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Evaluation of the temperature and molecular weight dependent migration of di(2-ethylhexyl) phthalate from isotactic polypropylene composites

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ABSTRACT

The development of a process for the bioremediation of di(2-ethylhexyl) phthalate (DEHP) blended in various polymers, with a low DEHP release rate, has become an essential mission in the packaging materials industry, especially for blood-component storage materials. Hence, polypropylene and DEHP composites were prepared to evaluate their DEHP release behavior at 90 °C and 25 °C. The physical and chemical properties of the composites were evaluated with various analytical tools. Polypropylene of three different molecular weights was used to compare the different DEHP releasing rates. The incorporation and migration of DEHP significantly followed the crystalline nature of the polymer matrix. The temperature-dependent migration behavior was evaluated by UV–Vis spectroscopy and LC/MS analyses. Among the three different molecular weight PP/DEHP composites, a significantly lower amount of DEHP was released from the higher molecular weight polymer composite due to its enriched crystalline nature. Moreover, the release behavior of DEHP was affected by the molecular weight and crystalline nature of PP, which can strongly hold the plasticizer, and therefore slow down its release. The high molecular weight iPP/DEHP composite may be suitable for blood-component backing materials because of its lower DEHP migration.

1. Introduction

In the packaging industry, the use of active packaging materials is an effective approach to sustain the quality of products during prolonged shelf times; the ecological interaction, or improved safety [1]. Therefore, although a variety of active packaging strategies have been demonstrated to be of affordable quality, wholesome, and safe, their application has been limited due to their package-related environmental pollution and disposal problems [2]. For example, the packaging materials used in disposable blood bags are used for the collection, storage, transportation, and transfusion of human blood and blood components. In this regard, plasticized poly(vinyl chloride) (PVC) is one of the most widely used materials in blood bags, however it does not have good handling characteristics, and lacks indispensable properties for the survival of red blood cells [3]. In addition, most PVC-containing medical products slowly liberate free chlorine, chlorine species (including phosgene), and dioxins, all of which are associated with carcinogenicity and other potential toxicities. Consequently, minimizing the use of PVC would result in a lower exposure to potential toxicities.

Research into the fabrication of single-use packaging materials that do not elute offensive effluents for medical applications has become an emerging field for health-care storage applications. Some thermoplastic elastomers (TPE) that have been most commonly used as substitutes of PVC include ethylvinylacetate (EVA), polyolefins, polyurethanes (PU), and fluoropolymers [4]. However, most of these plastics are not effective for the preparation of proficient packaging materials, and therefore required other additives such as plasticizers, antioxidants, or stabilizers to improve their properties without additional risks [5].

In order to produce plastics with a desired flexibility, plasticizers have long been used in various fields ranging from the automotive industry to health-care and consumer products [6]. Di-(2-ethylhexyl) phthalate (DEHP) was reported to be the most used plasticizer in PVC to endow it with flexibility [7]. However, leached DEHP was found in PVC/DEHP containers, causing toxic effects in humans. DEHP can easily enter the body through different pathways such as the skin, intestine, and other tissues due to their lipophilic nature [8]. The introduction of DEHP in the human body may cause cancer and generate endocrine

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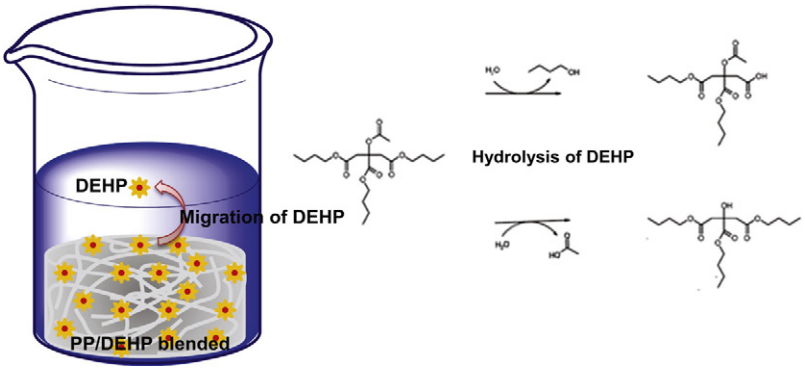

Fig. 1. Migration assay of DEHP and its hydrolysis process.

effects, particularly in young males. In order to avoid DEHP consumption, various methods have been applied to produce an appropriate DEHP substitute in blood components bags [9–10]. In this respect, the selection of an appropriate polymer matrix may be an important factor for reducing the migration of DEHP active agents. The development of a semi-crystalline polymer matrix based on new composite materials may be suitable for the reduction of the active agents. In this regard, polypropylene (PP) is an ideal material due to its chemically resistant nature, excellent mechanical properties, and easy processing. Hence, DEHP embedded in a PP matrix could minimize DEHP leaching due to the structure of the composite, and therefore could improve the mechanical and barrier properties of the polymer matrix.

In this study, a novel PP/DEHP composite was synthesized to evaluate the migration behavior of DEHP from a polymer composite matrix. In order to evaluate the DEHP migration, three different molecular weights of PP were used at two different temperatures, and they were compared through the influence of their crystalline domains. The migration of DEHP was affected by the molecular weight and crystalline nature of PP. Furthermore, the physical properties of the blend can be improve blood-component bag materials through their degree of crystallinity and controlled DEHP migration, which may play a vital role in blood compatibility.

2. Experimental

2.1. Materials

Polypropylene with various molecular weights such as amorphous polypropylene (aPP) with an average Mw of ~14,000 and an average Mn of ~3700; isotactic polypropylene (iPP12) with an average Mw ~ 12,000 and an average Mn ~ 5000; and isotactic polypropylene (iPP250) with an average Mw ~ 250,000 and average Mn ~ 67,000 were purchased from Sigma-Aldrich, Taiwan. Di(2-ethylhexyl) phthalate (DEHP) was purchased from Acros-Organics, Taiwan.

2.2. PP/DEHP blend

In order to prepare the PP/DEHP composites, a calculated amount of DEHP was introduced into the PP matrix using a melt blend. First, DEHP was added to PP to a concentration of 30% (w/w), and then the PP/DEHP blend was mixed by melt blending at 180 °C for 8 h. The melt-blended samples were cooled to room temperature for further experiments.

2.3. DEHP migration assay design

To evaluate the DEHP migration analysis, the PP/DEHP blended samples were added to an aqueous solution, and then they were extracted at two different temperatures (25 °C and 90 °C). As mentioned in Fig. 1, the DEHP extractions occurred through the hydrolysis of DEHP.

2.4. Characterization

Fourier transform infrared (FTIR) spectra of the composites were recorded on a Nicolet 6700 (Thermo Scientific) FT-IR spectrometer. The morphology of the composites was characterized using an FE-SEM with a JSM 6330F (JEOL). The PP/DEHP composite was characterized by wide-angle X-ray diffraction (WAXD) with a Bruker AXS D2 Phaser type X-ray diffractometer. A Perkin Elmer Pyris differential scanning calorimeter, equipped with an intra-cooler, was used to determine the melting and crystallization temperature of the PP/DEHP blend. Furthermore, a Jasco V-670 Ultraviolet-Visible spectrometer was used to evaluate the DEHP migration assay.

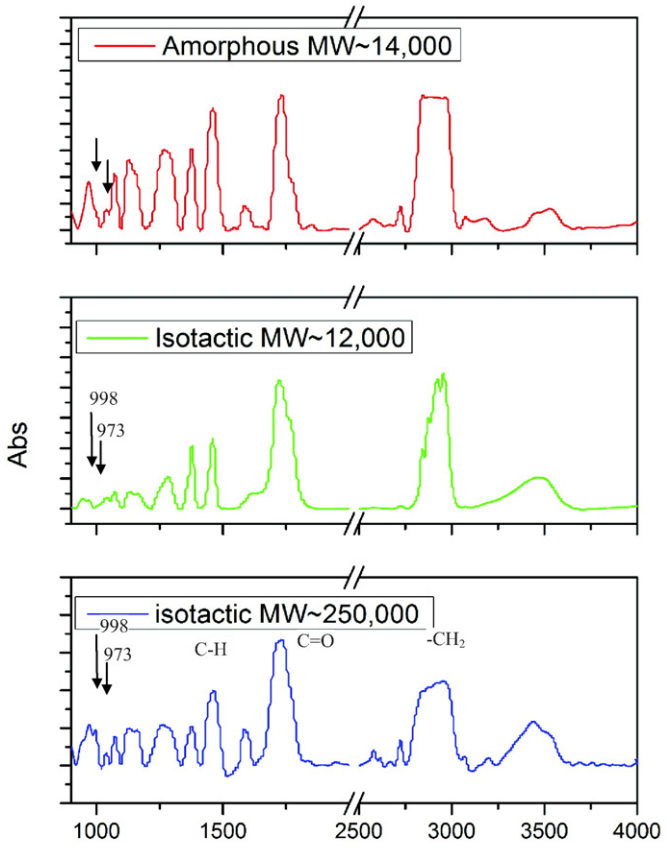

Fig. 2. FT-IR spectroscopy evidence for iPP/DEHP composites.