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FULL LENGTH ARTICLE

Porous membrane modifier as a new trend for deoiling process

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Abstract Porous membranes are prepared through micro phase separation of immiscible polymers consisting of hydrophobic polymer (polystyrene) and hydrophilic polymer (poly(2-vinylpyridine)). The greatest difficulties during petrolatum deoiling are related to the filtration stage for obtaining microcrystalline wax. The present study deals with the addition of porous membrane as modifier for the crystal structure of solid hydrocarbons, which will be the cornerstone in rearrangement and reformulation of new hard crystals in deoiling process. XRD and SEM photographs were used to evaluate the crystallinity and crystal sizes of the separated hard waxes.

1. Introduction

Porous polymers have found use for numerous applications, such as foams, membranes, filters, chromatography media, and solid support. These materials have many useful properties including low density, good thermal and electric isolation, and high specific surface. Various methods have been investigated to produce such scaffolds with different porosity and surface structures, using a range of materials [1–3].

Poly (N-vinylpyridine) (PNVP) was selected as a membrane due to its strong polarity, which gives good compatibility with other polymers while avoiding unstable morphologies that give rise to poor mechanical properties [4–8]. Lu et al. [9] reported the exceptional water or methanol sorption selectivity of PVA/PNVP blends that implied PNVP seemed to be a potential material for preparing the membrane. Recently, PNVP has been used as a stabilizer to improve the oxidative and mechanical properties of the membranes [10]. These results show that PNVP's hydrophilic groups play an important role in controlling permeability.

Blends comprising water soluble and water insoluble polymers are known to give unique properties to the prepared membranes [11], by the solution casting technique. Polymer blends have ternary systems comprising the two polymers and the solvents are used to study the influence of their phase behavior on the properties of the blend. In this study we present a method for preparing porous polymer membranes with adjustable microstructures. This method is based on micro phase separation of polystyrene (PS) and polyvinyl pyrrolidone (PVP) polymer in order to form a three-dimensional network.

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Petroleum waxes were considered as by-products in the dewaxing of lubricating and gas oils. They were used as components of furnace residual fuel oil. Today they are available petroleum products. The commercial petroleum waxes may be divided into three principal groups: paraffin waxes, microcrystalline waxes and petrolatums. Microcrystalline waxes are microcrystalline products, solid at room temperature and usually produced from heavy petroleum distillates or residues or tank bottoms [12,13].

In solvent dewaxing and deoiling processes; the processes of manufacture and refining of petroleum waxes respectively; crystallization takes place from solution. The precipitation of wax crystals during cooling is a function of two important processes: crystal nucleation and crystal growth. Both of crystal nucleation and crystal growth characterize the crystallization phenomenon of waxy crudes [14].

Petrolatum separated from residual feedstock during the manufacture of lubricating oil; a by-product of the dewaxing process; usually contains from 20 to 50 wt.% oil. Refined petrolatums and microcrystalline waxes varying in properties can be produced by selective removal of the oil and low melting waxes from the petrolatum crude. The process is commonly called solvent deoiling or wax recrystallization process. The Wax recrystallization process is the most prevalent deoiling technique. It is sometimes called wax fractionation process and it is used for fractionating all types of crude waxes. Our previous studies revealed that some different grades of petroleum waxes can be produced by fractional crystallization of light, middle, heavy slack waxes and crude petrolatums at ambient temperature by using different solvents [15–18].

Commercial processes for dewaxing and deoiling residual feedstocks are complex and laborious. The greatest difficulties are related to the stage of filtering slurries of solid hydrocarbons that tend to form an intercrystalline structure. In improving processes for obtaining solid hydrocarbons, use is made of various additives that have a modifying effect on the structure of solid hydrocarbons. The effect of a modifier on the crystallization of solid hydrocarbons is usually rated on basis of the melting point and the oil content in the wax.

The present study deals with the addition of polymer modifier plays as a nucleus which will be the cornerstone in rearrangement and reformulation of new hard crystals in deoiling process. This will lead to minimize the deoiling solvent ratio, which is better in plant design and cost conservation.

2. Materials and methods

2.1. Materials

Polystyrene (PS), poly (2-vinylpyridine) (PVP) and toluene were all purchased from Sigma-Aldrich Company.

One appropriate crude petrolatum (petroleum wax by product) obtained from Suez Oil. Processing Company (Marine Belayim crude) used in this study for studying the effect of membrane in improving the deoiling process for separation of microcrystalline waxes.

2.2. Synthesis of porous membrane polymers

Polystyrene (PS) and poly(2-vinylpyridine) (PVP) represent a good binary mixture system for preparing porous membranes due to their high immiscibility, similar density (1.04 g/mL), and nearly matched repeat unit molecular weight (PS, 104 g/mol; PVP, 105 g/mol). Porous PS/PVP membranes were prepared using the phase separation process [1] by blending of 60/40 weight percents of PS and PVP respectively. Sufficient time was given for the polymers to dissolve (4 h) and then 5–10% (w/v) polymer solutions (PS 23.6 g, PVP 23.6 g and Toluene 150 ml) were prepared in toluene. Then the polymer solutions were cast uniformly onto glass plates with a 200 μm doctor blade, which was then annealed in an oven at 60, 70, 80, 90, 100, 110 and 120 °C at various time intervals as 5, 10, 20, .30, 40, 60, 70 and 120 min, and thereafter residual solvents were evacuated, the film was separated from the glass substrate by floating on water.

2.3. Isolation of micro-crystalline waxes

2.3.1. Fractional crystallization technique

Suez crude petrolatum was subjected practically to one stage fractional crystallization using butyl acetate solvent at ambient temperature of 20 °C and solvent feed ratios (S/F by weight) ranging from 2:1 to 6:1 at fixed washing solvent ratio 2:1 to produce microcrystalline waxes [19–21].

A known weight of Suez crude petrolatum was dissolved in the corresponding amount of solvent in a beaker and heated till the mixture becomes homogenous. Then the mixture was cooled gradually at room temperature. The beaker and the buchner funnel were transferred to a controlled temperature unit and gradually cooled to the desired temperature. The beaker contents were transferred to the funnel and filtered through a Whatman filter paper No. 43 by using gentle suction. The wax cake was washed with additional solvent at the same temperature and added at small increments. Solvents were removed from the wax cake by distillation.

2.4. Addition of membranes

Membrane was used for studying its effect in improving the deoiling process for separation of microcrystalline waxes. Membrane was added to the petrolatum-deoiling solvent mixture in the percentages 0.05 and 1 wt.% based on the feed; at solvent feed ratio of 4:1 for dilution and at washing solvent ratio of 2:1 by weight at fractionating temperature of 20 °C.

2.5. Measurements and characterization

2.5.1. Physical characteristics

Suez crude petrolatum and the isolated waxes were physically characterized according to American Society for Testing and Materials (ASTM) standard methods [21]. The type of the isolated waxes was specified according to Technical Association of the Pulp and Paper Industry TAPPI-ASTM equation [22].

2.5.2. Molecular type composition

The total aromatic contents of suez crude petrolatum, and isolated waxes were determined using liquid solid column chromatography technique [23].

n-Paraffin contents for Suez crude petrolatum and isolated waxes were determined using gas chromatography technique (Perkin Elmer inst., Clarus 500, England).

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