



Original Research Paper

Novel method of the surface modification of the microcrystalline cellulose powder with poly(isobutyl vinyl ether) using mechanochemical polymerization



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ABSTRACT

The surface modification of microcrystalline cellulose (MCC) powder with poly(isobutyl vinyl ether) (PIBVE) chains of block copolymers of MCC and PIBVE (MCC-block-PIBVE) was produced by ball milling of MCC with isobutyl vinyl ether (IBVE) in vacuum at 77 K. The polymerization of IBVE was initiated by mechano-cations of MCC (MCC⁺) on the MCC powder surface in vacuum at 77 K. MCC⁺s located on the surface of MCC powder were produced by heterogeneous scissions of the β-1,4 glycosidic linkages comprising MCC main chain by ball milling in vacuum at 77 K, and existed on the powder surface of MCC in vacuum at 77 K as cations isolated from counter mechano-anions. The counterion-free MCC⁺s on the powder surface of MCC interacted with IBVE during milling, covalently bonded to IBVE, and simultaneously formed counterion-free cations (MCC-IBVE⁺) on the MCC powder surface. The counterion-free MCC-IBVE⁺s initiated a novel cationic polymerization of IBVE on the surface of MCC powder under vacuum, produced MCC-block-PIBVE, and gave rise to a surface chemical modification of MCC powder with MCC-block-PIBVE. This scheme is supported by ¹H NMR, FT-IR, ESR, GPC, and MO calculations.

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1. Introduction

A composite material is produced by mixing of polymeric material and filler; usually forming powder, to improve its physical property such as tensile strength. As the solid surface of powder plays a crucial role in dispersity in the composite material, in general, a surface modification of powder is carried out using various chemical compounds.

We have reported that a surface chemical modification of polymer powder was performed by production of a block copolymer on the powder surface using a mechanochemical polymerization in

vacuum at 77 K [1–16]. The mechanochemical polymerization was initiated by mechanoradicals which were produced by homogeneous bond scission of polymer main chain induced by ball milling. The growing polymers were covalently bonded to the surface, and resulted in block copolymers tethered on the surface. For example, the surface modification of polytetrafluoroethylene (PTFE) powder with poly(methyl methacrylate) (PMMA), i.e., the production of block copolymer composed of PTFE and PMMA (PTFE-block-PMMA) was performed by mechanical fracture of PTFE with poly(methyl methacrylate) (MMA) in vacuum at 77 K [1,8,10]. Furthermore, the block copolymer of microcrystalline cellulose (MCC) and PMMA (MCC-block-PMMA) was produced by the mechanochemical polymerization of MMA initiated by MCC mechano radicals which were induced by ball milling of MCC in vacuum at 77 K [16]. The surface modification by the block copolymer produced by mechanochemical polymerization has the advantage that a functional group located on the surface is not needed for bonding between polymer chain and the surface. However, a production of block copolymer, i.e., a surface modification by

Abbreviations: DFT, density functional theory; ESR, electron spin resonance; FT-IR, Fourier transform infrared; IBVE, isobutyl vinyl ether; MCC, Microcrystalline cellulose; MCC⁺, MCC mechanocation; MCC-block-PIBVE, block copolymer of MCC and PIBVE; MCC-IBVE⁺, counterion-free cation; MCCTA-block-IPBVE, acetylated MCC-block-IPBVE; ¹H NMR, ¹H nuclear magnetic resonance; PIBVE, poly(isobutyl vinyl ether); TMS, tetramethylsilane; XPS, X-ray photoelectron spectroscopy.

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mechanochemical polymerization is limited to a monomer which can progress through a radical polymerization.

To increase diversity of surface modification, a cationic monomer may be used in the polymerization of block copolymer on the surface.

Conventional cationic polymerization of vinyl compound has been achieved by various initiating systems in organic solvents based on carbocations stabilized through nucleophilic interactions. The initiating system involves the combination of counterions such as protonic acids and weak Lewis acids [17–20]. This system generates an initiating species composed of a counterion, and proceeds by the propagation of the growing species. Therefore, the conventional cationic polymerization produces a homopolymer having a highly controlled molecular weight with a narrow distribution. However, this conventional cationic polymerization cannot produce block copolymers due to a counter ion.

On the other hand, we have reported that the mechanical fracture of polymers under vacuum at 77 K induced heterogeneous bond scission of covalent bonds comprising the polymer main chain and simultaneously formed pair of chain-end-type anions (mechano-anion) and cations (mechano-cations) on the powder surface of polymers [21–26], and the yield of heterogeneous bond scission (ionic scission) was dependent on the ionic degree of the covalent bond [27–29]. For example, Fig. 1 shows pair formations of mechano-anions and mechano-cations of MCC by ball milling in vacuum at 77 K. These mechano-ions are produced by the heterogeneous scission of β -1,4 glycosidic linkages that comprise the main chain of MCC, and are trapped on the powder surface of the MCC. The yield of ionic scission of MCC under vacuum at 77 K was 0.692 ± 0.005 [29].

Herein, we show that a novel mechanochemical cationic polymerization of IBVE on the surface of MCC powder in vacuum at

77 K is initiated by MCC mechano-cations which are produced by mechanical scission of MCC main chain. The MCC mechano-cations are isolated from counter anion (counterion-free) and located on the surface of MCC powder in vacuum, and proceeds cationic polymerization of IBVE on the surface of MCC powder in vacuum at 77 K. This process produces MCC-block-PIBVE, and gives surface modification of MCC powders with PIBVE chains of MCC-block-PIBVE.

2. Material and method

2.1. Mechanical fracture of MCC

MCC (1.486 g, 9.17×10^{-3} mol, Aldrich) was added to a glass ball mill [30] equipped with an electron spin resonance (ESR) sample tube. The sample was dried at 0.6 Pa at 373 K for 6 h using a glass vacuum line. The glass ball mill was sealed off from the vacuum line by melting and placed in a Dewar flask filled with liquid nitrogen. The MCC in the glass ball mill was mechanically fractured using a homemade vibration glass ball mill apparatus [30] for 23 h at 77 K in vacuum. We carried out the mechanical fracture of MCC in vacuum at 77 K to avoid a side reaction forming peroxide radical or decaying chemical species.

After milling, the fractured MCC powder was dropped into the ESR sample tube attached to the top of the glass ball mill by quickly inverting the glass ball mill in liquid nitrogen.

2.2. Mechanochemical synthesis of MCC-block-PIBVE

MCC (1.486 g, 9.17×10^{-3} mol) in the glass ball mill was dried at 373 K for 6 h under vacuum at 0.6 Pa using the vacuum line. The

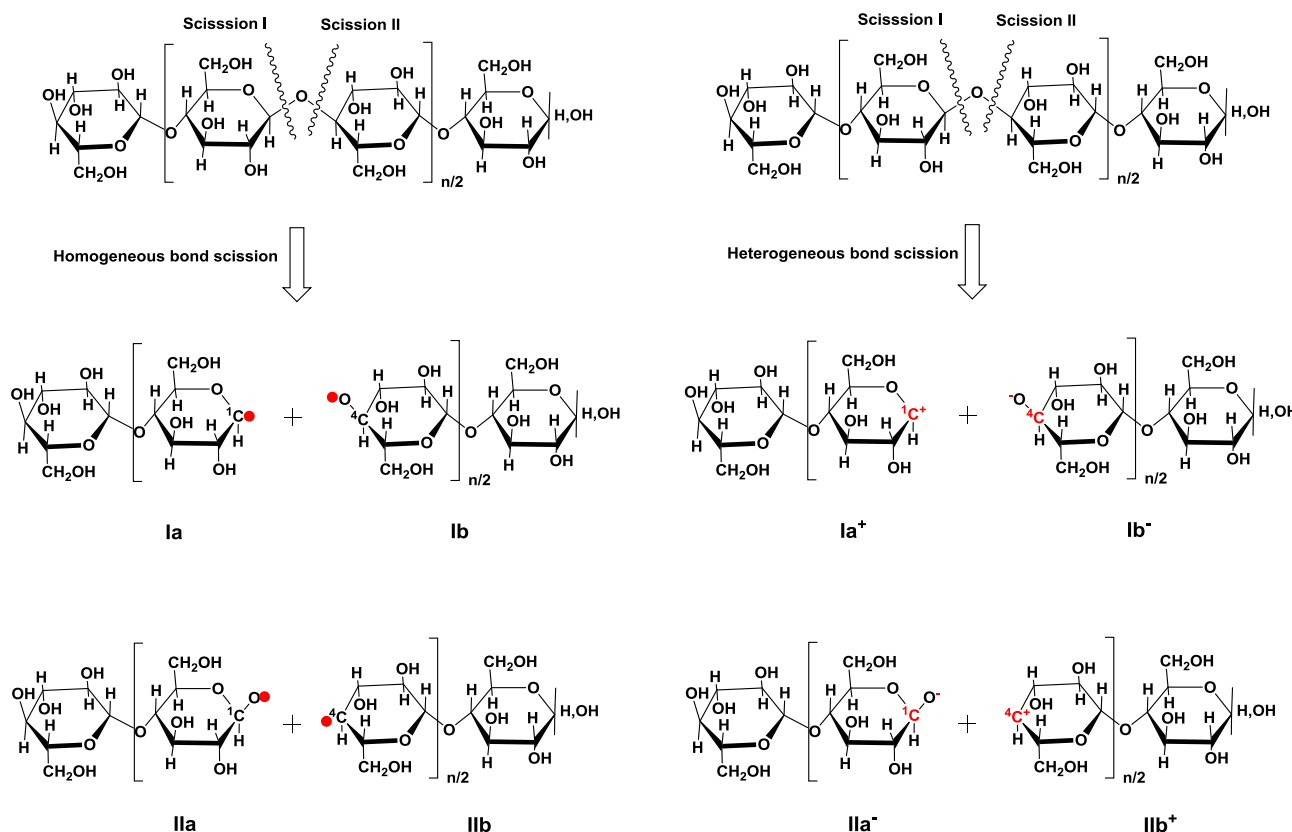


Fig. 1. Mechano-cations (MCC-Ia⁺ and MCC-Ib⁺) and mechano-anions (MCC-IIa⁻ and MCC-IIb⁻) are produced by the heterogeneous bond scission of β -1,4 glycosidic linkage of MCC induced by ball milling in vacuum at 77 K.

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