

Preparation, Characterization and Application of Polyaniline/Epoxyde Polysiloxane Composite Films^{*}

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Abstract Composites of polyaniline (PAn) and epoxyde polysiloxane (EPSi) are reported for the first time. EPSi is designed, synthesized and *N*-grafted onto the PAn backbone through covalent bonds. As-prepared EPSi-g-PAn composites are soluble in organic solvents and the corresponding films can be easily produced *via* a simple solution-casting procedure. The composite films combine the mechanical characteristics of EPSi and the chemical properties of PAn, enabling the facile introduction of the noble metal particles. The successful fabrication of the composites is confirmed by the investigation of the molecular structure, crystalline structure and microstructure of the materials. The resulting composite films containing noble metal particles are employed as the catalysts for the hydrogenation of phenol to produce cyclohexanone, which exhibit the convenience and recyclability for usage as well as the high catalytic activities, including the conversion ratio of 97%–100% and the selectivity as high as 84%–98%. The present work not only provides a new method to improve the processability of the conducting polymers but also describes a kind of composite materials that may display outstanding performances in industrial catalysis.

Keywords: Polyaniline; Epoxyde polysiloxane; Catalyst support; Phenol hydrogenation.

INTRODUCTION

Polyaniline (PAn) is a conducting polymer that has been attracting increasing attention because of its simple and reversible doping/dedoping chemistry enabling control over properties such as electrical conductivity, free-volume and optical activity^[1–3]. Nevertheless, polyaniline is difficult to be processed due to its insolubility in common solvents and infusibility^[4]. To achieve improved processability and mechanical properties, composite materials have been produced by simply blending the conducting polymer with insulating matrix polymers^[5–7]. The problem can also be partially solved *via* copolymerization between polyaniline and conventional polymers with reactive functional groups, generating the so-called pseudo graft/block copolymers^[8, 9]. However, these approaches usually result in poor mixing uniformity as well as decreased conductivity^[10]. To date, techniques for the preparation of composites containing conducting polymers are still urgent to be improved, in order to satisfy the increasing demands for practical applications^[11].

On the other hand, polysiloxanes (PDMS) have wide applications in industrial areas, resulting from the

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unique alternating silicon-oxygen (Si—O) units, which endow the materials with good flexibility, high or low temperature stability, environmental perdurability and film-formability^[12]. Moreover, PDMS can be facilely functionalized with sulfonic, amine, carboxyl and carbonyl groups, *via* copolycondensation or ring-opening polymerization of functional monomers, or direct hydrosilylation between olefins and poly(methylhydrosiloxane) (PMHS)^[13]. By combining the characters of functional PDMS and PAn through suitable approaches, it is possible to fabricate novel composite materials with outstanding and controllable properties^[14]. Recently, we have reported a new class of composites composed of PAn and carbonyl-functionalized PDMS, in which the hydrogen bonding between the amine or imine sites of PAn and the carbonyl groups of PDMS is believed to play a key role for the formation of the materials^[15]. However, up to our knowledge, no studies have been devoted to synthesize covalent-bonded PAn/PDMS composites *via* *N*-grafting of PAn, which is an important and routine reaction to modify PAn materials^[16, 17].

In the present paper, for the first time we describe a kind of PAn/PDMS composites prepared by chemical grafting with covalent bonds. PDMS with the side chains capped by the epoxy groups is designed and synthesized. By the *N*-grafting of such epoxide PDMS (EPSi) onto PAn, the organic solvent-soluble EPSi-g-PAn composites are obtained successfully and the corresponding films are fabricated through a simple solution-casting process. The composite films are further combined with particles of noble metals, and the resulting films containing metal catalysts are employed to induce the hydrogenation of phenol to synthesize cyclohexanone. The molecular structure, crystalline structure and microstructure of the composites are investigated attentively, and the catalytic performances of the composites are determined to be remarkable based on the measurements of the conversion ratio and the selectivity.

EXPERIMENTAL

Materials

Aniline (An) monomer was purchased from Aldrich and distilled under reduced pressure before use. Poly(methylhydrosiloxane) (PMHS, containing 0.46 wt% of reactive —H, M_n 1300), divinyl-terminated polymethylsiloxane (VPMS, M_n 930), vinyl alkoxy-terminated ether (F_6 , M_n 240) and chloroplatinic acid (H_2PtCl_6 , 80% isopropyl alcohol solution) were supplied by Nanjing Si Xin Co. Ltd., China. Allyl glycidyl ether (AGE) was obtained from Aladdin. Potassium tetrachloroplatinate (K_2PtCl_4), palladium chloride ($PdCl_2$), rhodium trichloride hydrate ($RhCl_3 \cdot nH_2O$), sodium hydride (NaH) and ammonium persulfate (APS) were purchased from Wanqing Co. in Nanjing, China. All other chemicals were analytical grade reagents and used as received.

Synthesis of Epoxide Polysiloxane (EPSi)

The hydrosilylation of AGE, F_6 and VPMS with PHMS was carried out in toluene at 120 °C. The total molar concentration of AGE, F_6 and VPMS was roughly equal to that of the available Si—H groups in PMHS. In a typical reaction, 100 μ L of the H_2PtCl_6 catalyst solution was added to a mixture of 6.0 g of PMHS (containing 27.6 mmol of Si—H), 1.87 g (16.4 mmol) of AGE and 1.29 g (1.4 mmol) of VPMS in 100 mL of toluene. The solution was kept at 120 °C for 6 h. Then 1.98 g (8.3 mmol) of F_6 was added into the mixture, and the reaction continued at 120 °C for another 6 h. The solvent was then evaporated to obtain the clear and highly viscous polymer with 83% yield.

Synthesis of the Leucoemeraldine Base of PAn (LEB)

Typically, 4.65 g (50 mmol) of An monomer was dissolved in 800 mL of 1 mol/L hydrochloric acid (HCl), and then 11.4 g (50 mmol) of APS dissolved in 50 mL of 1 mol/L HCl was added slowly with vigorous stirring. The reaction mixture was agitated magnetically for 24 h at room temperature. The formed precipitate was subsequently filtered, collected and dried in vacuum at 60 °C for 10 h, resulting in a green powder of the emeraldine salt of PAn. The product was then dedoped in excess 0.1 mol/L ammonia water ($NH_3 \cdot H_2O$) for 12 h to obtain the emeraldine base (EB) and dried in vacuum at 60 °C. The fully reduced LEB was prepared by refluxing the EB powder in 120 mL of phenylhydrazine at 120 °C for 24 h. The reaction mixture was filtered and washed exhaustively with methanol. Upon drying under vacuum at 80 °C for 20 h, a gray powder of the LEB of PAn was obtained with 75% yield.

N-grafting of PAn with EPSi (EPSi-g-PAn)

380 mg (15.8 mmol) of NaH was dissolved in 80 mL of dimethyl sulfoxide (DMSO). 1.3 g of LEB (7.2 mmol based on the repeating unit) was added to the solution, and the mixture was allowed to react at 40 °C for 24 h. Then 4.9 g of EPSi (containing 14.4 mmol epoxide groups) was added, so that the mole ratio of the repeating unit in LEB to the epoxide group in EPSi was 1:2. The reaction was kept at 30 °C for 24 h, and then the black mixture was poured into water, centrifuged, washed with toluene and dried under vacuum at 40 °C to get the EPSi-g-PAn product with 53% yield.

Preparation of EPSi-g-PAn Films and Combination with Noble Metal Catalysts

The EPSi-g-PAn samples were dissolved in *N*-methyl-2-pyrrolidone (NMP) to form 40 wt% solutions. The solutions were cast onto glass plates and heated in a constant temperature oven at 50 °C for 24 h to evaporate the solvent and form EPSi-g-PAn films. Without any additives added, three pieces of 1 cm² of the films were immersed into 20 mL of K₂PtCl₄, PdCl₂ and RhCl₃ (5 mmol/L in 0.1 mol/L HCl) aqueous solutions, respectively, and refluxed at 130 °C for 24 h. Then the composite films were taken out, washed with water, and dried under environmental temperature.

Hydrogenation of Phenol and Testing of Catalytic Activity

Briefly, the hydrogenation of phenol was carried out in a 100 mL stainless steel autoclave with a magnetic stirrer^[18]. In a typical experiment, after the adequate catalyst, 200 mg of phenol and 10 mL of water were added, the reactor was purged with H₂ for 20 min to remove the air inside the system. Then the reaction mixture was heated up to 100 °C with stirring. The products were periodically extracted, analyzed and identified by GC-MS. Conversion ratio (*C*) of phenol and selectivity (*S*) of cyclohexanone were calculated according to the following equations:

$$C = \frac{\text{mole of reacted phenol}}{\text{mole of initial phenol}} \times 100\%$$

$$S = \frac{\text{mole of cyclohexanone formed}}{\text{mole of initial phenol}} \times 100\%$$

Characterization

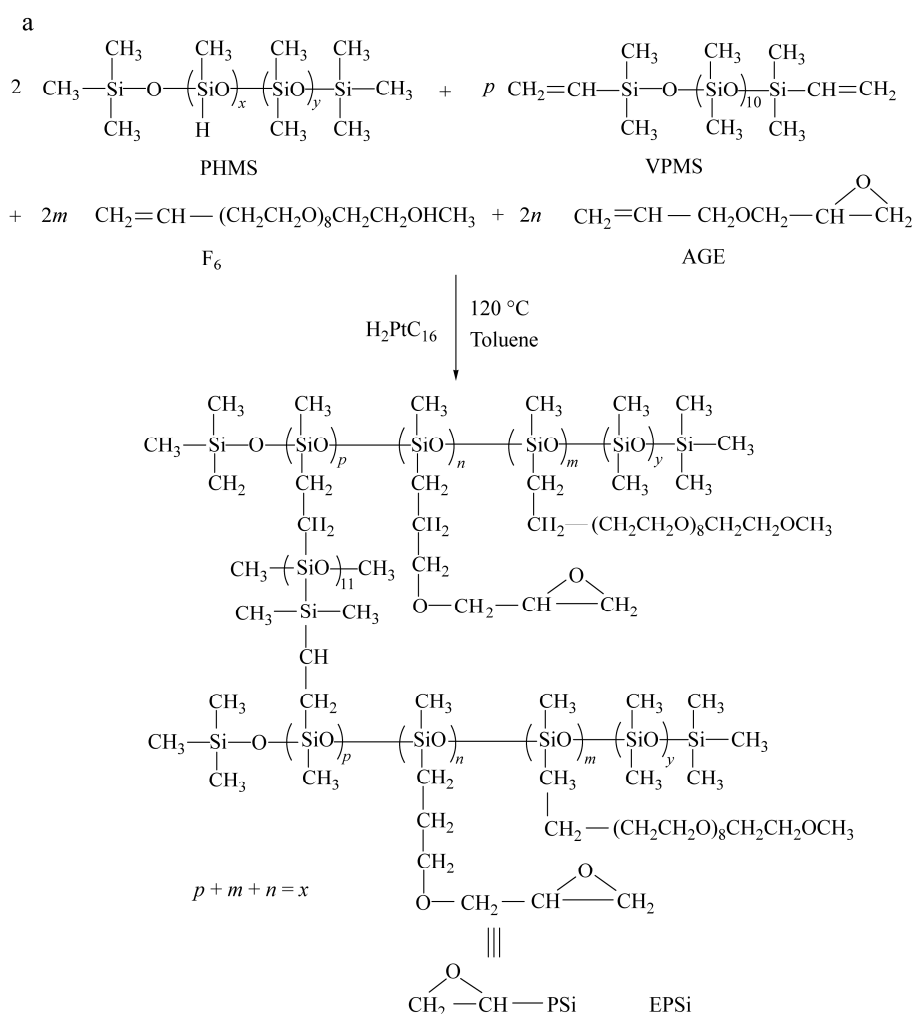
Number-average molecular weights (*M_n*) of the EPSi-g-PAn samples were determined by gel permeation chromatography (GPC, Waters 1515). Fourier-transform infrared spectra (FTIR) were recorded on a Bruker VECTOR22 spectrometer. UV-Vis absorption spectra were recorded on a UV-2401 spectrometer (Shimadzu, Japan). The EPSi-g-PAN samples were dissolved in DMSO-*d*₆ for ¹H-NMR measurements on a Bruker DRX-500 instrument. The morphologies of the resultant samples were characterized using scanning electron microscopy (SEM) with a HITACHI S-4800 instrument (Hitachi, Japan). Before SEM imaging, the samples were coated indirectly on a support tape and sputtered with thin layers of gold. The electrical conductivities were measured *via* the four-probe method at room temperature. The mechanical property was tested by the tensile stress-strain measurements (INSTRON 4466, Instron Co., England) at room temperature. Rectangular films with the dimension of 50 mm × 10 mm × 0.1 mm were examined at a crosshead speed of 2.0 mm/min to determine the tensile strength and the elongation at break. Gas chromatograph-mass spectroscopic analysis (GC-MS) was performed on GCMS-QP 2010 plus (Shimadzu, Japan). An inductively coupled plasma mass spectrometer (ICP, Perkin-Elmer SCIEX, Thornhill, Canada) was also used. X-ray photoelectron spectroscopy (XPS, ESCALB MK-II, VG Co., England) was performed under a base pressure of 1 × 10⁻¹³ MPa, using monochromatized Mg Kα X-rays, at *hν* = 1253.6 eV. Wide-angle X-ray diffraction (XRD) was taken with a Rigaku d/Max-Ra diffractometer using Ni-filtered Cu Kα radiation. The average crystalline size of the Pt, Pd and Rh particles was calculated according to the Scherer's equation on peaks of Pt(220), Pd(220) and Rh(220):

$$D = \frac{k \lambda}{\beta \cos \theta}$$

where $k = 0.9$, λ (the X-ray wavelength for Cu radiation) = 0.154056 nm, β is the half-height peak width, θ is the Bragg angle corresponding to the peak maximum, and D denotes the average diameter of the crystal pellets.

RESULTS AND DISCUSSION

The reaction mechanism for the synthesis of EPSi-g-PAn is proposed schematically in Fig. 1, which is also supported by several polymerization reactions in previous reported works^[19, 20]. In this way, two kinds of EPSi have been fabricated by the hydrosilylation of PMHS, VPMS, F₆ and AGE, employing different prescriptions (Table 1). Subsequently, partial deprotonation of —NH— groups in LEB is promoted using NaH in DMSO. The formed anions of LEB bring out the scission of epoxy groups and the formation of EPSi-g-PAn. The sample prepared without F₆ is denoted as EPSi-g-PAn-1, while the sample prepared with F₆ is denoted as EPSi-g-PAn-2 (Table 1). GPC measurements reveal that the M_n value increases from 5800 (the starting LEB) to 1.75×10^4 and 1.35×10^4 for the two samples, respectively, indicating that EPSi has been successfully grafted onto the LEB backbone. In the EPSi-g-PAn composites, the content of PAn is determined to be 7 wt%–10 wt%, depending on the prescription and the analytical methods.



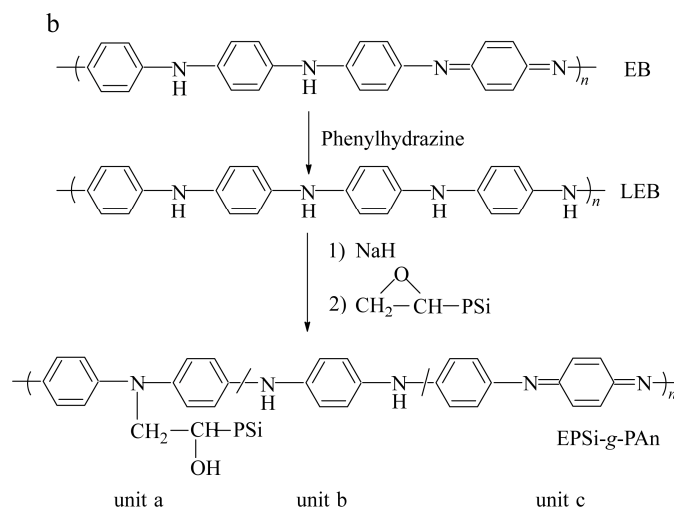


Fig. 1 Schematic description of the procedure for the preparation of EPSi-g-PAn: (a) synthesis of EPSi and (b) *N*-grafting of PAn with EPSi

Polymer	Prescription (g)				Analytical result	
	PMHS	VPMS	F ₆	AGE	M_n^a (g/mol)	PAn content (wt%)
LEB	—	—	—	—	5800	—
EPSi-g-PAn-1	6.00	3.84	—	2.20	1.75×10^4	9.56 ^b /8.71 ^c
EPSi-g-PAn-2	6.00	1.29	1.98	1.87	1.35×10^4	7.85 ^b /7.01 ^c

^a Measured by GPC; ^b Calculated from the data of content analysis of nitrogen element; ^c Determined by the ¹H-NMR method

The fully reduced LEB is used in this study in order to enhance the grafting ratio and avoid the side reactions, such as the cross-linking reaction^[21]. The UV-Vis absorption spectra prove the successful synthesis of LEB (Fig. 2). The spectrum of EB consists of two absorption maxima at around 325 nm and 630 nm, which are attributable to the δ - δ^* transition of the benzenoid rings and the absorption of the quinoid rings, respectively. For LEB, only one absorption peak is observable at 340 nm, originating from the π - π^* transition of the benzenoid rings^[22].

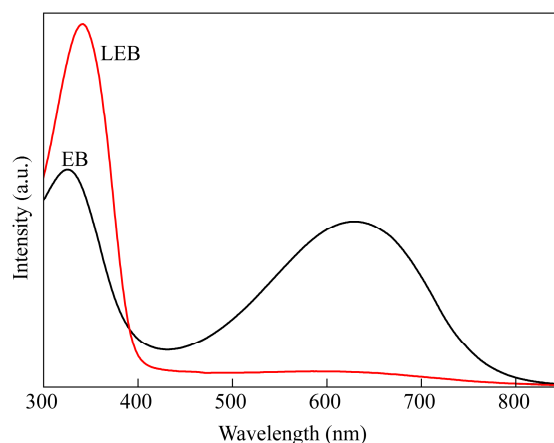


Fig. 2 UV-Vis absorption spectra of EB and LEB

As shown in Fig. 3, the FTIR spectra of EPSi-g-PAn-1 and EPSi-g-PAn-2 show the characteristic bands at 1120–1000 cm⁻¹ for —Si—O— stretching and 1258 cm⁻¹ for —Si—CH₃ stretching^[23]. For LEB, the bands at 1579 and 1487 cm⁻¹ are due to the quinoid and benzenoid ring deformation, and the band at 1280 cm⁻¹ is

assigned to $-\text{C}-\text{N}-$ stretching of a secondary aromatic amine^[24]. Comparatively, in the EPSi-g-PAn composites, the band corresponding to the benzenoid ring deformation shifts to 1496 cm^{-1} , while the $-\text{C}-\text{N}-$ stretching band shifts to 1295 cm^{-1} . Such spectral results imply the transformation of the molecular structure of the PAn component and provide another evidence for the grafting reaction between PAn and EPSi^[25].

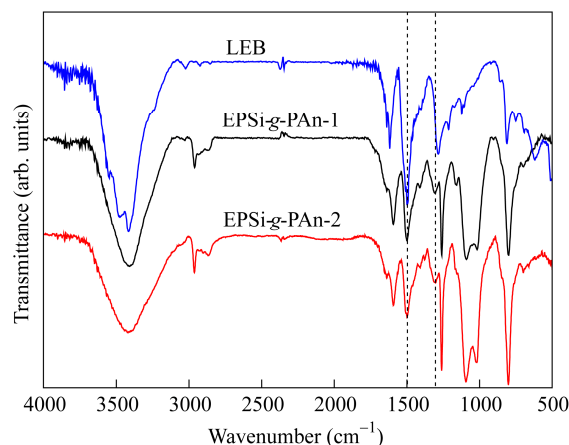


Fig. 3 FTIR spectra of LEB, EPSi-g-PAn-1 and EPSi-g-PAn-2

Figure 4 presents the ^1H -NMR spectra of EPSi-g-PAn-1 and EPSi-g-PAn-2 samples dissolved in $\text{DMSO}-d_6$. Four sets of peaks appear in the ranges of 0–0.2, 1.0–1.2, 2.4–2.8 and 3.2–3.6, which are ascribed to the hydrogens from $-\text{Si}-\text{CH}_3$, $-\text{Si}-\text{CH}_2-$, $-\text{C}-\text{CH}_2-$ and $-\text{CH}_2-\text{O}-$, respectively. In addition, peaks due to the hydrogens of the terminal $-\text{OH}$ at the grafted side chains (see Fig. 1b, unit a) appear in the range of 4.6–4.7, and the peaks at 7.0–7.3 are assigned to the hydrogens in the PAn rings^[15]. Again, the ^1H -NMR measurements testify the formation of the EPSi-g-PAn composites.

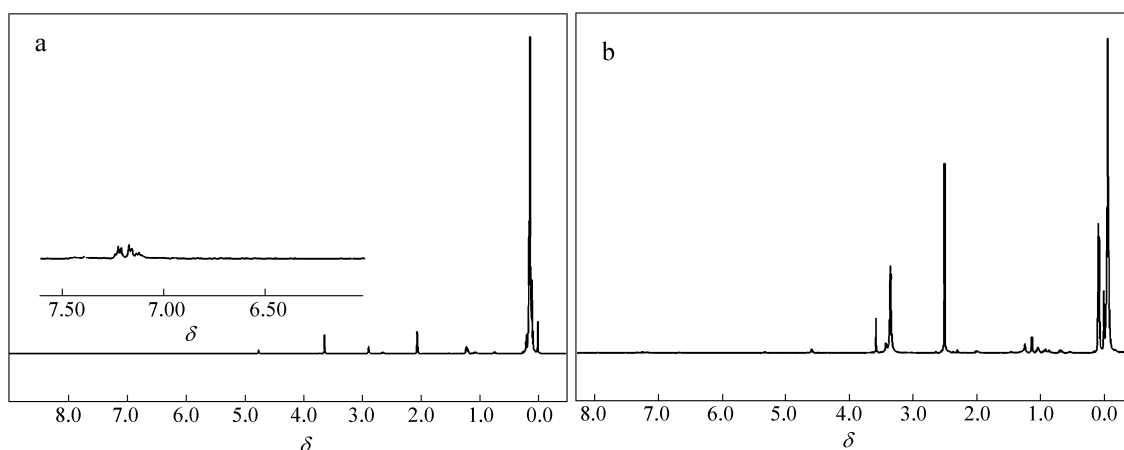


Fig. 4 ^1H -NMR spectra of (a) EPSi-g-PAn-1 and (b) EPSi-g-PAn-2

The as-prepared EPSi-g-PAn powders can be easily dissolved in organic solvents, such as NMP, and the corresponding films can be facily fabricated *via* the solution-casting process (see the Experimental section). After being protonated in 1 mol/L HCl solution, the doped composite films display electrical conductivities of 2.0×10^{-3} and $0.6 \times 10^{-3}\text{ S/cm}$ for EPSi-g-PAn-1 and EPSi-g-PAn-2, respectively. The data are lower than those of common protonated PAn^[26], however, these composite films may still be directly applied in the fields like antistatic and/or anticorrosive coatings^[27], where the electrical properties can satisfy the practical demands.

On the other hand, the composite films present favorable mechanical toughness, resulting from the excellent mechanical properties of the EPSi component^[28]. The stress-strain behavior of the composite films is shown in Fig. 5. The tensile strength and elongation at break of the EPSi-g-PAn-1 film are 4.3 MPa and 7.6%, respectively, while the EPSi-g-PAn-2 film breaks at a stress of 3.9 MPa and a strain of 8.1%. The improvement of the processability may be more important, which may remarkably enlarge the application fields for the composite materials. As an example, we employ the EPSi-g-PAn films as the catalyst supports for the hydrogenation of phenol to synthesize cyclohexanone, which is a significant reaction for the fabrication of Nylon-6 in the industrial production^[29].

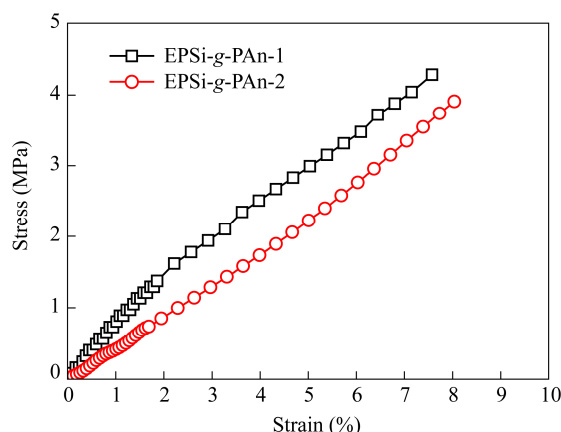


Fig. 5 Tensile stress-strain curves of EPSi-g-PAn-1 and EPSi-g-PAn-2 films

It has been reported that the particles of noble metals, such as platinum (Pt), palladium (Pd) and rhodium (Rh), possess the catalytic activity for the hydrogenation of phenol, and are typically synthesized from the metal ion solutions with low concentrations^[30]. In our work, choosing EPSi-g-PAn composite films as the catalyst support, five main advantages should be concerned. Firstly, PAn has quinoid (Q) and benzenoid (B) units along with amine and imine functional moieties, which can hold the metal complexes through nitrogen-metal coordination bond^[31]. Secondly, under certain conditions, PAn can play the role of the reducing agent and spontaneously induce the reduction of the metal ions^[32]. Therefore, no additive reducing agent is needed for the formation of the noble metal particles. Thirdly, the alternating silicon-oxygen units of EPSi endow the composite films with improved processability and mechanical properties, and the as-modified films combining the characteristics of PDMS with the PAn component are reported for the first time. Fourthly, in comparison with ordinary metal-PAn particles, the present composite films can be directly taken out from the catalytic system and facilely reused, which is important economically for the recovery of the noble metals^[33]. Finally, although some metal-PAn catalyst systems have been employed as the electrical-catalyst for the hydrogenation of unsaturated compounds^[34, 35], up to our knowledge, no studies have been devoted to the hydrogenation of phenol using modified PAn films as the chemical-catalyst.

The introduction of noble metal catalysts is accomplished simply by immersing the EPSi-g-PAn-1 films into the dilute solutions of the metal ions, and the formation and loading of the metal particles take place automatically upon heating. Figure 6 shows the SEM images of the surfaces of the EPSi-g-PAn/catalyst composite films prepared with and without stirring. It can be seen that Pt, Pd and Rh particles are generated without the addition of any reducing agents or structure-directing agents, which can be ascribed to the reductive characteristics of the PAn component in the composite films^[32]. It should be noted that the metal particles are smaller, more uniform, less aggregated and easier for deposition when the samples are prepared without stirring. It seems that the mechanical shearing may disturb the formation and deposition process of the metal particles. According to the SEM images, Pd and Rh particles are approximately spherical, and the diameters are about

50–100 nm (Figs. 6e and 6f). Interestingly, for the EPSi-g-PAN/Pt films, regular tetragonal prisms of Pt with a diameter of about 200 nm are detected on the surface of the composite films (Fig. 6d), suggesting that, in addition to chemical reduction, the EPSi-g-PAN films may also have the function of structure-directing for the formation of the microstructures^[36].

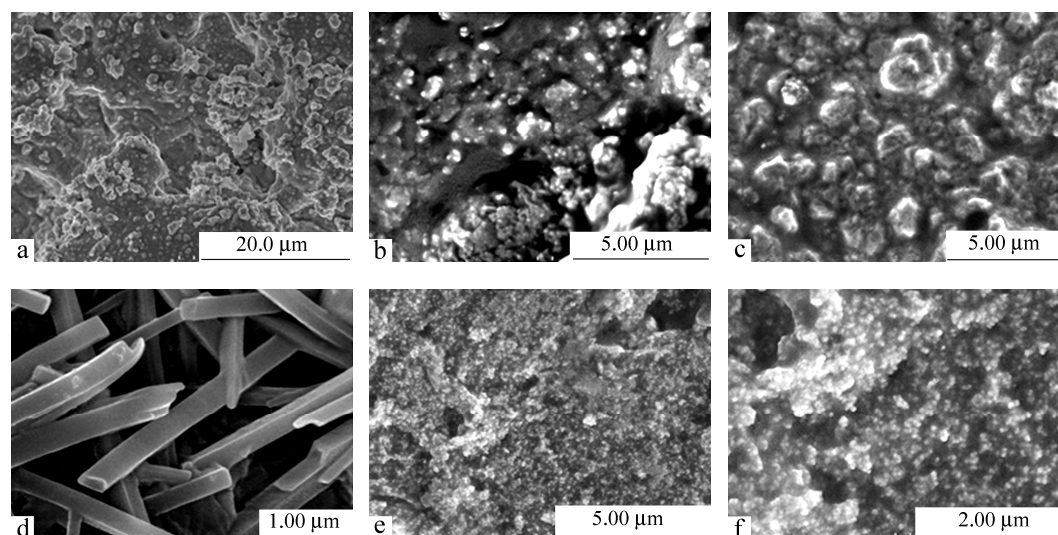


Fig. 6 SEM images of the surfaces of EPSi-g-PAN-1 films combined with (a, d) Pt, (b, e) Pd and (c, f) Rh particles (Synthetic condition: (a–c) with stirring, (d–f) without stirring)

The XRD patterns of the EPSi-g-PAN/catalyst films prepared without stirring are revealed in Fig. 7. As can be seen, all of the patterns contain broad reflections in the 2θ range of 15° – 38° , which correspond to the amorphous polymer phase^[37]. Additionally, the major diffraction peaks of Pt, Pd and Rh particles are observed^[35]. All peaks between 40° and 90° can be indexed as the Pt, Pd and Rh crystals with face-centered cubic (fcc) structures. For the EPSi-g-PAN/Pt film, the peaks at 40.9° , 47.6° , 68.7° and 82.4° are assigned to Pt(111), Pt(200), Pt(220) and Pt(311) crystalline plane diffraction peaks, respectively. For the EPSi-g-PAN/Pd film, the peaks at 40.9° , 47.6° , 68.8° and 82.8° are ascribed to Pd(111), Pd(200), Pd(220) and Pd(311) crystalline plane diffraction peaks, respectively. For the EPSi-g-PAN/Rh film, the peaks at 41.4° , 48.5° and 70.3° are

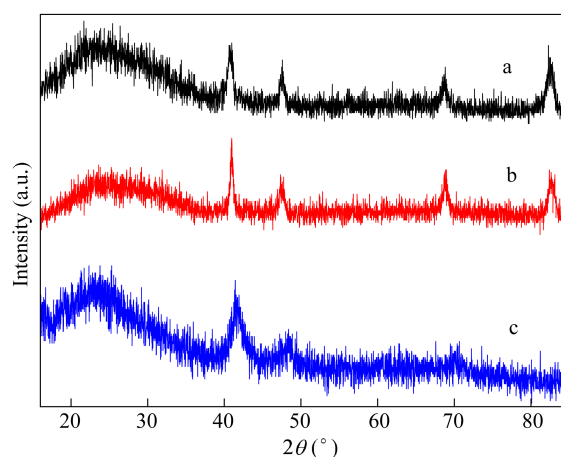


Fig. 7 XRD patterns of the composite films of (a) EPSi-g-PAN/Pt, (b) EPSi-g-PAN/Pd and (c) EPSi-g-PAN/Rh (The films were prepared without stirring.)

attributed to Rh(111), Rh(200) and Rh(220) crystalline plane diffraction peaks, respectively. According to the Scherer's equation^[35], the average sizes of the crystallites present in the samples have been calculated to be 4.38, 5.04 and 3.54 nm for Pt, Pd and Rh, respectively.

Although the presence of metallic Pt, Pd and Rh in the systems is confirmed by the XRD measurements, XPS analysis is carried out to provide further information about the electronic state of the noble metal and verify if they are deposited onto the films only in the metallic state. As displayed in Fig. 8, the Pt(4f) line shows a pair of peaks from the spin-orbital splitting of the $4f_{7/2}$ and $4f_{5/2}$ regions due to metallic Pt (71.0 eV) and oxide species (74.0 eV), respectively^[38]. The two peaks imply approximately the ratio of metallic Pt^0 to the oxide species is 50:50. Low-binding-energy doublet at 335.0 eV ($Pd3d_{5/2}$), 340.0 eV ($Pd3d_{3/2}$) and 308.0 eV ($Rh3d_{5/2}$), 311.0 eV ($Rh3d_{3/2}$) are attributed to the Pd^0 and Rh^0 species, indicating the presence of Pd and Rh metal particles, respectively^[39]. In the present case, XPS results prove that the EPSi-g-PAN/catalyst films have a Pt^0 loading content of about 50%, while the values for Pd^0 and Rh^0 is almost 100%. Herein, it should be pointed out that for the EPSi-g-PAN/Pt film, the higher binding energy component is due to Pt^{IV} species such as PtO_2 or $Pt(OH)_4$, and it is quite difficult to determine what oxygen-containing groups, O^{2-} , OH^- or H_2O , are bonded to the platinum^[40].

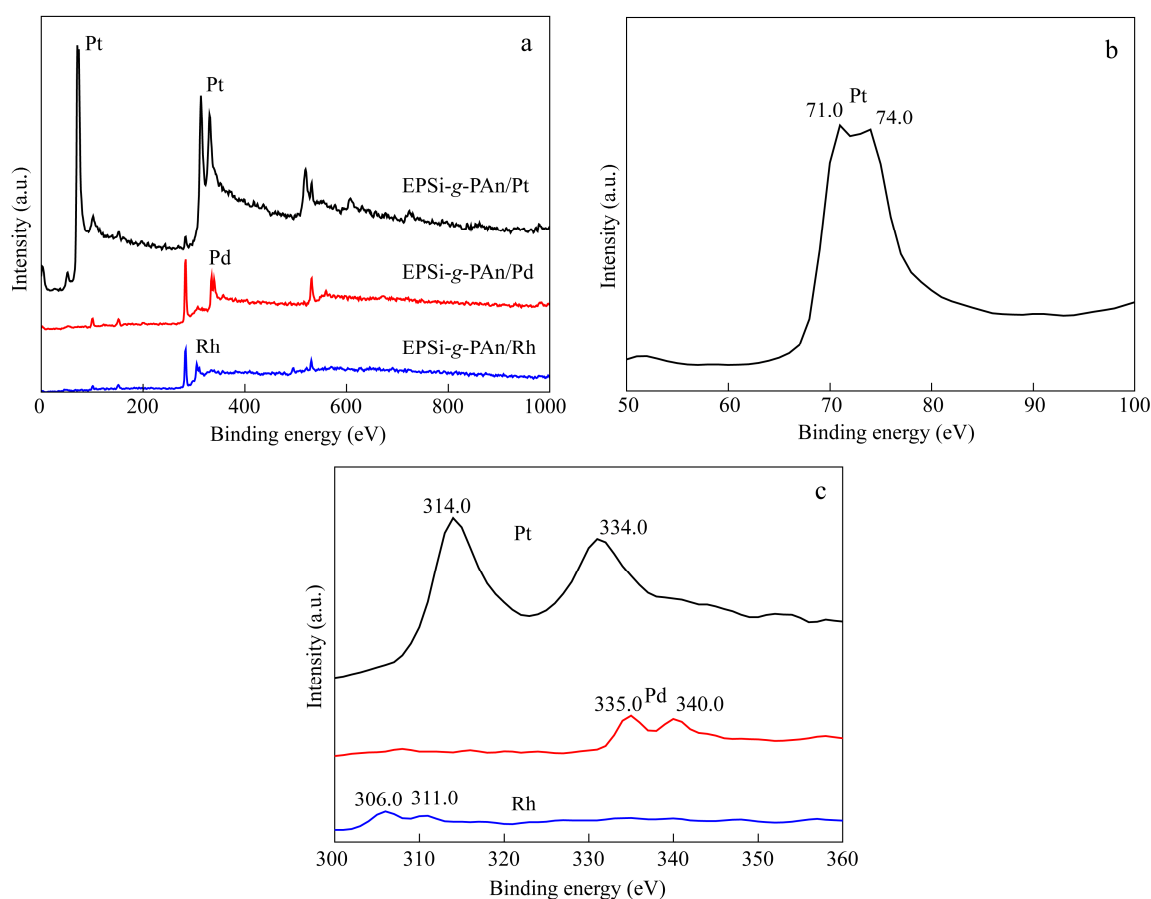


Fig. 8 (a) XPS spectra of the EPSi-g-PAN/catalyst composite films, and magnified curves for (b) Pt(4f) and (c) Pt(4d), Pd(3d), Rh(3d) bands (The films were prepared without stirring.)

The EPSi-g-PAN films combined with noble metals can be employed as the catalytic materials for the hydrogenation of phenol by directly immersing the composite films into the reaction systems. The catalytic performances are listed in Table 2. Excellently, the conversion ratio of phenol can readily achieve 97%–100% in 90 min, while the selectivity of cyclohexanone is in the range of 84%–98%. For comparison, the conversion

ratio is 80% with a selectivity of 74% when commercial Pd@C catalyst is used^[18]. It has been reported that the hydrogenation reaction occurs mainly between the phenol molecules adsorbed on the support nearby the metal particles and the hydrogen molecules activated on the metal sites^[41]. Hence, it is reasonable to believe that the nature of the supports and the methods for the loading of the noble metals determine the morphology, size and distribution of the metal particles, and in turn influence the catalytic activities through the electronic interactions. Although a range of materials, including zeolites, activated carbon, graphite and carbon nanotube, has been applied as the supporting materials for the Pt-, Pd- and Rh- based catalysts^[42–45], the EPSi-g-PAN films described in the present work are outstanding for the high conversion ratio and selectivity of the corresponding catalytic films. Additionally, from the data in Table 2, it seems that the EPSi-g-PAN/Pd and EPSi-g-PAN/Rh films are more effective than the EPSi-g-PAN/Pt film. Such result may be reasoned from the fact that the particle size of Pt is much larger than that of Pd and Rh, while the content of the metallic state is lower for the EPSi-g-PAN/Pt film, which have been detected through the SEM and XPS measurements, respectively.

Table 2. Catalytic performances of the EPSi-g-PAN films containing noble metals

Catalytic film	Quality of film (g)	Metal content ^a (wt%)	Conversion ratio ^b (%)		Selectivity ^c (%)
			50 min	90 min	
EPSi-g-PAN/Pt	0.072	15.6	45	97	84
EPSi-g-PAN/Pd	0.068	8.3	88	100	93
EPSi-g-PAN/Rh	0.182	3.1	79	99	98

^a Determined by ICP analysis; ^b Measured by GC-MS; ^c Measured by GC-MS after reacting for 90 min
The catalytic reaction was carried out in 10 mL of aqueous solution containing 200 mg of phenol.

Furthermore, the EPSi-g-PAN/catalyst films are found to be recyclable for the hydrogenation of phenol. After the simple separation by directly taking the films out from the reaction solution, the samples are investigated using XPS, from which it is discovered that the loading contents of the noble metals are decreased by only 2%–4%. According to SEM measurements, no obvious difference of the microscopic morphology is detected for the films after the cycling test. The low loss of the catalytic metals and the stability of the EPSi-g-PAN/catalyst films make the composites potential candidates as catalytic materials in the industrial production.

CONCLUSIONS

In summary, we have reported a kind of EPSi-g-PAN composites for the first time. EPSi is designed, synthesized and compounded with PAN through *N*-grafting reaction. Corresponding films are prepared *via* a simple solution-casting procedure. As-produced composite films combine the mechanical characteristics of EPSi and the chemical properties of PAN, which enables the facile introduction of the noble metal particles to form EPSi-g-PAN/catalyst films. The molecular structure, crystalline structure and microstructure of the materials are analyzed systematically to confirm the successful synthesis of the composites. The resulting composite films containing noble metal particles are found to possess high catalytic activities for the hydrogenation of phenol, leading to the conversion ratio of 97%–100% and the selectivity as high as 84%–98%. Industrially, the composites described in this work may be applied in a variety of catalytic systems because of the excellent performances, the usage convenience and the recyclability of the materials.

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