Polymeric membranes derived from immiscible blends with hierarchical porous structures, tailored bio-interfaces and enhanced flux: Potential and key challenges

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GRAPHICAL ABSTRACT
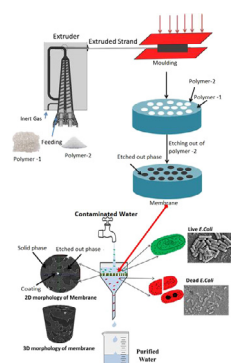
ARTICLE INFO

ABSTRACT

The review article presented here comprehensively highlights the various fundamental aspects of polymer blends from molecular level miscibility to the evolution of bi-phasic morphology, under different processing conditions, that are essential for exploring their potential in membrane applications. It also compares and contrasts the existing practices in membrane development such as phase inversion, track etching etc., for alternative and economical strategies to develop novel membranes. The key role of rheology on the evolution of morphology during processing and post-processing operations such as compression molding, annealing etc. has been discussed under the framework of different techniques for the preparation of thin membranes. The different hierarchical porous structures (micro and nano), developed by selectively etching one of the components from binary blends, and their application in separation technology have been highlighted and the results have been compared against the existing solutions. The effect of various processing parameters and ratio of the blend component that decides the final morphology of the membrane has been discussed. The unimpeded permeation of fluids is discussed with respect to the different morphology that is generated during their fabrication and the reasons for their clogging, fouling etc. have been extensively discussed. Further, different strategies like *in situ* and *ex situ* strategies modification of the membrane surface have been discussed with respect to antibacterial

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and antifouling properties. The efficacies of various *in situ* and *ex situ* strategies to render the surface antibacterial is elaborated with respect to water purification applications.

1. Introduction

The blending of two or more polymers to obtain desired mechanical and physical properties is an alternate economical solution in contrast to developing/synthesizing new polymers [1]. Polymer blending can yield properties that can be either additive or even synergistic as compared to individual components. Blending macromolecules with large molecular weight and structural conformations often results in low entropy of mixing leading to two-phase morphology. Thus, blending often leads to multi-phasic morphologies based on the thermodynamic and kinetic factors due to size and structural changes in polymer chains.

Blending of polymers can be carried out by mechanical mixing, solution mixing, latex blending, fine powder mixing and copolymerization etc. However, melt blending is an economical and effective way of designing new materials commercially [2]. As most of the polymer pairs are immiscible in nature, mixing two polymers results in heterogeneous morphologies [3] that exhibit weak interfaces and undesirable mechanical properties. Therefore, tailoring the interface is an essential criterion to obtain desired properties. The interface can be tailored either by physical modification like a block copolymer or chemical routes such as *in situ* formation of graft polymers at the interface. Thus tailoring the interface stabilizes the morphology by reducing the interfacial tension between the entities [4–6].

Morphologies generated during melt blending can be utilized for various strategic applications. The various morphologies that are often developed by blending are droplet matrix, sea-island and co-continuous (as shown in Fig. 1) morphologies. These have their own advantages and disadvantages with respect to various applications. These morphologies provide different transport phenomena, as will be discussed in the subsequent sections.

Polymeric membranes are traditionally synthesized either by stretching melt-cast of polymeric films, electro-spinning [10,11], tracking etching or thermally induced phase separation (TIPS) [12]. The commercial membranes are mainly composed of cellulose, polysulfone [13], polyvinylidene fluoride and polytetrafluoroethylene etc. [14]. The membranes are utilized to separate the contaminants from the feed stream. Therefore, membranes are in direct contact with the incoming feed stream that often contains microorganisms and particulates. The micro-organisms in the feed tend to adhere/attach to the surface. These form a biofilm due to microbial growth over time thereby clogging the active pores. This results in severe fouling of the membrane [15]. Biofilm further enhances the membrane resistance that increases the pumping cost. Hence, there is a great demand for manipulating the surface that can resist bacterial colonies to grow and prevent biofouling [16].

This article highlights the potential of immiscible polymer blends for separation technology. The underlying concepts of evolution of morphology during melt blending, rheology of the components influencing the final morphology, interfacial tension etc. are discussed in detail. The transportation of fluids through porous structures designed by selectively etching one of the components is discussed under the framework of different hierarchical porous structures that are developed by varying the concentrations of the components. The various strategies to develop polymeric membranes are discussed under the framework of existing solutions for water purification. In addition, various *in situ* and *ex situ* strategies that are currently being employed to resist biofilm formation are addressed alongside with different case studies.

2. Fundamentals of polymer blends

The underlying thermodynamics in mixing two polymers play a vital role in morphological development. For the blends to form a spontaneous single phase, Gibbs free energy of mixing (ΔG_m) should be negative, which is defined as:

$$\Delta G_m = \Delta H_m - T \Delta S_m \tag{1}$$

where, ΔH_m and ΔS_m are enthalpic and entropic contribution to mixing and T is the temperature. Further, $\left(\frac{\partial^2 \Delta G_m}{\partial \phi_i^2} \right)_{T,P} > 0$ where, ϕ_i is the volume fraction of ith component. Polymers generally have high molecular weight resulting in low entropic gain and thus ΔS_m will be small and positive. Thus, ΔH_m contribution should be exothermic for ΔG_m to be negative. However, most cases exhibit endothermic mixing, therefore the ΔG_m is positive. Thus, most of the polymer blends are phase separated i.e., they form immiscible blends.

The extent of phase separation can be suppressed if the components establish specific interactions between them. The specific interaction can be measured by mutual solubility which can be obtained by Hildebrand solubility parameter (δ). The difference in Hildebrand solubility parameter ($\Delta\delta$) of two polymer components should be as small as possible for better mutual solubility (miscibility) or compatibility [17,18]. It has been reported that δ is dependent on intermolecular interactions i.e. dispersion, hydrogen bonding and dipole–dipole interaction. The $\Delta\delta$ can be expressed as

$$\Delta\delta = \left(\Delta\delta_d^2 + \Delta\delta_p^2 + \Delta\delta_h^2 \right)^{1/2}. \tag{2}$$

The free energy density of mixing two polymers can be calculated by Flory–Huggins classical theory, which is defined as

$$\frac{\Delta G_m}{KT} = \left(\frac{\phi_A}{V_A N_A} \right) \ln \phi_A + \left(\frac{\phi_B}{V_B N_B} \right) \ln \phi_A + \frac{\chi \phi_A \phi_B}{V_m} \tag{3}$$

where, N_A represents the number of repeat units in polymer A with volume V_A and volume fraction ϕ_A, χ represents the Flory–Huggins interaction parameter, k is the Boltzmann constant at absolute temperature T (K). Similarly, N_B represents the number of repeat units in polymer B with volume V_B and volume fraction ϕ_B. The Eq. (3) can be utilized for predicting the phase diagram and the onset of phase separation can be evaluated via Flory–Huggins interaction parameter (χ) at the critical point (χ_c) which is defined as,

$$\chi_c = \frac{1}{2} \left(\frac{1}{\sqrt{N_A}} + \frac{1}{\sqrt{N_B}} \right)^2 \tag{4}$$

χ_c of blend represents the critical point above which the blends phase separate into two distinct phase in the blend. Assuming the molar volume (V_R) is identical for both A and B components, Eq. (3) can be rewritten as Eq. (5) for calculation of χ from interaction parameter between A and B can be calculated by their solubility parameter as

$$\chi = \frac{V_R}{RT} (\delta_A - \delta_B)^2. \tag{5}$$

From Eqs. (4) and (5), the miscibility in any pair can be predicted *apriori*. It has been reported that polymer pairs tend to be immiscible if χ/χ_c obtained is lesser than 1. But for certain cases like blends of PE and PEO, the ratio χ/χ_c obtained are 376 and 133