fine structures in various PMMA/PVDF blends,” two novel fine structures visualized by low-voltage transmission electron microscopy (LV-STEM) are discussed in relation to thermal properties and chemical interactions. The first structure is a nano-scale phase-separated structure composed of PVDF crystal domains and PMMA matrix in solution-casting blends, where the PVDF crystal domains have a size of approximately 200 nm, which can be described as a single molecule scale. This structure enables us to understand the melting point depression phenomenon from a morphological point of view, which has been previously understood only from thermodynamics. In concrete, the size of interface between the PVDF crystal domains and the PMMA matrix are related to the degree of melting point depression. It is also found that the low temperature melting components, which has been observed in previous studies are derived from the ultrafine PVDF crystals. The second structure is the “discrete random coil structure” in melt-mixing blends, in which the matrix is a mixture of amorphous PVDF and PMMA, and the PVDF molecules exist as random coils of approximately 300 nm in diameter containing PMMA molecules. This structure is also observed in blends that are quenched immediately after melt-mixing, so it can determine that the “miscible state of PMMA and PVDF” is visualized.

In Chapter 4 entitled “Investigation of crystallization behavior by thermal annealing of melt-mixing blends,” the crystallization of PVDF by thermal annealing is visualized and discussed in relation to their crystal structures. In the experiment, two PVDF resins prepared by emulsion polymerization and suspension polymerization are used to estimate the formation mechanism of “discrete random coil structure.” Due to the difference of polymerization method, the PVDF from the emulsion polymerization exhibits a higher β -crystal ratio and a higher quantity of molecular defects than the PVDF from the suspension polymerization. The PVDF used in Chapter 3 is from the emulsion polymerization method. From the result of experiment, the “discrete random coil structure” is not observed in the blends using PVDF from the suspension polymerization, and it is clear that the difference in the variety of PVDF is the dominant factor for the structure formation. From the discussion based on some of the other results, the formation mechanism of the “discrete random coil structure” is finally proposed as follows. The high β -crystal ratio or a high quantity of molecular defects of PVDF causes poor miscibility of PVDF and PMMA, which in turn forms structure. In addition, both two PVDFs formed peculiarly curved β -crystals after thermal annealing. On the other hand, a characteristic liner shape α -crystals are formed in the blends using PVDF from suspension polymerization.

In Chapter 5 entitled “Visualization of melting/crystallization behavior by In-situ AFM measurements,” in-situ AFM modulus mapping is performed using a heat stage to further understand the “discrete random coil structure.” The methods of quantitative temperature control and quantitative elastic modulus calculation, which are usually difficult in in-situ measurements, are described in detail. As a result of the measurements, the co-existence of random coils and curved β -crystals after thermal annealing, which could not be visualized by LV-STEM are observed. In addition, the crystallization of PVDF is also observed during the in-situ measurement, together with this result, it is revealed that the crystallization from

the “discrete random coil structure” progresses from the matrix region.

In Chapter 6 entitled “Conclusion,” this thesis is summarized, and future prospects are described.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note: Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1 copy of 800 Words (English).

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