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Separation of n-hexane/acetone mixtures by pervaporation using high density polyethylene/ethylene propylene diene terpolymer rubber blend membranes

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ABSTRACT

Polymer membranes were prepared by blending high density polyethylene (HDPE) with ethylene propylene diene terpolymer rubber (EPDM). These blend membranes were evaluated for the selective separation of n-hexane from acetone. The flux and selectivity of the membranes were determined both as a function of the blend composition and feed mixture composition. Results showed that polymer blending method could be very useful to develop new membranes with improved selectivity. Pervaporation properties could be optimized by adjusting the blend composition. The effects of blend ratio, feed composition, and penetrant size on the pervaporation process were analyzed. The permeation properties have been explained on the basis of interaction between the membrane and solvents and blend morphology. Flux increases with increasing alkane content in the feed composition.

1. Introduction

Separation of organic–organic mixtures using membrane separation technique is being investigated extensively owing to its great importance in chemical and petrochemical industries. Pervaporation (PV) is an energy-efficient membrane separation process, which has gained acceptance by chemical industries over the years because of its favourable economics, easy maintenance, and simplicity of the process [1–7]. The pervaporation process can be defined as a selective evaporation of a liquid mixture through a dense polymeric membrane. This method is applicable for the separation of azeotropic mixtures which are difficult to be separated by distillation, extraction of aromatic compounds from dilute solutions, separation of close boiling liquids, recovery of dissolved substances and the separation of organic–organic mixtures. High permeability, good selectivity, and stability are the important factors in choosing a suitable pervaporation membrane [8].

Pervaporation is defined as the selective evaporation of a component from liquid mixture through a membrane. In pervaporation, the liquid mixture to be separated is in direct contact with a membrane on one side and the permeated product is removed as vapor from the other side by applying a low pressure. Unlike other membrane separation processes, pervaporation involves a phase change of permeating species from the liquid to the vapor state. The mass transfer in a PV membrane is based on a solution-diffusion mechanism. The solution-diffusion mass transport involves three steps: (1) sorption of permeant from the feed liquid to the membrane; (2) diffusion of the permeant in the membrane; and (3) desorption of the permeant to the vapor phase on the downstream side of the membrane. The sorption and diffusion are considered as the rate-determining step of the mass transfer.

In recent years, there has been increased interest in the use of the pervaporation membrane separation process for the separation of organic liquid mixtures. Many researchers reported on the separation of binary liquid mixtures by this technique. Sinha et al. [2] reported the use of chemically modified polyvinyl alcohol membranes for the separation of methanol from its mixtures with toluene over the concentration range of 0.5–20 wt % methanol. Mixed matrix membranes based on chitosan and silicalites were used to separate toluene from its mixtures with methanol [9]. Both Polydimethyl siloxane(PDMS) as well as Polyoctylmethyl siloxane (POMS) membranes were applied for the pervaporation of industrial wastewater containing toluene [11]. The pervaporation dehydration of water–ethanol mixtures was investigated using the mixed matrix membranes prepared from natural rubber and crosslinked poly (vinyl alcohol) semi-IPN embedded with the zeolite [10]. A comprehensive review of polymeric membranes

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for pervaporation was published by Shao and Huang [12]. They investigated the potential pervaporation had for separating liquid mixtures in the areas of alcohol and solvent dehydration, organic(s) removal from water and organic/organic separations.

Generally, homopolymer membranes could not meet the demand of pervaporation. Polymer blend membranes are promising materials that can overcome the major difficulties associated with homopolymer system in the pervaporation process. Polymeric blend membrane is of great interest because it is the most versatile way of achieving materials with new desirable properties and also the least expensive [13]. Polymer blends are considered as physical mixtures of two or more polymers. In polymer blends, the properties are controlled by the microstructure of the blends. Polymer blend membranes are extensively used in the pervaporation membrane field for obtaining high-performance [14–19]. High density polyethylene (HDPE)/ethylene propylene diene terpolymer rubber (EPDM) blend membranes possess very good properties. To the best of our knowledge, the use of HDPE/EPDM blend membranes for the pervaporation process has not yet been examined.

The main objective of this work is to develop a new polymer membrane based on the HDPE/EPDM blend for the selective separation of aliphatic hydrocarbons from alkane–acetone mixtures by pervaporation. The alkane/acetone mixture has been chosen to perform a basic study on the pervaporation process using the membrane. The separation efficiency has been evaluated as a function of blend ratio and feed composition.

2. Experimental

2.1. Materials

High density polyethylene (HDPE-Relene, M60 200) of density 932 kg m^{-3} and melt flow index 20 g/10 min (at 230 °C/2.16 kg) was obtained from Reliance Industries Ltd. Hazira Gujarat, India. EPDM with an *E*/*P* ratio of 62/38 and a diene content of 3.92% supplied by Herdillia Unimers, New Mumbai was used. The solvents n-pentane, n-hexane, n-heptane and acetone (Merck India, Ltd., Mumbai, India) were distilled twice before use. All other ingredients were of laboratory reagent grade, supplied by Bayer India, Ltd., Mumbai, India.

2.2. Preparation of membranes

The blends were prepared in a Brabender plasticorder by melt mixing of the components at 160 °C and a rotor speed of 60 rpm. HDPE was melted for 2 min and then EPDM was added. The mixing was continued for 5 min. Dynamically vulcanized blends were also prepared by using three different vulcanizing systems such as sulphur, peroxide (DCP) and a mixture of sulphur and peroxide (mixed). In the case of dynamically crosslinked blends, after blending HDPE with EPDM, the curing agents were added and mixing is continued for 3 min. Membranes were prepared by compression molding the melt mixed blends in a hydraulic press at 170 °C (at 200 kg/cm^2 pressure). The thin membranes thus obtained were used for pervaporation experiments. The average thickness of the membrane was 0.2 mm.

The binary blends with varying compositions are noted as H_{100}, H_{70}, H_{50}, H_{30} and H_0 where the subscripts denote the weight % of HDPE in the blend. The formulation of the mixes used is given in Table 1.

2.3. Phase morphology studies

Scanning electron microscope (JEOL JSM 35C) was used to study the phase morphology of blends. The compression-molded samples were cryogenically fractured under liquid nitrogen and the EPDM phase was preferentially extracted from the samples using cyclohexane at room temperature for 5 days. Fracture surface was sputter coated with gold in a sputter coating machine (Balzers SCD 050) for 150 s.

Table 1
Formulation of mixes in phr.[a]

Ingredients	HDPE/EPDM 50/50 blend (crosslinking systems)		
	Sulphur	Mixed	Peroxide
EPDM	50	50	50
HDPE	50	50	50
Stearic acid	2	2	–
Zinc oxide	5	5	–
MBTS[b]	0.05	0.05	–
TMTD[c]	0.1	0.1	–
Sulphur	0.2	0.1	–
DCP[d]	–	0.5	1

[a] Parts per hundred rubber.
[b] Dibenzothiazole disulphide.
[c] Tetramethyl thiuram disulphide.
[d] Dicumyl peroxide.

2.4. Swelling studies

The swelling behavior of the membranes was assessed by immersing them in mixtures of n-hexane and acetone of different compositions at 28 °C for 72 h. After reaching equilibrium, the membranes were taken out from the mixtures, their surfaces wiped with a filter paper, and then they were weighed immediately in an electronic balance. The swelling ratio (*S*) was determined as

$$S = \frac{W_s - W_d}{W_d} \quad (1)$$

where W_d and W_s are the weight of dry and swollen membranes, respectively.

2.5. Pervaporation experiments

The pervaporation experiments were performed using the apparatus shown in Fig. 1. The permeation cell was assembled from two half-cells of column couplers made of glass and fastened with bolted clamps. The capacity of each half cell was around 100 mL, and the effective surface area of the membrane was 19.4 cm^2. The membrane was supported on a finely porous stainless steel plate with holes drilled in it. Vacuum at the downstream side was measured with a vacuum gauge. The membrane was kept in the

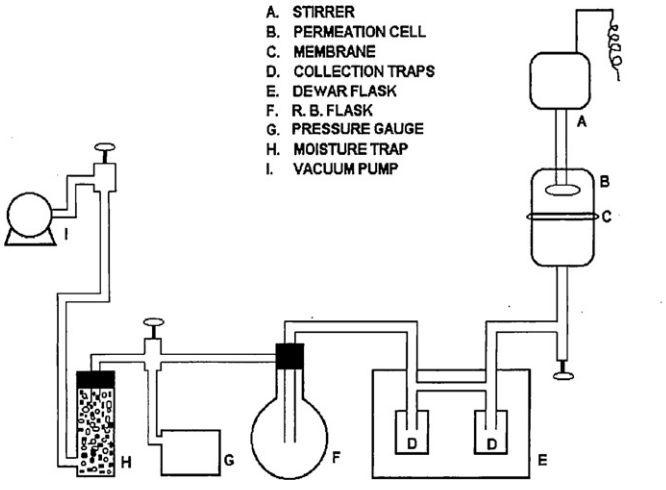

Fig. 1. Pervaporation apparatus.