

# Preparation of conducting composite particles of styrene–methyl acrylate copolymer as the core and graphite-incorporated polypyrrole as the shell by surfactant-free mini emulsion polymerization

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**Abstract** A series of nearly monodispersed poly(styrene–methyl acrylate) (SMA) copolymer latex particles were coated with polypyrrole having different graphite contents. The composite particles were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The d.c. conductivity and the electrochemical behaviour of the particles were studied by using a standard four-probe method and a cyclic voltameter respectively. The dependence of electrical conductivity of the composites on the concentration of graphite in the polypyrrole shell, the methyl acrylate content in SMA copolymer and the temperature was also investigated. The electrical conductivity of the samples can be tuned by varying the graphite content in the polypyrrole shell phase. The d.c. conductivity decreases with increasing methyl acrylate content in the core particles. Electrochemical study (at a scan rate of  $50 \text{ mV s}^{-1}$ ) reveals that the particles are sufficiently stable under redox potential and should find potential applications in various optoelectronic devices.

**Keywords** Core-shell · Mini-emulsion · Graphite · Copolymer

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## Introduction

Since their discovery in 1977 conducting polymers have been the subject of intensive research due to their many potential applications in organic electronics [1, 2]. However, there are serious processing and stability problems associated with pristine conducting polymers. Polymers like polypyrrole and polyaniline show excellent conductivity but they are often brittle in nature and have very poor film forming ability. Therefore considerable interest has recently been shown in combining conducting polymers with insulating polymers having good mechanical strength to produce core-shell conducting composites. These composite particles have manifold applications such as antistatic coatings, dampers, clutches, electrodes, separation membranes, electrochromic devices, electrochemomechanical actuators, and sensors [3, 4]. Core-shell conducting composites have two advantages. Firstly, depending on the type of core latex used, these conducting polymer-coated latex particles can have very good mechanical and processing properties. Moreover, the amount of conducting polymer used can be greatly reduced with an insulating polymer without much loss of conductivity by synthesizing a very thin conducting shell around the non-conducting latex core [5].

Latex particles coated with conducting polymers were first reported in 1987 [6]; and subsequently this approach has found widespread use [7–10]. Since 1995, Armes et al. have published a series of papers describing the coating of micrometre-sized polystyrene (PS) latexes with various conducting polymers, such as polypyrrole (PPy) [11], polyaniline (PAn) [12] and poly(3,4-ethylenedioxythio-

phene) (PEDOT) [13]. These authors also described a detailed study of the surface composition and morphology of these micrometre-sized, polypyrrole-coated polystyrene latexes. Other workers [14] synthesized styrene–butadiene latexes coated with polypyrrole using the  $\text{H}_2\text{O}_2$ – $\text{HBr}$ – $\text{Fe}^{3+}$  oxidant system. Huijs et al. [5, 14, 15] described the preparation of poly(butyl methacrylate) (PBMA) latex particles coated with polypyrrole and focussed on the influence of the amount of polypyrrole on the morphology and the conductivity of the core-shell latex particles. These authors also studied the effects of the thickness of PPy shell, the annealing temperature and the nature of the counter-anion on the film-forming ability of the latex. Ma et al. [16] prepared polyaniline/styrene–butadiene–styrene triblock copolymer (PANI/SBS) composite materials using emulsion polymerization techniques. Ruckenstein and Yang [17] obtained PANI/PS conducting materials using an oxidative polymerization method, in which sodium dodecylsulfate (SDS) aqueous solution was used as the continuous phase and benzene solution containing aniline and PS was used as the dispersed phase. Yassar et al. [18] also reported the polymerization of pyrrole using the  $\text{FeCl}_3$  oxidant in the presence of sulfonated polystyrene latexes. Liyan et al. [19] reported the preparation of conducting composite particles composed of styrene–butyl acrylate copolymers as the core and polypyrrole as the shell. Jang and Oh [20] successfully synthesized conducting-polymer nanoparticles with diameters of several nanometres by low temperature micro emulsion polymerization. Jang [21] reported the selective fabrication of amorphous polypyrrole nanoparticles with diameters of 2 nm, using micro emulsion polymerization at low temperature. Wang et al. reported the preparation of polyaniline-coated poly(styrene-*co*-styrene sulfonate) nanoparticles with diameters of 25–30 nm by using an in situ micro emulsion polymerization method [22].

In this paper we report the preparation of conducting core-shell particles with poly(styrene-*co*-methyl acrylate) (SMA) as the core and graphite-incorporated polypyrrole as the shell by surfactant-free mini emulsion polymerization. The dependence of electrical conductivity of the core-shell particles on the graphite content in the shell phase and temperature is investigated. We also report the effect of methyl acrylate content in the core phase on the conductivity of the composite particles.

## Experimental

### Materials

The monomers styrene (Sty) and methyl acrylate (MA) were obtained from Aldrich and washed with 4% NaOH

**Table 1** Conditions for the synthesis of core particles (values in grams)

| Ingredients                      | Core I | Core II | Core III | Core IV | Core V | Core VI |
|----------------------------------|--------|---------|----------|---------|--------|---------|
| Water                            | 120    | 120     | 120      | 120     | 120    | 120     |
| PVP                              | 0.7    | 0.7     | 0.7      | 0.7     | 0.7    | 0.7     |
| $\text{K}_2\text{S}_2\text{O}_8$ | 0.1    | 0.1     | 0.1      | 0.1     | 0.1    | 0.1     |
| Styrene                          | 5      | 5       | 5        | 5       | 5      | 5       |
| Methyl acrylate                  | 1      | 1.5     | 2        | 2.5     | 3.5    | 5       |

and distilled water to remove the inhibitors. Pyrrole (Aldrich), polyvinylpyrrolidone (PVP) (CDH Laboratory) and pure graphite (20  $\mu\text{m}$ ) (Aldrich) were used as received. Hydrochloric acid, potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ), methanol and ferric chloride were of analytical grade (Merck, Darmstadt, Germany) and used as received. Doubly distilled water was used for all purposes. All reactions were carried out under nitrogen atmosphere.

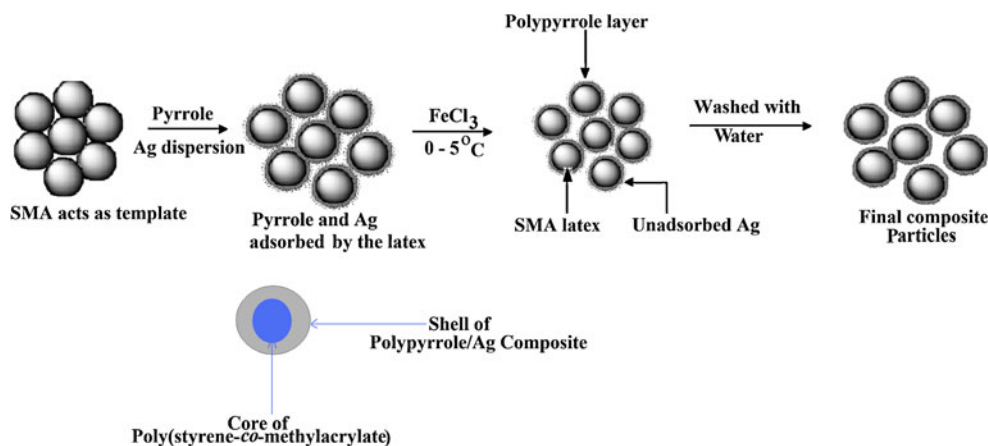
### Synthesis of styrene methacrylate latex (SMA)

The conditions for the synthesis of the core particles are given in Table 1. In a typical synthesis 120 mL of water was added to a 1-L resin kettle equipped with a mechanical stirrer, a nitrogen inlet, a condenser and a thermometer and purged with nitrogen for 0.5 h. Then 0.7 g PVP was added to the kettle and the temperature was raised to 70 °C; 0.1 g of  $\text{K}_2\text{S}_2\text{O}_8$  (in 10 mL water) was then added. A mixture of 5 g of styrene and 2 g of MA was added dropwise over 2 h via a dropping funnel whilst maintaining the reaction temperature at 70 °C. Polymerization was continued for a further 24 h and the mixture was then cooled to room temperature to afford the core latex.

**Table 2** Conditions for the synthesis of core-shell particles (values in grams)

| Ingredients       | CS I | CS II | CS III | CS IV |
|-------------------|------|-------|--------|-------|
| Core III particle | 4    | 4     | 4      | 4     |
| Water             | 50   | 50    | 50     | 50    |
| 5 M HCl           | 1    | 1     | 1      | 1     |
| $\text{FeCl}_3$   | 0.8  | 0.8   | 0.8    | 0.8   |
| Methanol          | 20   | 20    | 20     | 20    |
| Pyrrole           | 0.67 | 0.67  | 0.67   | 0.67  |
| Graphite          | 0    | 0.167 | 0.335  | 0.67  |

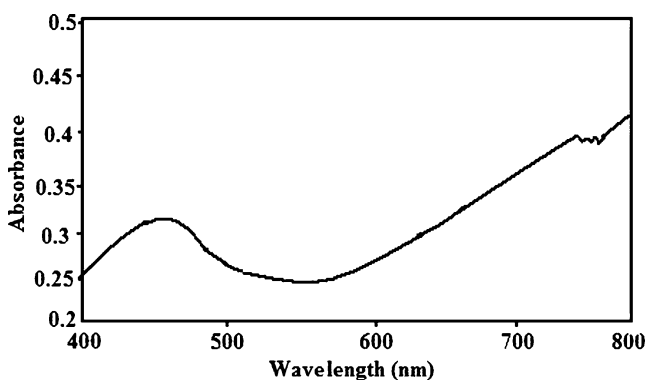
**Scheme 1** Schematic representation of the formation of the core-shell composite particles



### Synthesis of composite core-shell particles

A series of core-shell particles were prepared by taking core III (Table 1) as the core component. The conditions for the preparation of the core-shell particles are given in Table 2. In a typical synthesis an emulsion containing 4 g of the SMA latex (core III) was added to a three-necked round bottom flask equipped with a thermometer and dropping funnel and then diluted with 50 g of distilled water. The pH of the mixture was adjusted to around 1 by adding 1 g 5 mol/L HCl. To this latex 0.8 g of  $\text{FeCl}_3$  (in 20 g methanol), 0.67 g of pyrrole and varying amounts of graphite (0%, 0.25%, 0.50%, 1% w/v of pyrrole) were added in turn under a nitrogen atmosphere. The mixture was stirred for 24 h at 0 °C. The resulting black precipitates were isolated by filtration and washed several times with water and ethanol to remove unreacted monomer and unadsorbed graphite particles. The prepared composites were dried in a vacuum oven at 50 °C. A schematic representation of the synthesis is given in Scheme 1.

In another experiment a series of core-shell particles were prepared by taking different cores (cores I–VI of Table 1) as the core component. The graphite content in the polypyrrole shell phase was 1% in all the core-shell particles. All other ingredients were the same as stated in Table 2.



**Fig. 1** UV-visible spectrum of polypyrrole

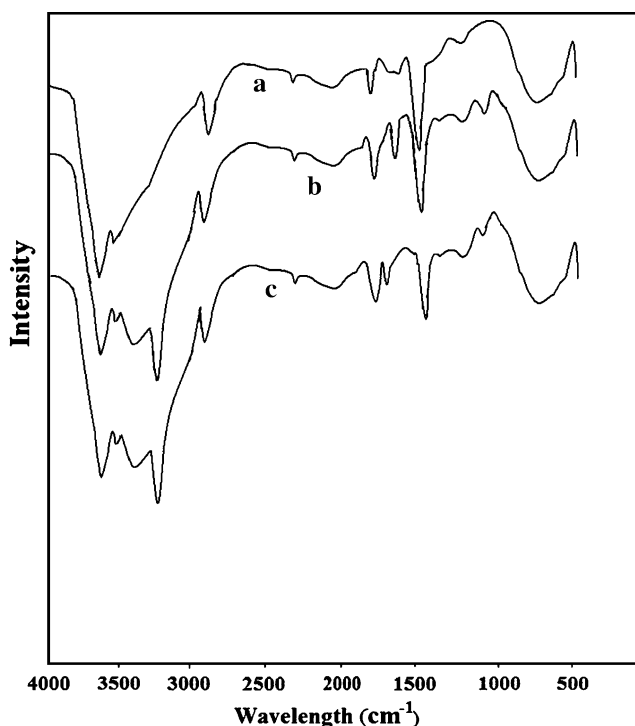
### Solvent extraction experiments

Excess tetrahydrofuran (THF) (20 mL) was added to ca. 100 mg of dried PPy-coated SMA powder at room temperature and this solution was left to stand overnight. The resulting black residues were filtered, washed with THF and dried overnight in a vacuum oven at 60 °C.

### Characterization

#### UV-visible spectroscopy

The UV-visible absorption spectra of the samples in 1-methyl-2-pyrrolidone solvent were recorded in the range



**Fig. 2** IR spectra of a SMA latex, b polypyrrole and c core-shell particles

300–800 nm using a Shimadzu UV-2550 UV–visible spectrophotometer.

#### Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of the core-shell composite particles were recorded in a KBr medium on a Nicolet Impact-410 IR spectrometer (USA) at room temperature in the region  $4,000-450\text{ cm}^{-1}$ .

#### X-ray diffraction (XRD)

Powder XRD data were collected on a Rigaku Miniflex X-ray diffractometer (Tokyo, Japan) with Cu  $K\alpha$  radiation ( $\lambda=0.15418\text{ nm}$ ) at 30 kV and 15 mA with a scanning rate of  $0.05^\circ/\text{s}$  in the  $2\theta$  range from 10 to  $70^\circ$ .

#### Scanning electron microscopy

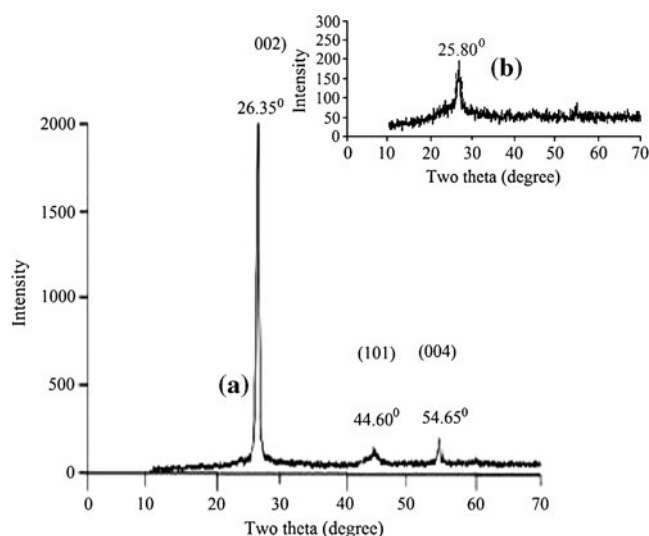
SEM micrographs of the core-shell particles were taken with a Jeol-JSM-6390L V scanning electron microscope. Latex samples were sputter coated with platinum of thickness of  $200\text{ \AA}$ .

#### Transmission electron microscopy

For the TEM analysis a Philips EM 400 was used with an acceleration voltage of 100 kV. All images were taken at a magnification of 60,000 or 120,000. For the TEM measurement, latexes were first sonicated, and the samples were prepared by dropping highly diluted latexes on the carbon-coated copper grid and dried in a vacuum oven at room temperature.

#### Thermogravimetric analysis

Thermal analysis was done in a Shimadzu TA-60 thermogravimetric analyser. A preweighed amount of the latex was loaded in a platinum pan and heating was done under nitrogen atmosphere at a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  in the range of  $0-700\text{ }^\circ\text{C}$ .



**Fig. 3** XRD patterns of **a** core-shell particles and **b** polypyrrole

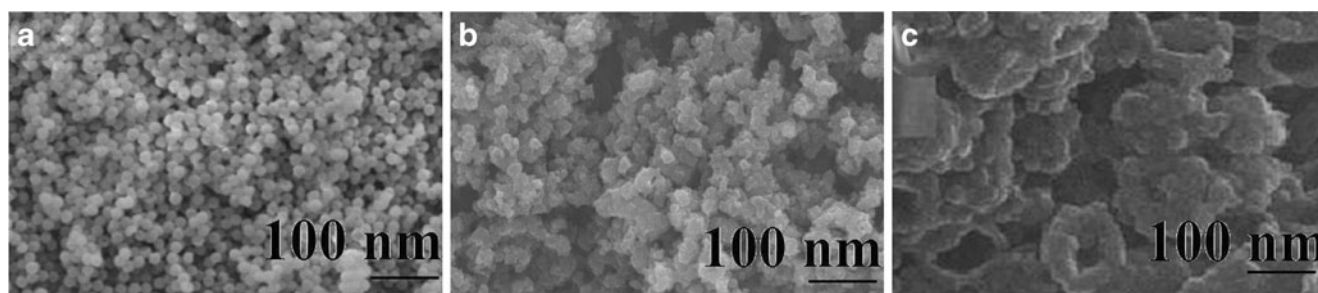
#### Electrical conductivity

Pellets of the composite latex were made with a compression-molding machine with hydraulic pressure. High pressure was applied (1.5–2 ton) to the sample to afford round-shaped hard pellets (diameter=1.5 cm, thickness=2 mm); these pellets were used to measure the conductivity.

The electrical conductivity of the composite latex was measured with a four-probe technique in the temperature range  $300\text{ K}\leq T\leq 433\text{ K}$ . The current–voltage ( $I$ – $V$ ) characteristics were studied with a Keithley 2400 source meter (USA) at room temperature in the frequency range 102–106 Hz. The conductivity of the composite was calculated with following equation:

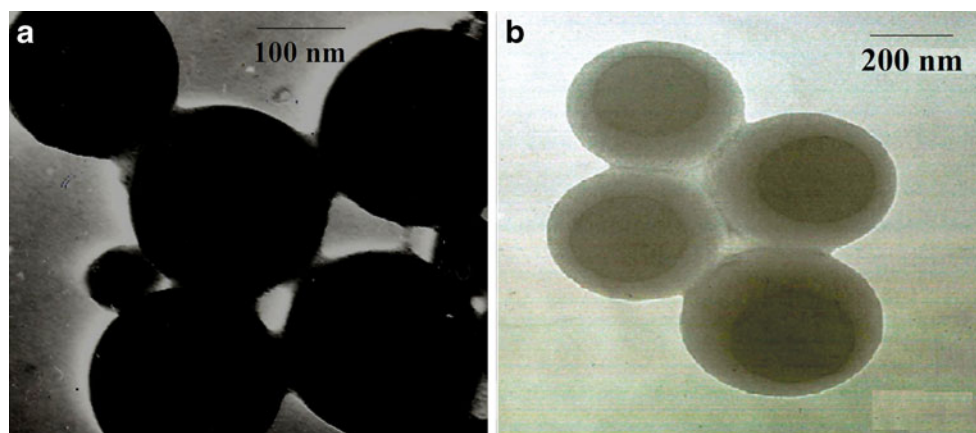
$$\rho = (V/I)2\pi S \quad (1)$$

Where  $\rho$  is the resistivity of the sample,  $V$  is the applied voltage,  $I$  is the measured current through the sample, and  $S$  is the distance between the probes.



**Fig. 4** SEM images of **a** SMA latex, **b** core-shell composite particles and **c** core-shell composite particles after extraction with THF

**Fig. 5** TEM images of **a** SMA latex and **b** core-shell composite particles



### Cyclic voltammetry (CV)

Electrochemical measurements were performed on a Sycopel AEW2-10 electrochemical workstation (UK) with an Ag/AgCl reference electrode, a platinum wire as a counter electrode, and the latex films on indium tin oxide (ITO) coated glass as a working electrode. The electrochemical characteristics of the polymer solution in *N*-methylpyrrolidone (NMP) were investigated by CV scanning in 0.1 M hydrogen chloride (HCl) in acetonitrile at a scan rate of 50 mV/s. A solution of 0.1 M KCl prepared in 10 mL acetonitrile was used as supporting electrolyte.

## Results and discussion

### Polymerization

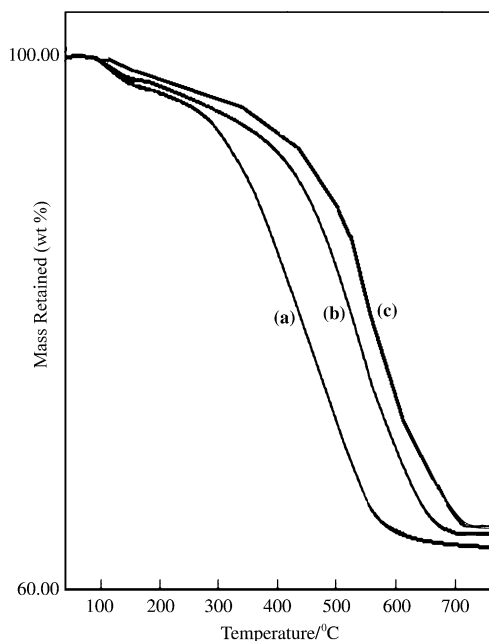
Copolymer particles of styrene and methyl acrylate were formed by surfactant-free mini emulsion polymerization. These latex particles were used as template for the polymerization of pyrrole. The surface of the copolymer particles adsorbs pyrrole and graphite, and polymerization was performed by redox coupling reaction on the surface of the copolymer latex. The amount of pyrrole is low and forms a near uniform layer over the latex particles and results in core-shell morphology. The unadsorbed graphite particles are removed by washing with water and ethanol. (Scheme 1)

### UV-visible spectroscopy

Figure 1 shows the UV-visible spectra of polypyrrole. The peak at 460 nm is associated with the  $\pi$ - $\pi^*$  transition of the heterocyclic ring of polypyrrole. The broad peak at around 800 nm is believed to be due to the extended coil of polypyrrole chain indicating a well-conjugated system [23]; this peak may be attributed to the  $\pi$ - $\pi^*$  transition of the aromatic heterocycles of the polypyrrole ring.

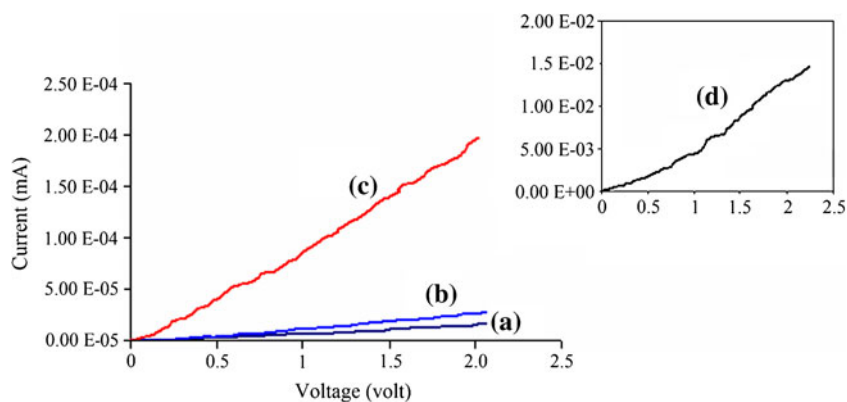
### IR spectroscopy

The FTIR spectra of SMA latex, pure polypyrrole and the polypyrrole/graphite composite are shown in Fig. 2. The broad strong bands at  $3,433\text{ cm}^{-1}$  correspond to the absorption of N-H stretching of polypyrrole. The band at  $2,926\text{ cm}^{-1}$  corresponds to the stretching vibration of the C-H bond. The absorption at  $1,578\text{ cm}^{-1}$  was assigned to the C=C ring stretching of pyrrole. The band at  $1,380\text{ cm}^{-1}$  is due to C-H vibrations. The band at  $1,042\text{ cm}^{-1}$  is due to in-plane deformations of the C-H and N-H bonds of pyrrole rings. The peak at  $1,727\text{ cm}^{-1}$  and  $1,165\text{ cm}^{-1}$  correspond to C=O and C-O stretching of poly(methyl acrylate). The absorption at  $1,578\text{ cm}^{-1}$  was shifted to  $1,638\text{ cm}^{-1}$  in the graphite-incorporated core-shell particles.



**Fig. 6** TGA analysis **a** polypyrrole, **b** polypyrrole/graphite particles and **c** core-shell composite particles

**Fig. 7** I–V plot of the core-shell particles with **a** 0% graphite, **b** 0.25% graphite, **c** 0.50% graphite and **d** 1% graphite



This may be attributed to the conjugation between the C=C of pyrrole and the graphite surface. Thus from the IR spectra it may be confirmed that the core-shell particle contains both the SMA latex and the graphite-incorporated pyrrole phase.

#### XRD analysis

The XRD patterns of polypyrrole and the core-shell composite particle are shown in Fig. 3. The XRD pattern of polypyrrole shows a characteristic peak at  $25.8^\circ$ , whereas the XRD pattern of the core-shell composite particles showed the characteristic peaks at  $26.35^\circ$ ,  $44.60^\circ$  and  $54.65^\circ$  corresponding to the (002), (101) and (004) planes of an hexagonal system. This indicates the presence of graphite in the core-shell composites. The peak of polypyrrole is not visible in the core-shell composites due to its very low intensity (ca. 200). The ‘d’ spacings for the core-shell composites are 3.34, 2.02 and  $1.67 \text{ \AA}$  for their corresponding peaks at  $26.35^\circ$ ,  $44.60^\circ$  and  $54.65^\circ$  respectively. This indicates the incorporation of the graphite particles on the PPy matrices.

#### Morphology of core-shell latex

##### SEM analysis

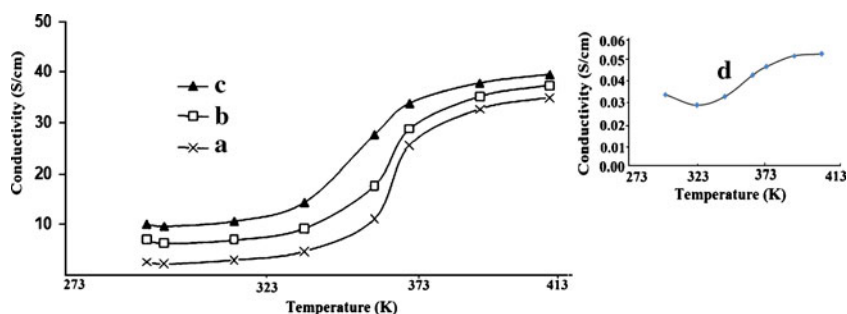
Figures 4a and b are SEM images of the SMA latex and the graphite-incorporated polypyrrole coated SMA latex. Figure 4c is a SEM image of the polypyrrole-coated SMA latex after treatment with excess THF; the THF dissolves

the SMA latex in the core and leaves a void in the interior, resulting in “broken egg shell” morphology. This SEM analysis reveals beyond any reasonable doubt that core-shell morphology was achieved with the SMA latex as the core and graphite-incorporated polypyrrole as the shell. The SEM image reveals that the SMA core particles are nearly monodispersed, and their size.

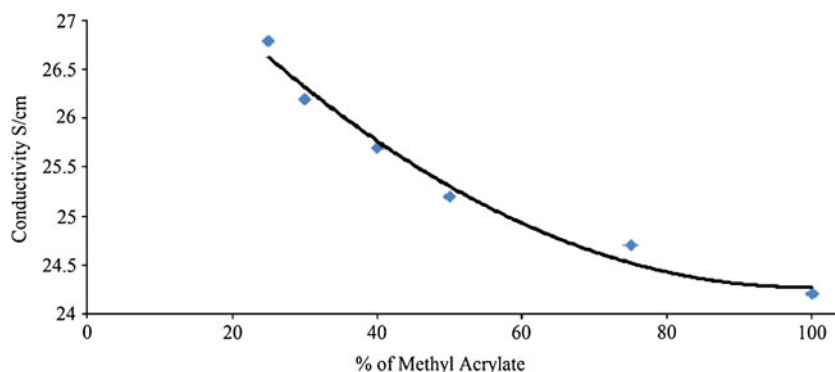
##### TEM analysis

Figures 5a and b are TEM images of the SMA latex particles and the SMA/PPy-graphite composite particles. Figure 5a shows that the SMA particles are nearly monodispersed with size ranging from 220 to 250 nm; the particles’ spherical shape may also be confirmed. As shown in Fig. 5a, micro aggregates of SMA particles occurred when the water medium was evaporated. This is because PMA has a relatively low  $T_g$  and hence exhibits good film formation properties at room temperature. In Fig. 5b it can be seen that the conducting shell is formed as a layer on the SMA surface. The polypyrrole overlayer appears to be reasonably continuous, with little or no evidence of bare patches. This is consistent with the core-shell morphology of the resultant particles. The TEM image reveals that the core-shell particles are almost uniform with size ranging from ca. 380 to 410 nm. The increase in size of the core-shell particles in comparison with the core particles gives further evidence of the formation of polypyrrole layer over the SMA core.

**Fig. 8** Conductivity vs temperature curve of the core-shell particles having **a** 0.25% graphite, **b** 0.50% graphite and **c** 1% graphite, and **d** pristine polypyrrole



**Fig. 9** Plot of conductivity of the composite particles vs methyl acrylate content in the SMA latex



### TGA analysis

The thermogravimetric profiles of PPy, PPy/graphite (G) and SMA-PPy/G composites are given in Fig. 6. In all cases the weight loss at 398 K reveals the loss of moisture/adsorbed solvent from the polymer matrix. The major degradation occurred at 573 K for PPy, at 673 K for PPy/G composites and at nearly 700 K for the core-shell composite particles, showing that the thermal stability is improved in the core-shell composites.

### Electrical behaviour

#### Current–voltage relationship

Figure 7 shows the current–voltage relationship for the SMA-PPy/G composites having different graphite contents. All the synthesized core-shell composites showed semiconducting behaviour. For all the samples, the potential

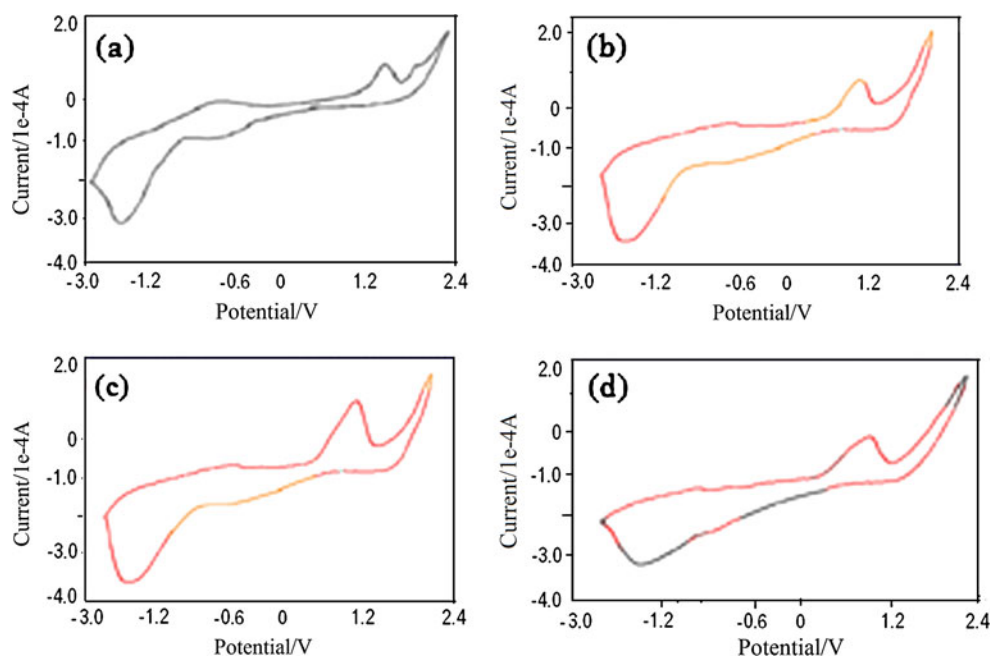
difference (in volts) increases linearly with the applied current (in milliamps) and the percentage content of graphite in the polypyrrole phase (shell)—a characteristic of semiconductors; hence it may be concluded that the core-shell composite particles are of semiconducting nature.

#### Direct current electrical conductivity

The conductivity of the SMA-PPy/graphite core-shell composite particles varied widely from 19.3 to 26.8 S/cm depending on the graphite content in the shell phase. Thus in the pellet of SMA/PPy-graphite composite particles, interfacial conductive paths consisting of the PPy-graphite shell were formed, and efficient charge transport through the materials occurred without much interference from the electrically insulating SMA component.

Figure 8 shows the variation of conductivity of pristine polypyrrole and the core-shell composite particles in the temperature range of 293 K <math>T</math> <math>413</math> K; in both the cases

**Fig. 10** Cyclic voltammogram of the composite particles having **a** 0% graphite, **b** 0.25% graphite, **c** 0.50% graphite and **d** 1% graphite



**Table 3** Electrochemical data of PPy and PPy/G composites

| Core-shell composites | $\phi_{\text{onset}}^{\text{ox}}/E_{\text{HOMO}}$ | $\phi_{\text{onset}}^{\text{red}}/E_{\text{LUMO}}$ | $E_{\text{ec}}^{\text{g}}$ (eV) |
|-----------------------|---|--|---------------------------------|
| 0% Graphite           | 1.50/−6.21  | −1.40/−3.31  | 2.90                            |
| 0.25% Graphite        | 1.40/−6.11  | −0.5/−5.21   | 1.9                             |
| 0.5 Graphite          | 1.35/−6.06  | −0.4/−5.11   | 1.75                            |
| 1% Graphite           | 1.3/−6.01   | −0.35/−4.36  | 1.65                            |

conductivity increases with increasing temperature. At high temperature inter- and intra-chain hopping increases thereby increasing the mobility of the charge carrier. This high charge carrier mobility ultimately results in increasing conductivity at high temperature [24–26]. With 1% incorporation of graphite in the polypyrrole shell phase conductivity increases from 26.8 S/cm at 298 K to 51.6 S/cm at 413 K. This gives evidence beyond any reasonable doubt that the newly synthesized core-shell composite particles are of semiconducting nature. However the curves reveal that the conductivity of pristine polypyrrole is very low even at high temperature. (0.05 S/cm at 413 K). This value increases significantly with incorporation of graphite in the polymer phase.

The electrical conductivity of the core-shell composite depends not only on the concentration of graphite in the polypyrrole shell but also on the methyl acrylate content in the SMA latex. When the other conditions are the same, the electrical conductivity of the core-shell composites can be tuned to a certain extent by varying the soft monomer methyl acrylate content in the SMA copolymer latex. The relationship between the conductivity and the methyl acrylate content in the SMA latex of the core-shell composites having 1% graphite in the polypyrrole phase is shown in Fig. 9. The decrease of conductivity may presumably be attributed to the increase of soft segment in the surface of the core-shell composite particles with increasing methyl acrylate content in the SMA latex. As the amount of soft content increases efficient charge transport becomes and hence electrical conductivity decreases.

#### Electrochemical behaviour

Figure 10 shows the cyclic voltammogram of the core-shell composite particles with different graphite contents in the shell phase. The electrochemical band gaps ( $E_{\text{ec}}^{\text{g}}$ ) of the samples were calculated by using the following formulae [27]:

$$\text{HOMO} = -[\phi_{\text{onset}}^{\text{ox}} + 4.71] (\text{eV}), \quad (2)$$

$$\text{LUMO} = -[\phi_{\text{onset}}^{\text{red}} + 4.71] (\text{eV}), \quad (3)$$

$$E_{\text{ec}}^{\text{g}} = (\phi_{\text{onset}}^{\text{ox}} - \phi_{\text{onset}}^{\text{red}}) (\text{eV}), \quad (4)$$

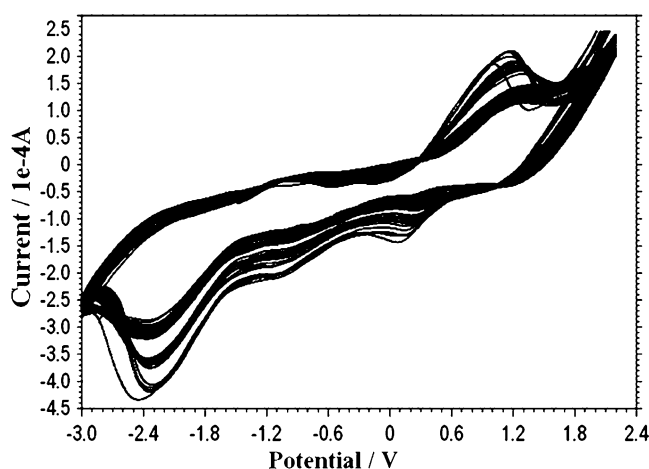
where the units of  $\phi_{\text{onset}}^{\text{ox}}$  and  $\phi_{\text{onset}}^{\text{red}}$  are volts vs. Ag/AgCl. The values obtained are listed in Table 3. The

electrochemical band gap for PPy was calculated from voltammograms and was found to be 2.90 eV, whereas in the core-shell composite particles band gaps decreased (1.9 to 1.65 eV) with increasing content of incorporated graphite in the polypyrrole shell phase. The incorporation of graphite resulted in change in electronic band structure manifested as a new mid-gap being created and hence a decrease of band gap occurs [25].

The electrochemical stability of the core-shell composite particles was investigated by carrying out successive cyclic voltammetry up to the 100th cycle. Figure 11 reveals that the cathodic and anodic peaks are nearly symmetrical above each other and have minimum separation. Thus it may be inferred that the core-shell composite particles are sufficiently redox stable to have manifold potential applications in the field of opto-electronics.

#### Conclusions

Graphite-incorporated polypyrrole is coated on poly(styrene-co-methyl acrylate) core by surfactant-free mini emulsion polymerization. TEM micrographs showed distinct contrast difference between the core and shell phase, revealing that the resulting SMA/PPy-graphite composite particles possess core-shell morphology. The resultant composite particles have a diameter of nearly 120 nm. Powder XRD study confirms the incorporation of graphite in the polypyrrole



**Fig. 11** Successive electrochemical cycles of the composite particles (1% graphite) up to the 100th cycle



shell phase. TGA study shows that the core-shell particles are sufficiently thermal stable and sustain up to 700 K. The d.c. conductivity of the core-shell composite particles may be tuned in the range from 19.3 to 26.8 S/cm at room temperature by varying the graphite content (from 0.25 to 1%) in the polypyrrole shell. The d.c. conductivity increases with increasing temperature. Conductivity of the core-shell composite particles not only depends on the graphite content and temperature but also on the methyl acrylate content in the SMA core. The conductivity decreases with increasing methyl acrylate content. The electrochemical study reveals that the composite particles possess excellent electrochemical reversibility having charge capacity almost unchanged up to the 100th cycle.

## References

1. Wiersma AE, Vd Steeg LMA, Jongeling TJM (1995) *Synth Met* 71:2269
2. Singh A, Singh NP, Singh P, Singh RA (2010) *J Polym Res*. doi: [10.1007/s10965-010-9392-6](https://doi.org/10.1007/s10965-010-9392-6)
3. Skotheim TA, Elsenbaumer JR, Reynolds (eds) (1998) *Handbook of conducting polymers*, 2nd ed. Marcel Dekker, New York
4. Pickup NL, Sharpio JS, Wong DKY (2001) *J Polym Res* 8:151
5. Huijs FM, Lang J, Kalicharan D (2001) *J Appl Polym Sci* 79:900
6. Wang J (2009) *Adv Mater* 21:1137
7. Armes SP, Gottesfeld S, Beery JG, Garzon F, Agnew SF (1991) *Polymer* 32:2325
8. Wu TM, Chang HL (2008) *Compos Sci Technol* 68:2254
9. Khan MA, Armes SP (2000) *Adv Mater* 12:671
10. Huijs FM, Vercauteren FF, Kalicharan D, Hadziioannou G (1999) *Synth Met* 102:1151
11. Lascelles SF, Armes SP (1995) *Adv Mater* 7:864
12. Aoki K, Chen J, Ke Q (2003) *Langmuir* 19:5511
13. Khan MA, Armes SP (1999) *Langmuir* 15:3469
14. Huijs FM, Lang J (2000) *Colloid Polym Sci* 278:746
15. Huijs FM, Vercauteren FF, Hadziioannou G (2002) *Synth Met* 125:395
16. Xie HQ, Ma YM, Guo JS (1999) *Polymer* 40:261
17. Ruckenstein E, Yang SJ (1993) *Synth Met* 53:283
18. Yassar A, Roncali J, Garnier F (1987) *Polym Commun* 28:103
19. Liyan H, Wenbo H, Zhengping L, Qingyue Z (2005) *Chin Sci Bull* 50:971
20. Jang BJ, Oh JH (2005) *Adv Funct Mater* 15:494
21. Jang J, Oh JH, Stucky GD (2002) *Angew Chem Int Ed* 41:4016
22. Wang Y, Shi Y, Xu X, Liu F, Yao H, Zhai G (2009) *Colloids Surf A Physicochem Eng Asp* 345:71
23. Rai AR, Prom-Jun A, Ouajai WE, Ouajai S (2008) *J Met Mater Miner* 18:27
24. Konwer S, Pokhrel B, Dolui SK (2010) *J Appl Polym Sci* 116:1138. doi:[10.1002/app.31633](https://doi.org/10.1002/app.31633)
25. Liu J, Wan M (2001) *J Mater Chem* 11:404
26. Leeuw DM, Simenon MJ, Brown AR, Einerhand REF (1997) *Synth Met* 87:53
27. Bhadra S, Singha NK, Khastgir D (2007) *J Appl Polym Sci* 104:1900