



Biocompatible poly(vinyl alcohol) nanoparticle-based binary blends for oil spill control



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ARTICLE INFO

Article history:

Received 21 April 2016

Received in revised form 8 August 2016

Accepted 19 August 2016

Available online 19 September 2016

Keywords:

Poly(vinyl alcohol)

Nanoparticles

Binary blends

Oil cleanup

Chitosan

Starch

ABSTRACT

In the current study, biocompatible and biodegradable blends based on poly(vinyl alcohol) nanoparticles – PVAn mixed with either chitosan (Ch) or starch (St) – were prepared and investigated as nanoabsorbents for oil elimination from wastewater. The use of water/dimethyl sulfoxide (DMSO) as a mixed solvent is the key factor for preparing aggregated PVAn, which is further mixed with Ch or St. Nanoblends were applied as oil absorbents, and the results showed that PVAn/St possess high adsorption capacity than PVAn/Ch and PVAn. The maximum sorption capacities ($q_{g/g}$) of the PVAn/Ch sorbents for hydraulic oil, kerosene, and toluene were 33.6, 73.96, and 93.1 g/g, respectively. The absorbed oil could be rapidly recovered by simple mechanical squeezing and reused without any other modification. The blends showed excellent reusability and could be reused for at least 10 times with minimal losses. The current study demonstrates the application of these blends as an ideal alternative sorbent for oil spillage cleanup.

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1. Introduction

Oil released through industrial wastes, oil leakage and oil spills can have a catastrophic effect on the environment and aquatic system (Godduhn and Duffy, 2003). Current methods for cleaning oil spills on water include mixing of oil with water using the dispersion method, in-situ burning bioremediation, collection of oil from the water surface, and the use of polymeric sorption materials (Roulia et al., 2003; Boopathy et al., 2012; Buist et al., 2011; Pan et al., 2014). Among these methods, oil-adsorbing materials have been extensively investigated because they are cost-effective and efficient for easy oil recovery. Oil absorbents can be roughly divided into three categories: organic natural sources (such as active carbon, rice straw, and fibers; Bayat et al., 2005; Sun and Sun, 2002; Annunciato et al., 2005), inorganic mineral products (perlite, silica, and zeolites; Bastani et al., 2006; Syed et al., 2011; Sakthivel et al., 2013), and synthetic polymers (polymer sponges, rubber, and polyacrylate; Pan et al., 2014; Lin et al., 2005; Zhang et al., 2013). These materials have been recently investigated and applied practically, but the drawbacks of these materials, such as low absorbability and instability during the absorption process, hamper their applications as oil absorbents.

Recently, polymeric nanoabsorbent materials have been extensively investigated in the removal of oil from oil spill sites, which has largely contributed to reduce environmental pollutions. Besides, the oil absorbent categories mentioned above, polymer blending is an interesting approach for preparing polymeric materials with new properties. Poly(vinyl alcohol) (PVA) is a linear polyhydroxy polymer that is prominent among nontoxic, biodegradable, and biocompatible polymers. Moreover, PVA can be produced on an industrial scale at relatively low cost and has a broad range of hydrolysis and degree of polymerization. These properties encouraged several research groups to investigate PVA as a candidate for environmental applications (Atta et al., 2013). Polysaccharides have emerged recently as economic materials for the removal of contaminants from the main sources (El-Menshawey et al., 2008; Salama et al., 2015). Chitosan, the second most abundant natural polysaccharide, is a biocompatible polymer with a good film-forming ability and was studied recently for enhanced oil recovery. Zheng et al. prepared CoFe₂O₄ chitosan magnetic nanoparticles with core-shell structure. These superparamagnetic nanoparticles could reduce surface and interfacial tension without any other additives. Moreover, chitosan nanoparticles showed good salt resistance (Zheng and Lian, 2015).

Starch, a biopolymer composed of two homopolymers – amylose and amylopectin, is an attractive raw material with low cost and renewability to produce biodegradable films for different applications (Xu et al., 2005). Several previous studies have reported that the blends of chitosan and starch with PVA have good mechanical, thermal, and tensile strength compared to individual polymer (Yang et al., 2004; Tang and

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Alavi, 2011; Grande and Carvalho, 2011). In the field of food packaging, starch/PVA supported with *Grewia optiva* fiber and methyl methacrylate-grafted fibers showed good thermal stability and antibacterial activity against both gram-negative and gram-positive bacteria (Singha et al., 2015). However, the properties of PVA mainly depend on the solvents and on the preparation methods (Hyon et al., 1989). For example, PVA prepared by repeated freeze-thawing cycling showed interesting features of transparency and a high modulus (Peppas and Stauffer, 1991). Wolf et al. reported that PVA was soluble in either water or dimethyl sulfoxide (DMSO) separately, but phase-separation change occurred with mixtures of both water and DMSO. Because of the reduction in solvency with some composition of the mixed solvent, the presence of both water/DMSO mixture is termed cononsolvent (Wolf and Willms, 1978). Moreover, nanosized particles of PVA with a narrow pore-size distribution can be obtained in water/acetone as solvents (Akl et al., 2013).

In the current study, we report the development of a facial and cost-effective method for blending PVA nanoparticles with chitosan or starch to form a uniform nanomembrane that can be used for oil spill recovery. The mechanical properties, including hydrophobicity of the prepared membrane and the oil-sorption capacities, of these binary nanoblend sorbents for toluene, kerosene, and hydraulic oil were investigated.

2. Materials and methods

2.1. Materials

The polymers used were PVA powder with polymerization degree of 2000 and saponification degree of 98% was purchased from Across; Chitosan (Ch) with molecular weight 400,000 Da and degree of deacetylation 98% was obtained from Challenge Bioproducts Co. (Taichung, Taiwan). Starch (corn starch; St) was supplied by CDH India. All other reagents were chemical grade and used without further purification.

2.2. Preparation of PVAn nanoparticles

PVAn (2 g) was dissolved in 300 ml water at 70 °C for at least 2 h and then equilibrated at room temperature (RT) with 250 rpm stirring overnight. For clear and homogeneous solution, 27 ml of DMSO was added dropwise with vigorously stirring for 45 min. The solution was then stored at 10 °C for 2 days; it turned to a pale blue solution. This indicates shrinking of long chains of PVAn to nanoparticles.

2.3. Preparation of PVAn/Ch and PVAn/St binary nanoblends

A 2% w/v solution of Ch was prepared in 2% aqueous acetic acid, while a 3% w/v starch solution was prepared in water. Subsequently, 50:50 wt/wt of PVAn/Ch or PVAn/St was mixed to form a homogeneous clear solution. The mixture was continuously stirred for 5 h in a mechanical stirrer (250 rpm). The blended films of PVAn/Ch or PVAn/St were obtained by casting the polymer solutions onto the tissue culture polystyrene Petri dishes and dried at 50 °C in an oven.

2.4. Characterization of nanoblends

The chemical structures of PVAn, PVAn/Ch, and PVAn/St were analyzed by Fourier transform infrared (FTIR) spectrometer (Nicolet, NEXUS-670). Transmission electron microscope (TEM) images were acquired with a JEOL JEM-2100 electron microscope at $\times 100$ k magnification, with an acceleration voltage of 120 kV. The surface morphology of the porous PVAn, PVAn/Ch, and PVAn/St was observed by a scanning electron microscope (SEM; JEOL JXA-840 A) operating at 5 kV. The mechanical strength of the nanoblends was evaluated with a tensile-compressive tester (LR10K, LLOYD Instruments, USA). The hydrophobicity was measured by an OCA 20

contact-angle system using contact angles (Data Physics, Germany) at RT. The average contact angle value was obtained by measuring the same sample at three different positions.

2.4.1. Procedures of oil removal

Three different types of oils, including toluene, kerosene, and pump oils, were selected to examine the efficiency of the PVAn, PVAn/Ch, and PVAn/St nanoblends. Physical constants of the selected oils are listed in Table 1. All tests for oil removal were conducted at 25 °C. Blends of PVAn, PVAn/Ch, and PVAn/St were cut with dimensions of 3×3 mm. The blends were weighted, immersed in 100 ml oils, and the weight of the absorbents was monitored as a function of time. The swollen membranes were removed from the oils at certain intervals, and their weights were recorded at time (t) after the blends were held at least for 15 s to drip off the residual surface liquid. The absorption capacity (Q_t) at time (t) was calculated according to the following equation:

$$Q_t (\text{gg}^{-1}) = \frac{m_t - m_0}{m_0} \quad (1)$$

where m_0 (g) and m_t (g) are the weights of the dry blend at time $t = 0$ and the total weight of the wet blends at time t , respectively.

2.4.2. Selectivity test

To investigate the strong oil adsorption selectivity of the blends in the aqueous medium, a small amount of oil was poured into a beaker to obtain a layer nearly equal to 2 mm above the water level. Subsequently, the (3×3 mm) blend samples were placed on the surface of the oil/water mixture, and the weights of the blends were monitored; after 30 min of absorption, the wet sorbents were removed, drained for 5 min, and weighed according to Eq. 1.

3. Results and discussion

3.1. Characterization tools of the PVAn nanoparticle-based blends

According to the chemical structure of water/DMSO as solvents, the behavior of the donor/acceptor and dipole moments of each component could manipulate these molecular interactions, which would change with the compositions of the solvent mixture to form more stable (water)₂/DMSO complexes at approximate volume fraction (Φ) = 0.54, resulting in polymer/poor and polymer/rich phases (Takahashi et al., 2003).

Fig. 1 shows TEM images of PVAn, PVAn/Ch, and PVAn/St. PVAn are mainly aggregated with particle sizes <50 nm. In contrast, PVAn/Ch showed a highly monodispersed network with the size average of 88.5 nm. The most interesting result here is the uniform size, shape, and dimension of the formed nanoparticles PVAn/Ch, which may be originated from the cationic charges present around the particles. After mixing with starch, PVAn/St showed heterogeneous morphology with fine rich needles with a length of the order of 50–100 nm. These needles exhibit a common preferred orientation.

Fig. 2 shows the FTIR spectrum of PVAn-based blends. The pure PVAn membrane prepared in water/DMSO 2:1 (v/v) solution shows sharp absorption bands at 3387, 2939, 1411, 1370, 1212, and 1039 cm^{-1} attributed to –OH of axial stretching, CH₂ stretching, H–OH deformation, CH–O deformation, –CH wagging, and C–O stretching band, respectively

Table 1
Properties of the selected oils.

Oil type	Viscosity (cp) at R.T.	Specific gravity (R.T.)
Toluene	0.59	0.867
Kerosene	58	0.890
Hydraulic oil	82.7	0.783

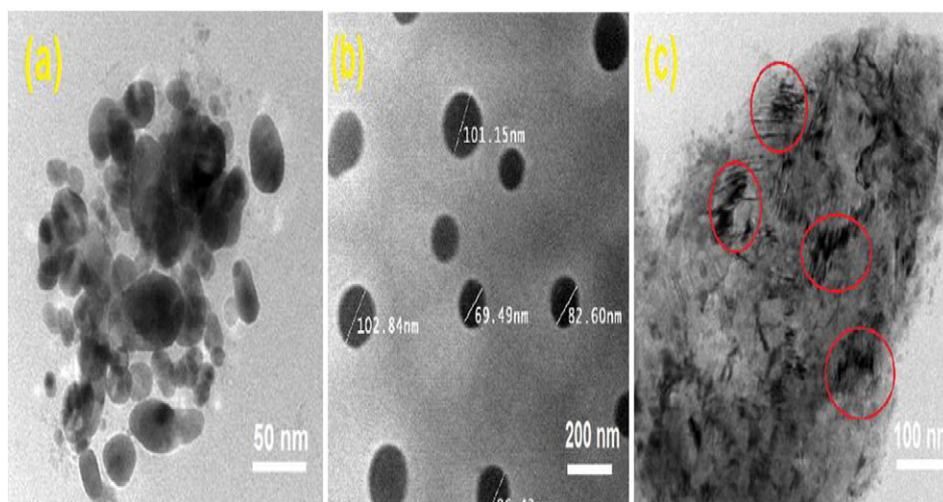


Fig. 1. TEM images of (a) PVAn, (b) PVAn/Ch, and (c) PVAn/St.

[26]. The shortened peak at 1726 cm^{-1} was related to the ester band of the binary blends PVAn/Ch, indicating definite interactions between PVAn and Ch. The most noticeable change detected in the FTIR was the shift that occurred in the peaks at 3387 cm^{-1} to expand and reduce to 3479 cm^{-1} for both $-\text{OH}$ and $-\text{NH}$ stretching vibration of PVAn

nanoparticle and Ch because of the molecular interactions of the $-\text{OH}$ groups; this indicated that these groups were present in a chemical environment, earthly exposed to scarce H.b interactions, which lead to reduction in band intensity (Grande and Carvalho, 2011).

In case of PVAn/St blend (Fig. 2, spectrum c). The stretching vibration of C—O in C—C—O in the glucose ring in starch was related to the peaks at 997 and 852 cm^{-1} . The change in peak intensity at 3355 cm^{-1} confirmed the interaction between PVAn nanoparticle and St because of increase in the total number of $-\text{OH}$ groups of both polymers (Cano et al., 2015). These results support that the H.b polymer PVAn chains, Ch and St, can interact to a certain degree of polymer compatibility, which is related to the specific solvent of the phase-separation behavior for the combination of PVAn/Ch and PVAn/St.

Fig. 3 shows the SEM of the cross-section of the different films. PVAn nanoparticle film had a continuous and broken interconnected network fibril structure and exhibited cavities ranged from small and large sponge-like pores. For PVAn/Ch binary blend, increasing the viscosity of the solution leads to lower degree of entanglements and slower dynamics of phase separation. Moreover, the formation of a soluble complex between PVAn nanoparticle and Ch may delay the phase-separation behavior, which leads to some holes between the phases, which is in agreement with the TEM confirmation (Wang et al., 2015a, b). When PVAn nanoparticles were blended with St, a mixture of both spherical particles and elongated fiber-like structures were formed. However, this blend consisted of fine spacious needles with particle sizes in range of 100 nm (Chin et al., 2011).

Generally, for dynamic recovery, the blends should simply possess a good mechanical property to withstand compression of sorbents (Zhu et al., 2015). Fig. 4 shows the mechanical properties of the different blends. Both tensile strength and break elongation increase with increasing Ch and subsequent St loading in the membranes. For PVAn/St, the tensile strength showed a steep linear increase until 200% strain, and then reached a plateau until failure. However, the incorporation of Ch in the blend resulted in a slightly lower tensile strength, but showed the largest elongation among the blends. PVAn nanoparticle showed a sudden steep increase, and then showed a plastic deformation and slow extension mode until failure. The improvement in mechanical properties of $\text{St} > \text{Ch} > \text{PVAn}$ blend membranes can be attributed to the biocompatibility and relative facility of obtaining materials with enviable properties without any significant changes or investments on the conventional process. Thus, PVAn/Ch or PVAn/St blends are a versatile technological solution to obtain polymeric materials with myriad specifications and a good mechanical property (Guimaraes et al., 2015).

Fig. 5 shows the water-contact angle for PVAn nanoparticle-based blends only with toluene to investigate the hydrophobicity and

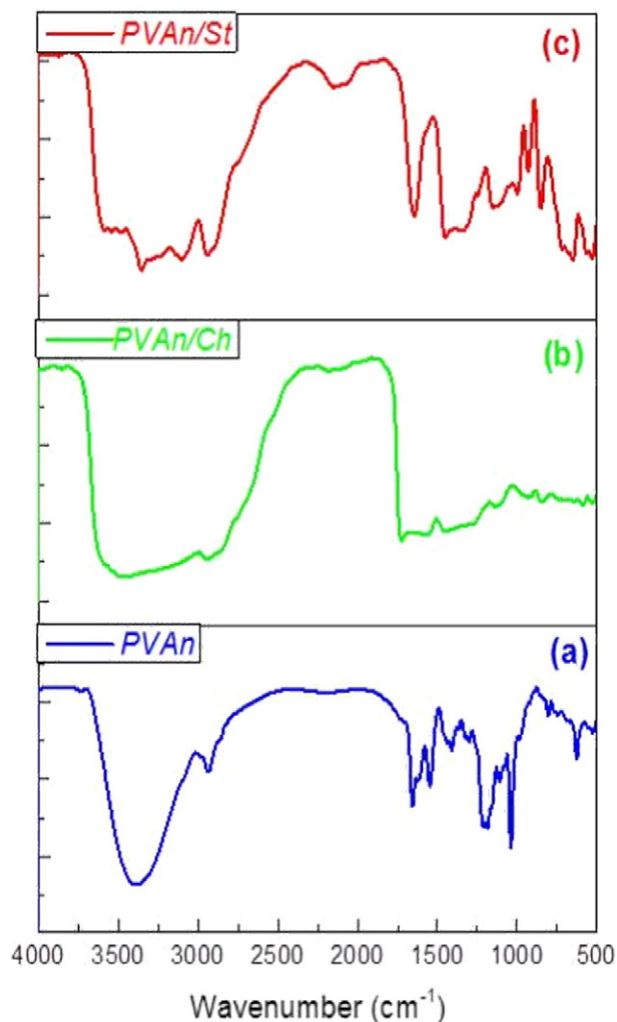


Fig. 2. FT-IR spectra of (a) PVAn, (b) PVAn/Ch, and (c) PVAn/St.

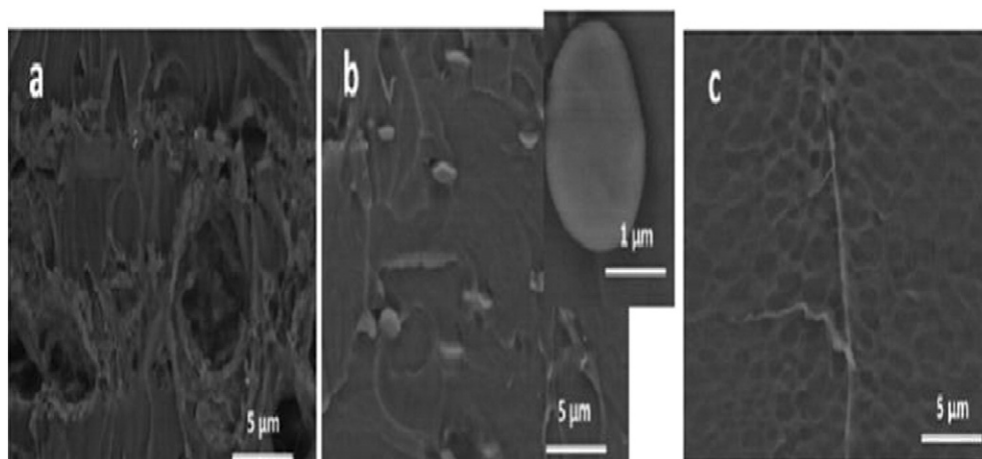


Fig. 3. SEM micrographs of the cross-section for (a) PVAn, (b) PVAn/Ch, and (c) PVAn/St.

oleophilicity properties. From the figure, we can see that all the samples showed superhydrophobic features with water droplets on the surface of the hydrophobic blends and contact angles 105° , 114° , and 131° (± 3) for PVAn, PVA/Ch, and PVA/St, respectively. A higher increase in PVAn/St blend water-contact angle was observed, which may be attributed to the increased roughness and rigidity due to surface-blending properties resulting from intrinsic hydrophobicity of St and underneath air pocket trapped in the porous texture based on the Cassie–Baxter surface model (Marmur, 2003).

3.2. Oil absorption kinetics

Oil absorption kinetic is a very important parameter that characterizes the efficiency of the nanoblends as an absorbent. The absorbents with nanoscale structure could be rapidly penetrated by suitable solvents. Consequently, the absorption equilibrium can be reached within a short time (Bayat et al., 2005; Abdeen and Moustafa, 2016). Fig. 6 depicted that the adsorption efficiency of oil increases with time and then rapidly reached a constant value, beyond which nearly no more oil was further absorbed from the solutions. These results suggested that the equilibrium time varied according to the viscosity of the oil. In low-viscous oils such as toluene, the PVAn, PVAn/Ch, and PVAn/St

blends can reach absorption equilibrium after 20, 15, and 10 min, respectively, while in case of kerosene, a medium viscous oil, the equilibrium state was achieved at 25, 20, and 15 min, respectively. However, in high-viscous oils such as hydraulic oil, at least 20 min are required to reach absorption equilibrium. For oils with low/medium viscosity, the oil molecules move faster and can diffuse into the nanoblend network in a shorter time, which also lead to the solvation of the polymer network simultaneously. Thus, this type of absorption process is dominated by the diffusion step. In contrast, for heavy hydraulic oil, slow diffusion of oil molecules is observed, which leads to slow solvation, indicating that the equilibrium would take a long time (Yin et al., 2016). In addition, the results revealed that oil absorption was rapid at the initial stages of the contact period especially with PVAn/St blend, and this observation was based on the fact that a massive number of vacant surface sites were available for absorption during the initial stage, and after a lapse of time, the remaining weak surface sites were difficult to be occupied because of the repulsive forces between the solute molecules of the nanoblend and the bulk phases. This observation suggested that the surface of the nanoblends were hydrophobic in nature and mainly absorbed oil rather than water (Chin et al., 2014).

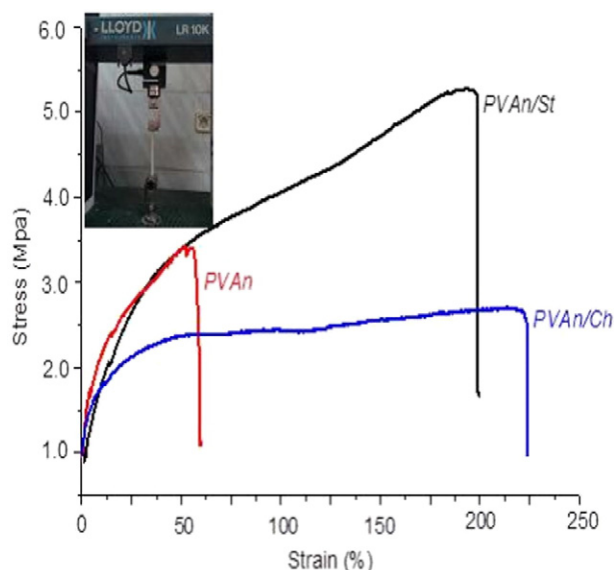


Fig. 4. Typical stress-strain curves of PVAn-based nanoblends.

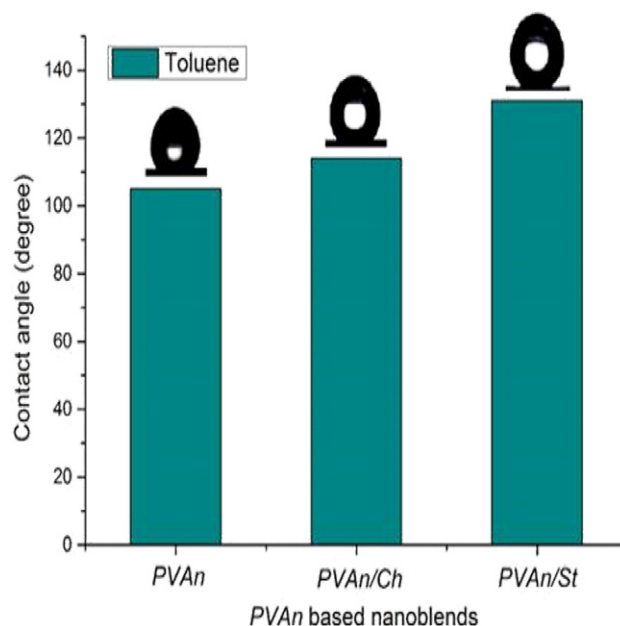


Fig. 5. Contact angles measurements of the fabricated nanoblends.

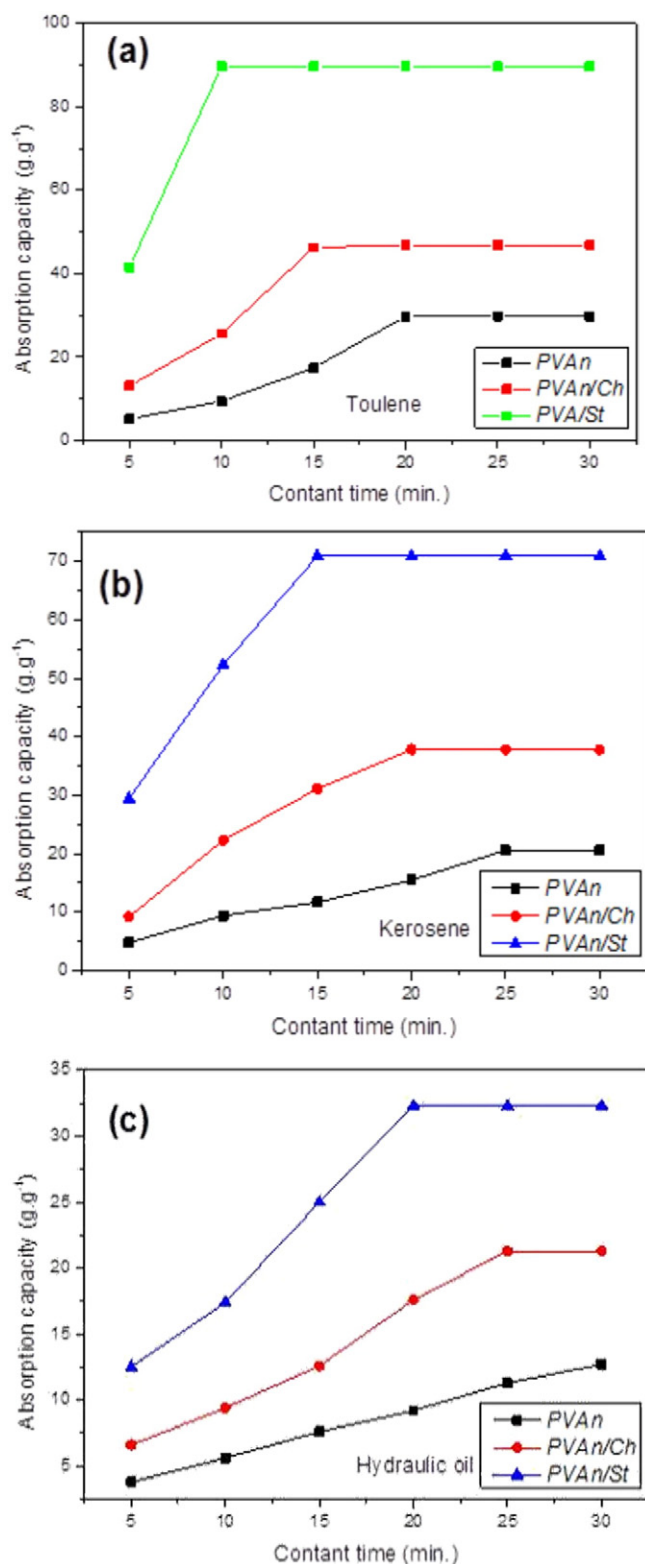


Fig. 6. Oil absorption capacity (g/g) versus time for nanoblends.

3.3. Absorption capacities and selectivity

The blend sorbents were immersed into the different selected oils for 30 min, and as shown in Fig. 7, the saturated absorption capacity was obtained. The absorption capacities of PVAn nanoparticle in toluene, kerosene, and hydraulic oil are 31.9, 23.4, and 13.06 (g.g⁻¹),

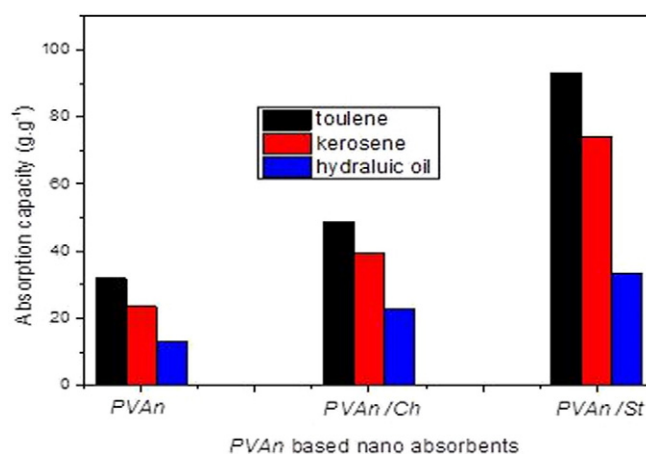


Fig. 7. Maximum oil capacities for PVAn-based binary nanoblends.

respectively, whereas those of PVAn/Ch are 48.7, 39.3, and 22.7 (g.g⁻¹), respectively. The PVAn/St absorbs 93.1 g of toluene, 73.9 g of kerosene, and 33.6 g of hydraulic oil. Apparently, PVAn/St blend had the highest oil absorption capacity, and this is due to the polymer blending approach that improves the absorption capacity for different oil products, particularly with hydrophobic PVAn/St blend because of the versatility to incorporate interesting properties on the membrane; moreover, it has a profound ability to simultaneously modify the membrane properties during the phase-inversion process (Qiu et al., 2009).

3.4. Selectivity for oil slick

When a hydrophobic blend was placed in the oil/water mixture, it repelled water and the selectivity of absorbed oil was complete and rapid (Fig. 8a), exhibiting excellent selectivity. To confirm oil selectivity by blends, only 0.02 wt.% of water was elected in the recovered oil. Fig. 8 shows the absorption capacities of the polymer blends for the same oils mixed with the water phase.

The blends exhibited excellent oil absorption capacities; for example, PVAn/St blend absorbed 99.2 g of toluene, 75.6 g of kerosene, and 36.9 g of hydraulic oil, which was similar to the results obtained from pure oil media with a slight increase of 1–3%, indicating that the as-prepared superhydrophobic blend membranes readily absorb oil from water. In addition, the oil-filled membranes buoyed on the water surface without oil release.

3.5. Reusability

To recycle PVAn-based nanoblends and to collect absorbed oil, simple roll squeezing could easily recover the oil loaded on 0.3 g of blend

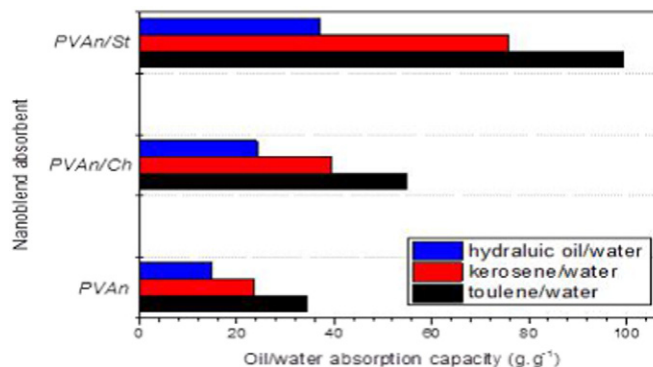


Fig. 8. Saturated absorption capacity of nanoblends in various oil/water mixtures.

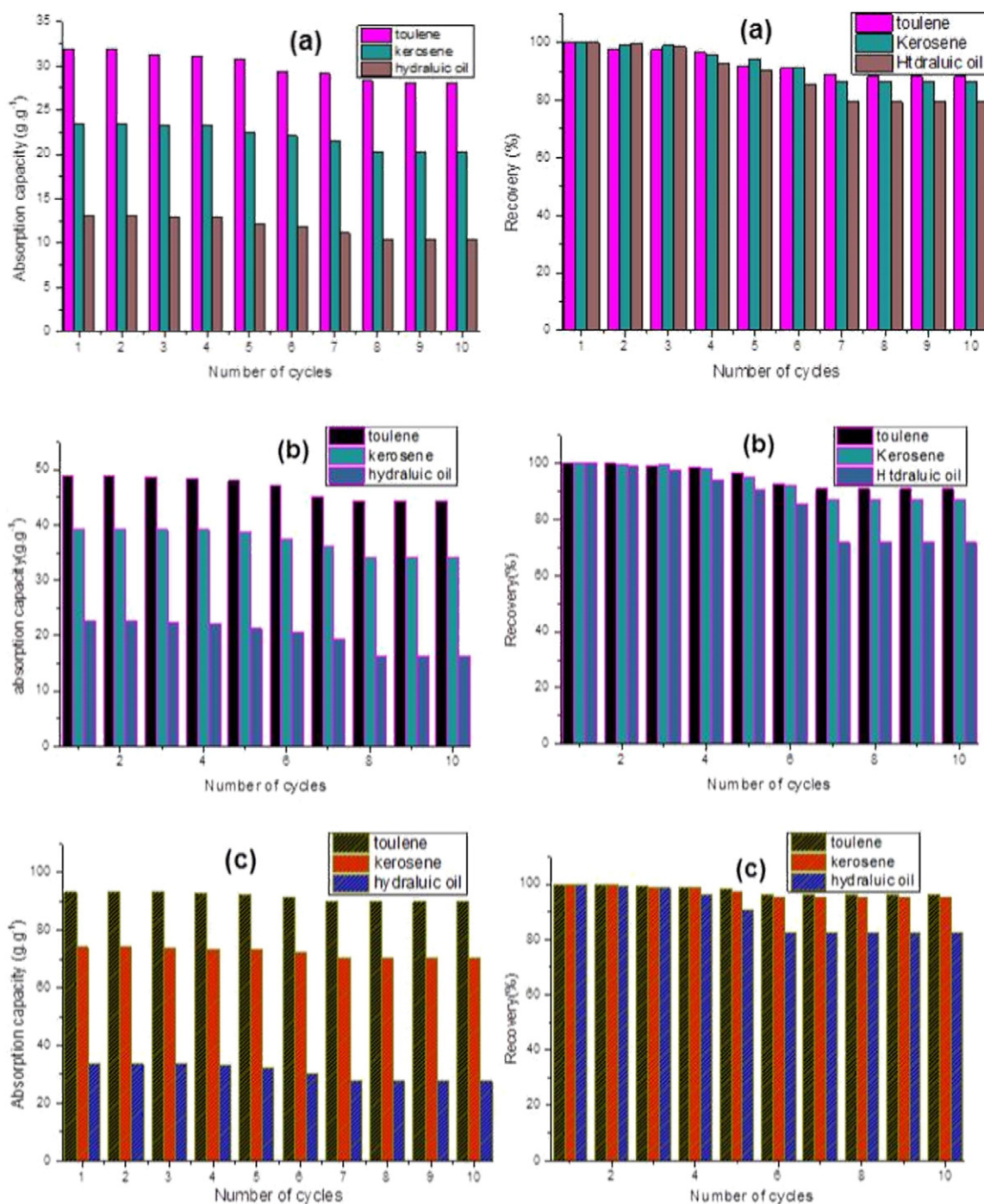


Fig. 9. Repeated absorption capacity and adjacent recovery (%) of nanoblends for selected oil sorption: (a) PVAn, (b) PVAn/Ch, and (c) PVAn/St sorption cycles.

(3 × 3 mm). This method is more eco-friendly than heat treatment or burning off the oil reported previously (Wang et al., 2015a,b). Fig. 9 shows the reusability performances of the hydrophobic PVAn nanoparticle-based blends. Apparently, a decrease in the oil-sorption rate occurs only during the first six cycles with capacity that do not exceed approximately 1–6 g blend per gram of oil, which represent recoveries between 71.8% and 96.3%. Subsequently, the oil-sorption capacities appeared to become constant. Excellent reusability and recovery are attributed to the good mechanical properties and good hydrophobicity. In addition, the squeezed PVAn/St reached saturated absorption point rapidly once it was in contact with oils, regardless of the kind of oils, indicating specifically the PVAn/St nanoblend is an efficient oil absorbent and can be used in practical applications for oil spill cleaning.

4. Conclusion

Green/bio-based PVAn blends were prepared by surfactant-free emulsion polymerization using water/DMSO as cosolvent. PVAn binary blended with Ch and St was developed to fabricate strong mechanical nanoblends. The prepared PVAn/St exhibited rapid absorption rate within 10 min. The saturated absorption capacities were up to 93.1 g/g with PVAn/St, which is approximately 2.77 times higher than that of PVAn and 1.25 times higher than that of PVAn/Ch. When using oil/water mixture, as a simulated oil slick system, the nanoblends showed higher absorption capacity and excellent selectivity. The absorbed oils can be recycled by applying manual pressure by simply rolling the nanoblends with hand, and an oil recovery rate of 96.3% was attained. Nanonetwork,

strong mechanical property, and hydrophobic surface can contribute to superior performance, which gives an ideal solution for absorbing oil spills by using these nanoblends.

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