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Pervaporation-aided Esterification of Trifluoethanol with Methacrylic Acid through New Acid-resistant PVA Membrane

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INTRODUCTION

Pervaporation-combined esterification is an important field of the membrane reactor [1], in which pervaporation membranes with dehydration property are adopted to allow selective permeation of water, i.e., by-product, from reaction mixtures and thus, highly enhance the conversion of thermodynamically limited esterification [2-6]. The above pervaporation membranes have been mainly prepared by a crosslinking reaction of PVA with dialdehyde, diisocyante and diacid. However, they show poor stability under acid conditions due to the presence of unstable functional groups like acetals, urethanes and esters.

In this study, newly crosslinked PVA membranes were prepared via crosslinking between PVA and ethylene glycol diglycidyl ether (EGDE). The basic pervaporation properties of the PVA membranes crosslinked with different EGDE contents were investigated for TFEA/water and MA/water, and pure TFEMA, respectively. The esterification reaction of TFEA with MA using the PVA membrane was investigated with three main parameters - initial molar ratio of TFEA/MA, reaction temperature and catalyst content - at a fixed ratio of membrane area to reactant volume.

EXPERIMENTAL

For the membrane preparation, PVA/EGDE aqueous solutions were cast and thermally crosslinked to produce acid-resistant polymer networks connected with chemically stable alkyl chains and ether groups. ATR/IR and DSC observations and swelling test were used to characterize PVA membranes prepared with various contents of EGDE. The basic pervaporation properties of the membranes were investigated with TFEA/water, MA/water and pure TFEMA by varying EGDE content and operating temperature. The esterification reaction of TFEA with MA using the PVA membranes was also carried out at a fixed reaction mixture volume and the effect of reaction temperature, catalyst content and initial molar ratio of TFEA/MA on the TFEMA conversion was investigated.

RESULTS AND DISCUSSION

New acid-resistant PVA membranes crosslinked with different EGDE contents were prepared for the application to pervaporation membrane reactors. The esterification of TFEMA using TFEA and MA in the presence of sulfuric acid was used as a reaction model. The ATR-IR, DSC and swelling degree measurements confirmed that the PVA membranes were crosslinked with ether groups (C-O-C) and the

crosslinking density of the membranes increased with the EGDE content. The swelling degree of the PVA membranes in TFEA increased with increasing the EGDE content in the reaction solution due to the enhanced affinity between TFEA and the membranes. Pervaporation experiments showed that the permeation flux increased and the separation factor decreased with higher EGDE content due to the enhanced miscibility of the membranes toward TFEA. The esterification experiment of TFEA with MA was performed using the PVA membrane crosslinked with 2 wt% EGDE and it was found that the TFEMA conversion for pervaporation-esterification increased with increasing reaction temperature, amount of sulfuric acid and initial molar ratio. The highest conversion to TFEMA was about 90% at following reaction conditions; reaction temperature 90℃, an amount of catalyst 2.5 wt% and initial molar ratio 1.7.

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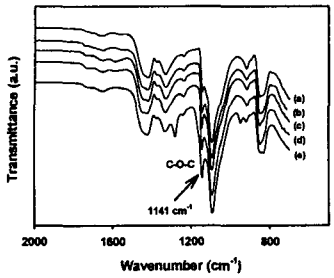

Fig. 1. ATR-IR spectra of PVA membranes crosslinked with different EGDE contents: (a) PVA, (b) 2 wt% EGDE, (c) 5 wt% EGDE, (d) 10 wt% EGDE, (e) 20 wt% EGDE.

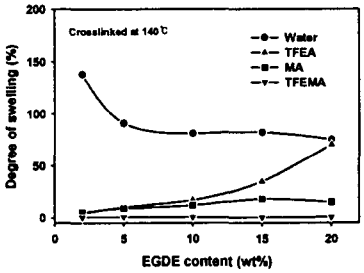

Fig. 2. The degree of swelling of the PVA membranes on the four components of esterification

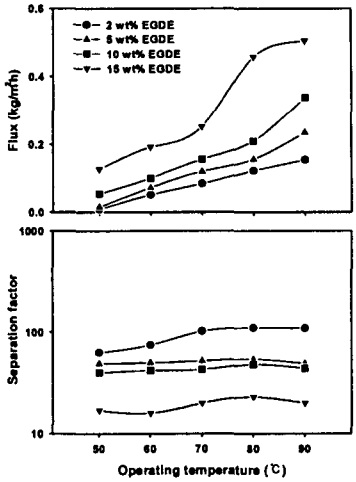

Fig. 3. Effect of operating temperature on pervaporation performance of PVA membranes crosslinked with different EGDE contents in a 96 wt% aqueous TFEA solution.

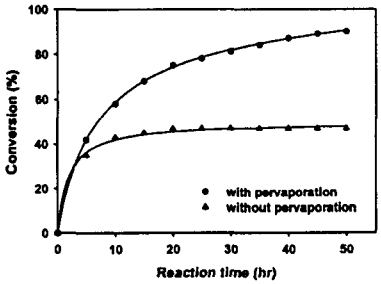

Fig. 4. Effect of pervaporation on conversion to TFEMA (T=90℃, R_0=1.7, C_{cat}=2.5 wt%, S/V=55 m^{-1}).