Bull. Mater. Sci. (2021)44:236
https://doi.org/10.1007/s12034-021-02529-9

Molecular transport of aliphatic alcohols through expanded polystyrene–polyvinyl alcohol thin films

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MS received 3 March 2021; accepted 15 May 2021

Abstract. Expanded polystyrene (EPS) and polyvinyl alcohol (PVA) blend film was prepared by the non-solvent-induced phase separation method. FESEM analysis revealed the porous nature of the polymer membrane. The pore size and density were found to increase with higher loading of PVA. Mechanical testing showed that the incorporation of PVA into the EPS matrix improved Young's modulus and tensile strength. The wettability of the film was determined by the degree of swelling (DS) and water contact angle measurements. A sharp increase in water absorption capacity and reduction in contact angle were observed for the polymer membrane with higher PVA content. Mass transport behaviour of the as-prepared film was determined using different aliphatic alcohols viz. methanol, ethanol and 2-propanol. The polymer film containing 10% PVA was taken as the optimum blend ratio since it exhibited good permeation capacity and mechanical strength. The selectivity of vapour permeation of the blend film between 2-propanol and acetone was studied.

Keywords. Mass transport; permeation; polymer membrane; aliphatic alcohols.

1. Introduction

Polymeric membranes are widely used in partitioning of organic compounds from mixtures and in food packaging industry [1–3]. The charge and porosity of the membrane affect the degree of selectivity between solvents. For better selectivity, the polymer film must possess remarkable chemical and thermal stabilities. The structure, morphology and mechanical strength of the polymer film determine the permeability and selectivity [4,5].

Porous polymeric membranes are used for solute separation either by microfiltration or ultra-filtration. Those with uniform pore diameters are symmetric, whereas with variable pore diameters, are asymmetric. If the pores with diameter between 0.1 and 10 µm, are used for microfiltration and the membranes with pore diameter between 0.001 and 0.1 µm, are used for ultra-filtration [6]. Permeation method using polymer membranes is simple, low-cost and superior compared to general methods of separation of compounds from solvents with respect to environmental and health considerations [7]. The permeation of organic solvents and gases through modified polymer films depend on nature of polymer chain, curing agents, fillers and temperature [8,9].

The molecular interactions between the polymer chains affect their transport properties. Tailor-made polymer blends with versatile transport properties are well demanded in industrial applications. Swelling studies are crucial to know the life time of polymer utensils which come in contact with solvents [10]. It has been found that most of the hydrophilic membranes used for the separation of water from methanol have low selectivity between water and methanol [11], but allow the separation of methanol from higher homologues [12]. Pervapouration and vapour permeation occur equally through these membranes [13]. In the pervaporation process, as the azeotropic mixture contains large amounts of methanol having substantial heat of evaporation, many membrane layers are required to compensate the heat lost during the vapourization of permeated methanol. So, vapour permeation can be considered as superior to pervapouration [14,15].

Expanded polystyrene (EPS) is extensively used in insulation and packing processes. It is attractive because of its low-price and ease of processability. Polymer wastes are generally disposed of by land filling or incineration. Due to its huge volume, EPS cannot be transported economically to dumping sites. Incineration of it, produces toxic gases and may cause severe environmental pollution. Blending of EPS with suitable polymers convert it into value-added products having specialty properties [16,17]. Polyvinyl alcohol (PVA) is a nontoxic, biodegradable and biocompatible polymer with high stability, miscibility and good opto-electrical properties [18]. Being transparent and non-expensive, it is a suitable component for the fabrication of thin films with good flexibility and permeability against air and foul-smelling vapours [19,20]. The poor mechanical strength and high hydrophilicity of PVA can be compensated by blending EPS with PVA [21].

Here, we report the fabrication of free-standing EPS/PVA blend films via the non-solvent induced phase separation (NIPS) method using N-methyl-2-pyrrolidone (NMP)/water system. Mechanical properties, such as tensile strength, Young's modulus and percentage elongation were determined. The hydrophilicity of the as-prepared EPS/PVA film was monitored by the degree of swelling and contact angle measurements. The parameters, such as permeability, selectivity in vapour permeation and temperature dependence were studied to determine the controlled permeation of aliphatic alcoholic vapours. This is the first report of the utilization of waste EPS in the fabrication of polymer membrane with selective permeability to organic solvents.

2. Materials and methods

PVA ($M_w \sim 20{,}000$ g mol^{-1}), NMP, acetone, methanol, ethanol and 2-propanol were purchased from Fisher Scientific, Mumbai, India. Waste EPS was collected from packaging materials, cleaned and chopped into smaller pieces. Millipore water was used for all the experiments.

2.1 *Synthesis of EPS/PVA blend film*

NIPS method was adopted to prepare blend film. To EPS solution at 60°C (15 wt% in NMP), different amounts of PVA (0, 5, 10, 20 and 30 wt%) were added and stirred magnetically under 600 rpm for 2–3 h. The homogeneous solution was then casted on to a glass plate by using a film applicator (Elcometer: Model-3540). The thin films (200 μm) were immediately dipped in a coagulation bath containing the non-solvent (water) and immersed for 24 h. They were dried and kept in a desiccator [20]. The films were coded as PSA0, PSA5, PSA10, PSA20 and PSA30, where the digits denote the wt% of polyvinyl alcohol with respect to EPS. Beyond 30%, the mixture was found to lose homogeneity.

2.2 *Characterization*

The polymer films were characterized by FTIR spectroscopy (Agilent-Technologies-Cary 630-ATR), X-ray diffraction (Rigaku Miniflex-600: 40 kV and 20 mA current) and field emission scanning electron microscopy (Supra 55VP FESEM) analysis. Mechanical strength of the films (rectangle pieces 1 × 5 cm) was measured by using UTM, Shimadzu AG-X plus 10 kN with a cross-head speed of 5 mm min^{-1}.

2.3 *Degree of swelling and contact angle measurement*

Rectangular pieces (2 × 2 cm^2) of the films were accurately weighed and immersed in 10 ml of distilled water for 24 h in small covered bottles. The polymer films were taken out, wiped well and weighed [22]. Degree of swelling was calculated from the following equation:

$$\mathrm{DS}(\%) = \frac{(W_1 - W_0)}{W_0} \times 100, \qquad (1)$$

where w_0 and w_1 are the weights (g) of the dry and wet films, respectively. The contact angle of the blend films was determined using goniometer (GBX Digidrop) with water as the probe liquid.

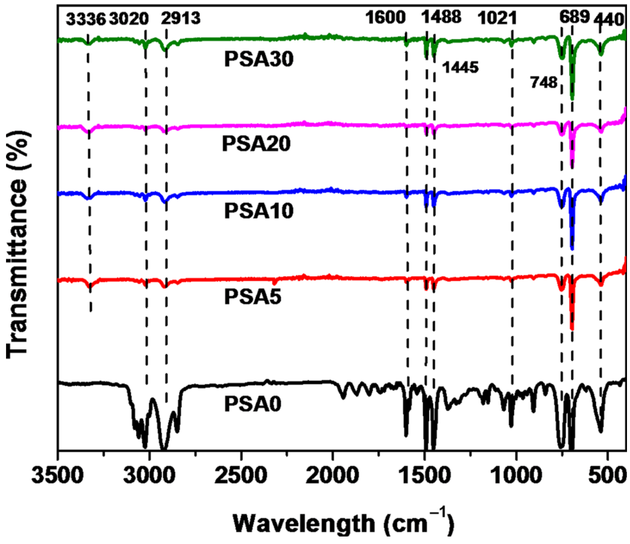

Figure 1. FTIR spectra of PSA0–PSA30 films.

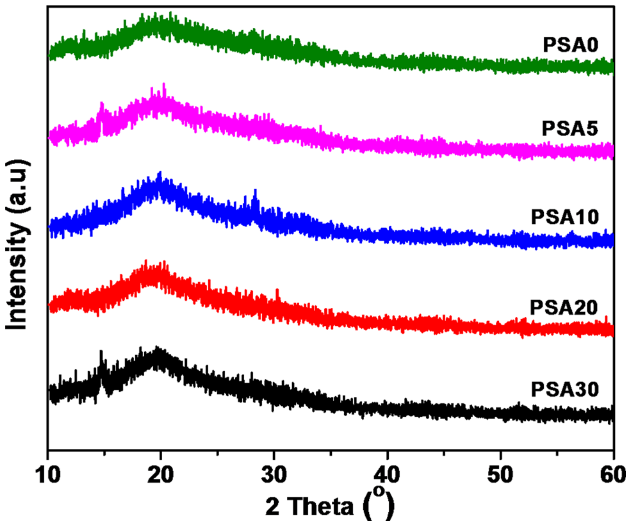

Figure 2. XRD pattern of PSA0–PSA30 films.

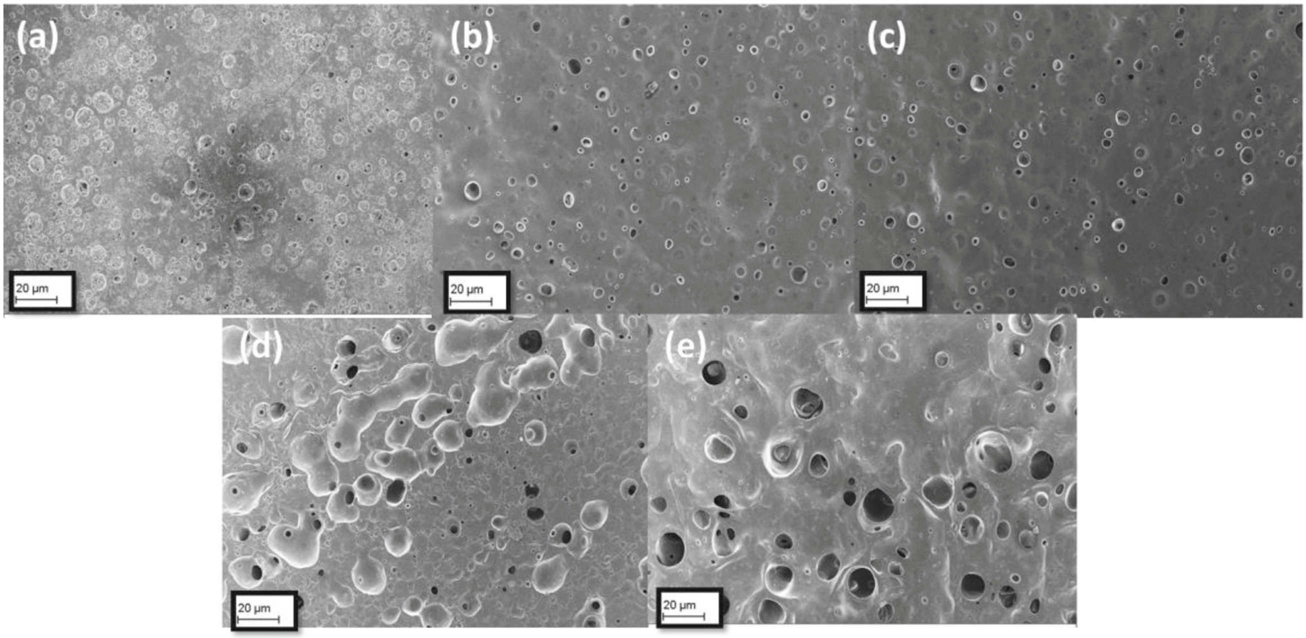

Figure 3. FESEM images of (**a**) PSA0, (**b**) PSA5, (**c**) PSA10, (**d**) PSA20 and (**e**) PSA30 films.

2.4 *Permeation of aliphatic alcohols*

The vapour permeability of the as-prepared polymer films was studied using three different aliphatic alcohols viz. methanol, ethanol and 2-propanol. Three permeation vials were filled with 5 ml of alcohols and covered with thin films. They were weighed at regular intervals of time (10 min) for 3 h. Triplicate measurements were done with the variation of ±0.0001–0.0002 g. The dependence of temperature on permeability was studied with 2-propanol, whereas the differential separation capacity was analysed using 2-propanol/acetone mixture [23].

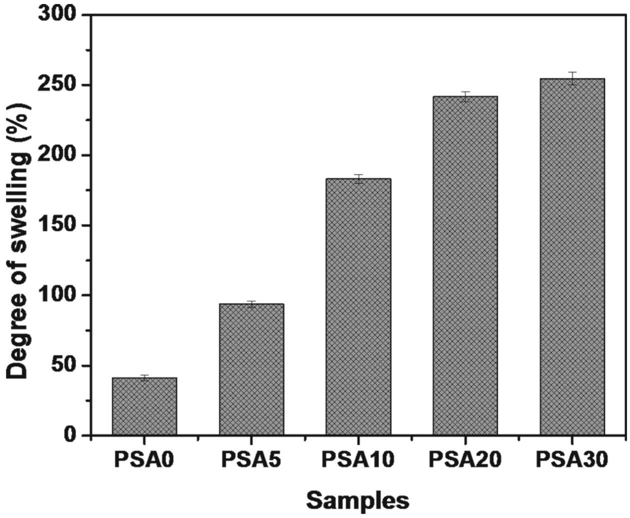

Figure 4. Swelling behaviour of PSA0–PSA30 films.

3. Results and discussion

3.1 *FTIR analysis*

In the FTIR spectra of the blend films (figure 1), it can be seen that the absorption band around 3050–2900 cm^{-1} correspond to the –CH aromatic and aliphatic stretching vibrations. The peaks around 1500–1400 and 1100–1000 cm^{-1} represent the C–H deformation and –C–O stretching vibrations, respectively. The spectrum also exhibits substituted benzene ring peak near 750 cm^{-1} and the C=C stretching peak around 1490–1440 cm^{-1}. The peak around 3300 cm^{-1} is attributed to the –OH stretching vibration of PVA moiety which confirmed the presence of residual PVA content within EPS matrix [24,25].

3.2 *XRD analysis*

XRD patterns of pristine EPS and the blends (figure 2) exhibit broad and strong peaks in the range of 19.3–19.5°. It can be seen that the addition of PVA into the PS matrix cause a small shift in 2θ and slight reduction in diffraction peak intensity. Even though PVA exhibits a semi-crystalline structure with a large intense peak in the same range, the blends show more amorphous nature as evident from the diffraction pattern [26].

3.3 *FESEM analysis*

Figure 3 shows the FESEM images of PSA0–PSA30 blend films. PSA0 exhibits almost plane surface with a very few

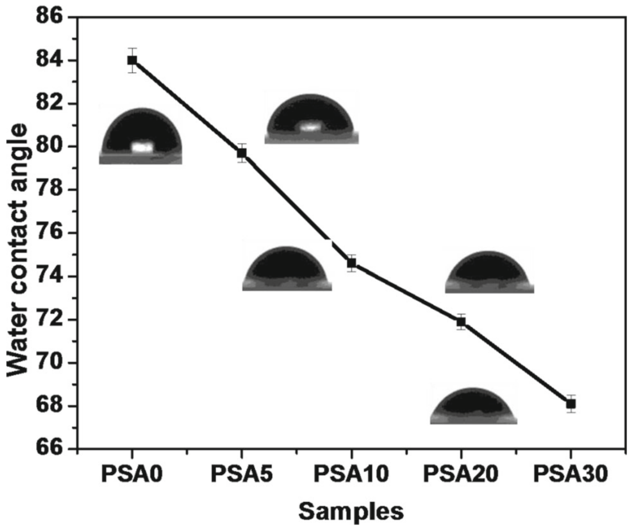

Figure 5. Water contact angle.

number of pores. This can be due to the diffusion of trace amounts of polymer into the non-solvent (water) and as a result, pores are created on the sub-layer of the blend film. As evident from the FESEM images, the porous nature of the blend film increases with higher loading of PVA. The size and pore density show linear increase from PSA0–PSA30. Pore size of EPS was found to increase from 3.02 to 6.741 μm when 10% of PVA blended with it. The optimum pore size for PSA10 enables it to be used as a suitable polymer membrane with good permeability [6].

3.4 *Hydrophilicity studies*

3.4a *Degree of swelling:* The water absorption capacity of the blend films is revealed from the swelling studies as shown in figure 4. The swelling behaviour gradually increases from 41.55% for PSA0 to 254.65% for PSA30. This is due to the increase in the hydrophilicity of the blend films with higher PVA loading.

3.4b *Water contact angle:* Figure 5 displays water contact angle (WCA) values and images of PSA0–PSA30 films. The contact angle of EPS (84 ± 2°) was found to decrease to 68.1 ± 3° for PSA30. This means that the

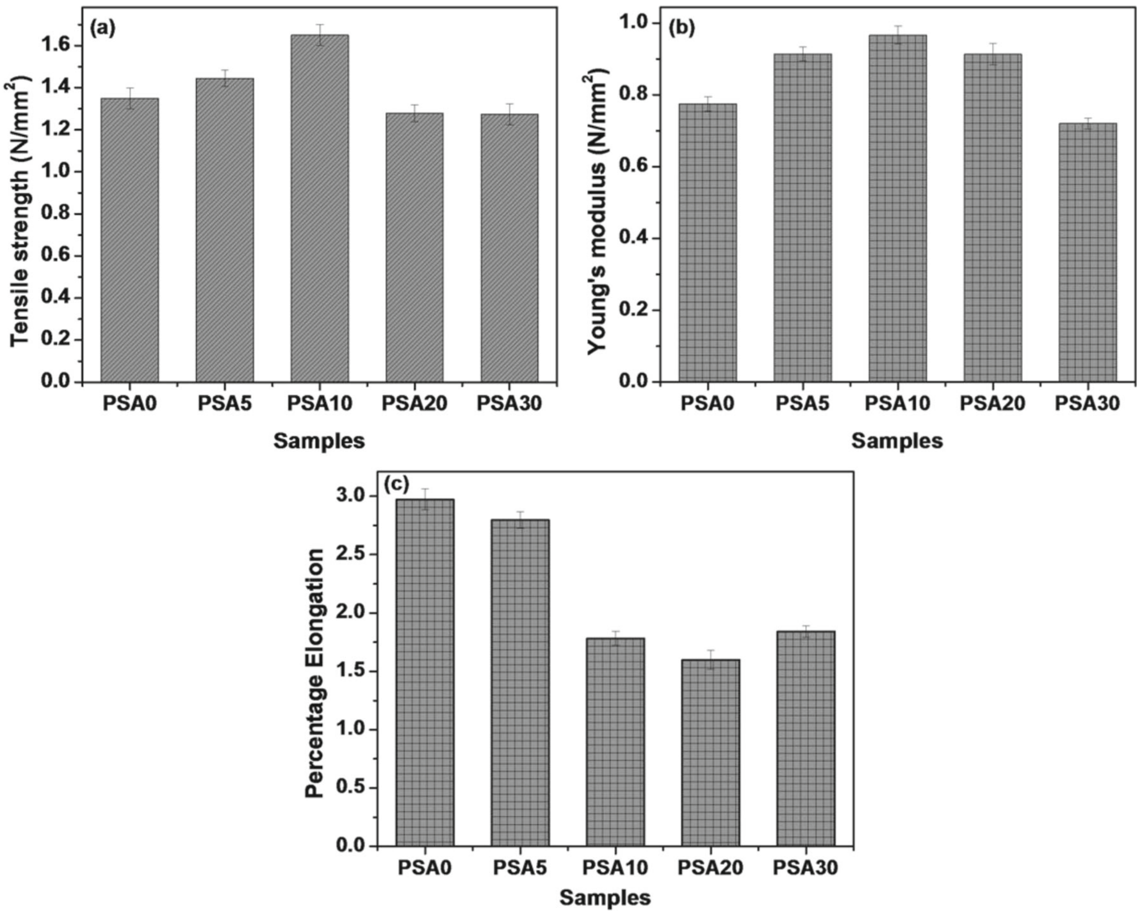

Figure 6. (**a**) Tensile strength, (**b**) Young's modulus and (**c**) % elongation of films.

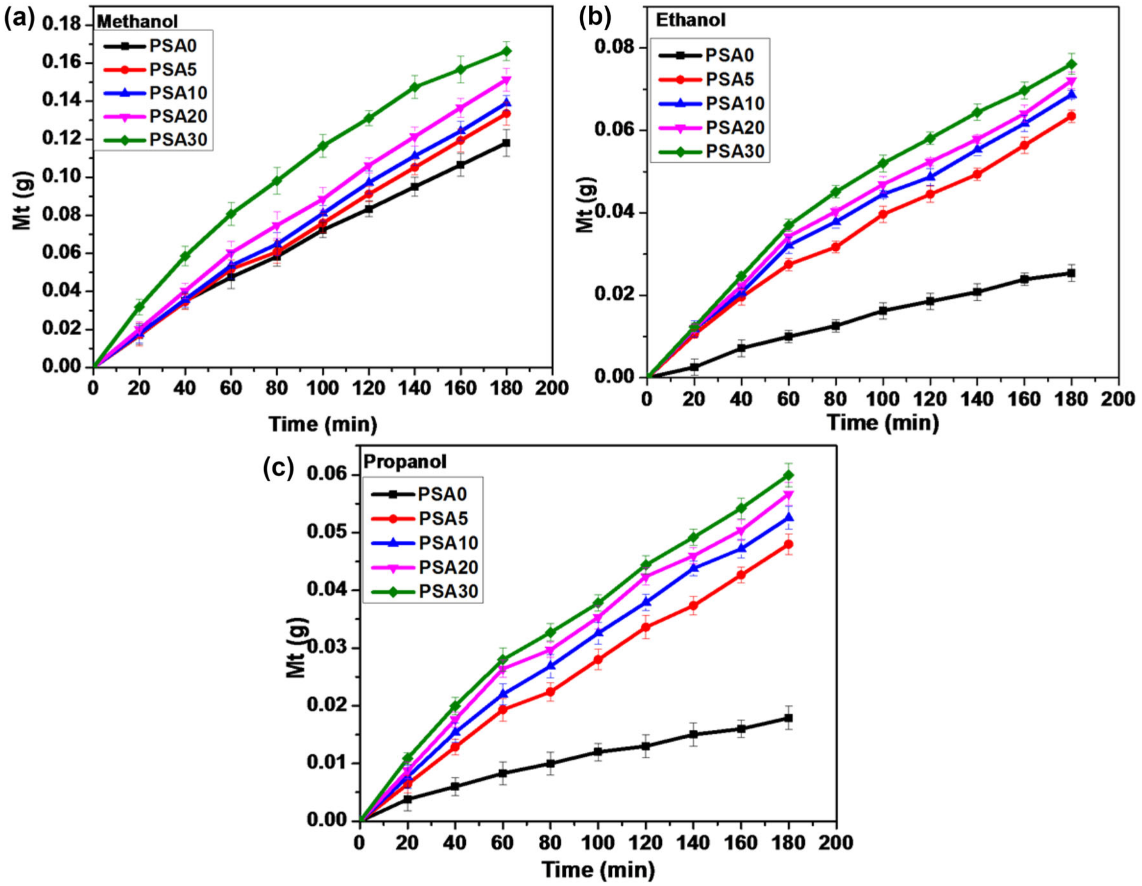

Figure 7. Permeation of (**a**) methanol, (**b**) ethanol and (**c**) 2-propanol through blend films.

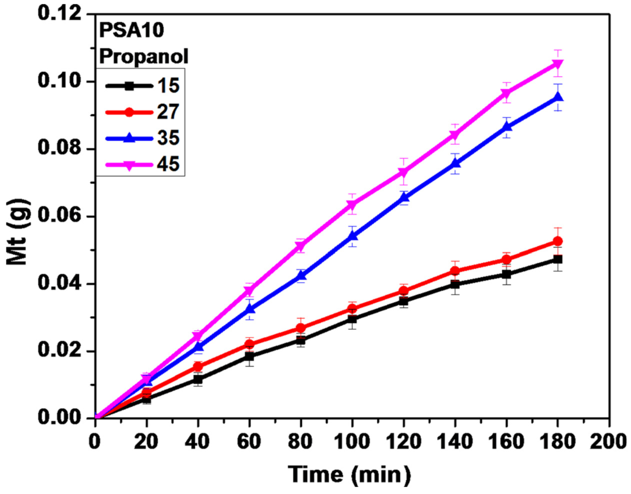

Figure 8. Effect of temperature on permeation.

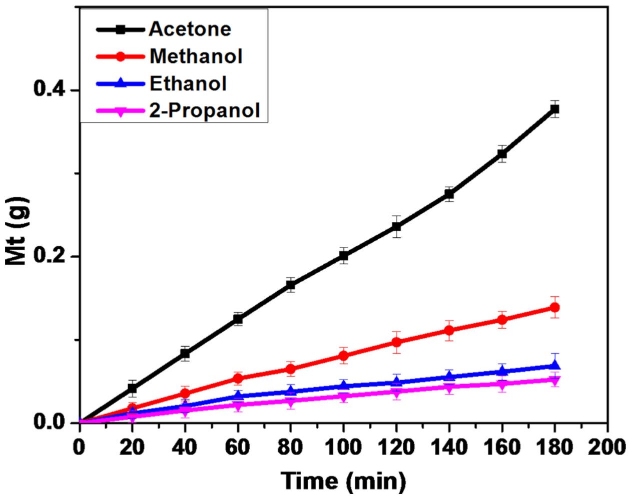

Figure 9. Permeation of organic vapours across PSA10 film.

Table 1. Physical parameters of solvents.

Solvents	Boiling point (°C)	Vapour pressure at 25°C (Pa)	Molecular mass (g mol^{-1})
Methanol	64.7	12798.9	32.04
Ethanol	78.37	5866.19	46.07
2-propanol	82.5	4399.6	60.1
Acetone	56.0	206843	58.08

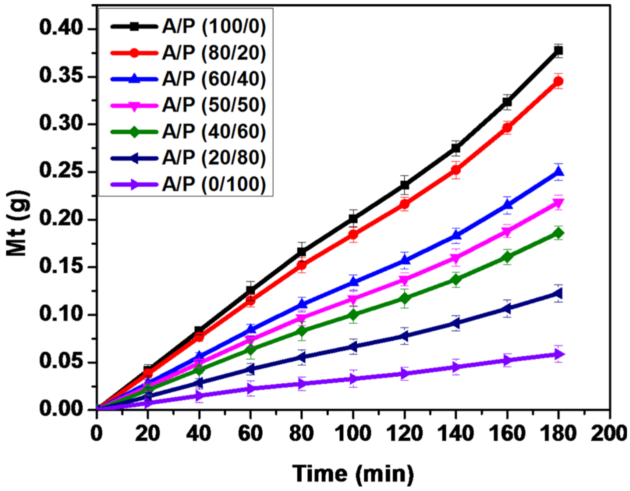

Figure 10. Permeation of 2-propanol/acetone mixtures.

hydrophobic EPS has acquired hydrophilicity by blending with PVA.

3.5 *Mechanical properties*

Figure 6a–c illustrates the mechanical strength of the blend films. There is a considerable variation in percentage elongation, tensile strength and Young's modulus of the blend film. The tensile strength increased gradually up to PSA10 and then decreased. It is expected from the FESEM images; due to the increased porosity at higher loading level. Similar trend is observed for Young's modulus also. As we know the % elongation is inversely proportional to Young's modulus and the former show gradual decrease up to PSA10. In other words, the incorporation of PVA into the EPS matrix improved the Young's modulus and tensile strength with decreased % elongation which indicate better compatibility between the constituents along with improved strength and stiffness [27].

3.6 *Vapour permeation properties for alcohols*

Figure 7a–c shows the variation in permeation of methanol, ethanol and 2-propanol with time through the films for 3 h. The rate of permeation of the aliphatic alcohols is proportional to the time of transport. It can be seen that the permeation capacity of the blend film increases with the amount of PVA and is due to the higher porosity of the blend film as evident from the FESEM image. Since PSA10 shows good mechanical properties with superior permeation characteristics, we selected it as the optimum composition for further solvent transport studies.

3.7 *Temperature dependence of vapour permeation*

Figure 8 shows the effect of temperature on vapour permeation through PSA10 film. The permeability is found to increase linearly with temperature. This is due to the enhanced macromolecular flexibility of the polymer film and kinetic energy of the organic penetrants at high temperature [9].

3.8 *Permeability and nature of penetrant*

Figure 9 illustrates the variation of permeation of the different organic vapours, viz. methanol, ethanol, 2-propanol and acetone across PSA10 film for 3 h. The homogeneous dispersion of the components and also the uniformity in pore size as evident from the FESEM image indicates the good permeability characteristics of PSA10 film. Acetone is permeated more through this film and 2-propanol the least. The physical parameters of the solvents are given in table 1.

3.9 *Selectivity in vapour permeation*

Figure 10 shows the variation of permeability of mixtures of 2-propanol and acetone in different composition. It can be seen that acetone permeates at a higher rate than 2-propanol and also permeability decreases with increase in the amount of alcohol. The higher permeability of acetone than 2-propanol through PSA10 film permits the separation of mixtures of these solvents using the as-prepared polymer membrane.

4. Conclusions

Waste EPS and PVA blend films were prepared and characterized. FTIR and XRD analyses data proved the existence of PVA content within the EPS matrix. FESEM analysis showed that the pore size and density were found to increase with higher loading of PVA. Mechanical testing showed that the incorporation of PVA into the EPS matrix improved the Young's modulus and tensile strength. Water absorption capacity and hence, hydrophilicity were found to increase linearly with PVA content in the blend film. The contact angle of EPS (84 ± 2°) was found to decrease to 68.1 ± 3° for PSA30. This means that the hydrophobic EPS has acquired hydrophilicity by blending with PVA.

Vapour permeability measurements showed the good permeation capacity of the polymer membranes for the transport of aliphatic alcohols. In addition to its higher mechanical strength, the homogeneity in dispersion and uniform pore size as evident from the FESEM image indicated the superior permeability characteristics of PSA10 film. Hence, it was found to be the optimum blend film and used to study the selectivity of vapour permeation between 2-propanol and acetone. The present investigation illustrates a simple method of preparation of free-standing polymer film with selective permeability for organic vapours. The utilization of waste EPS (thermocol) and conversion into useful products is an environmentally sustainable and economically viable green policy.

Acknowledgements

This work has been supported by UGC-innovative programme and DST-FIST programmes of Nirmalagiri College, Nirmalagiri, Kannur, Kerala, India.

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