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Development of a Sustainable Resource Based Conducting Composite of Polyaniline-Poly(esteramideurethane)

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Polymers synthesized from coconut oil as a precursor find scarce applications. Polyesteramide urethane synthesized from coconut oil, a natural resource, is a dough-like material, unusable in our study. Upon loading with polyaniline it becomes tough and flexible. Composites of ClO₄⁻ doped polyaniline with coconut oil based poly(esteramide urethane) (CPEAU) were prepared by a solution blending technique, using different ratios of polyaniline (2 wt%, 4 wt% and 8 wt%). The composites were further characterized by FT-IR, DSC, TGA, XRD, and SEM. Conductivity was found to be in the range $2.5 \times 10^{-5} - 5.7 \times 10^{-4} \text{ Scm}^{-1}$. The composite was found to show weak hydrogen bonding interactions between PANI and CPEAU at 8 wt% loading.

Keywords polyaniline, polyesteramide urethane, composite, conductivity

Introduction

Polyaniline is one of the most extensively investigated intrinsically conducting polymers having commercial significance due to its good conductivity, and environmental stability, as well as ease of synthesis (1–3). However, the poor processibility of polyaniline limits its commercial applications (4, 5). One of the widely applied strategies to overcome this deficiency of polyaniline is the formation of its blends with commercial polymers, which incorporates the mechanical properties of the polymer matrix and the electrical conductivity of polyaniline. Solution blending of polyaniline has been exhaustively investigated by several authors using commercial polymers such as poly(styrene-co-butadiene) (6), polystyrene (7), poly(methacrylate) (7), poly(amic acid) (8), poly(epichlorohydrin-co-ethylene oxide) (9), etc.

Polyurethane possesses a unique combination of elastic properties of rubber and toughness of a metal. Lately, blends of polyurethane with PANI have attracted the attention of several researchers as they hold potential for application as a roller in electrostatic spray, EMI shielding, chemical, as well as biological sensors (10–13), etc.

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Several authors have reported the synthesis of PANI/PU blends by adopting different techniques. Spirkova et al. (14) prepared an anisotropic PANI/PU composite by first preparing polyaniline via oxidative polymerization of anilinesulphate. A polyurethane network was then prepared from trihydroxy(poly oxy propylene) (PPT) and diisocyanate–diphenylmethane, using dibutyltin dilaureate (DBTL) as a catalyst for urethane formation. Liao et al. (15) have reported a series of novel conducting IPNs prepared by sequential polymerization of maleimide terminated polyurethane (UBMI) and dodecylbenzenesulphonic acid doped PANI. Wang et al. (16) have studied conducting PU-amine terminated PANI oligomeric powder dissolved in NMP.

Apart from the mentioned synthetic procedures, some authors have used castor oil as a precursor to synthesize polyurethanes. Siddaramiah (17) synthesized interpenetrating networks of castor oil based polyurethane with PMMA and loaded 12.5% PANI doped with camphor sulphonic acid. Malmonge (18) also prepared a castor oil based polyurethane, blended it with PANI dissolved in NMP, obtaining conductivity up to 10^{-2} S/cm upon 10 wt% PANI loading.

Polyurethanes can also be synthesized from other vegetable oils through the formation of hydroxyl terminated polyesteramide (19–21). Normally, saturated oils are not used as precursors for polymers because of the absence of unsaturation, which is required for curing. Coconut oil based poly(esteramide urethane) is a dough like substance which is unusable for our purpose. In the present study, we report the synthesis of composites of coconut oil based poly(esteramide urethane) and PANI, prepared via solution blending. We expect the loading of polyaniline in CPEAU to provide toughness to the composite, resulting in the formation of free standing films. The composite has been characterized by FT-IR, DSC, TGA, XRD and SEM analysis.

Experimental

Aniline (Merck, India) was distilled twice under vacuum and stored in a refrigerator prior to use. Coconut oil (M/s Atul Chemicals Pvt. Ltd., Delhi, India) was de-waxed and purified. Toluene-2,4 diisocyanate (TDI), dibutyl tin dilaureate (DBTL) (Merck, Germany), phthalic acid, xylene, diethanolamine, methanol (Merck, India) and perchloric acid (Qualigens Chem., India) were of analytical grade, and were used as such.

Synthesis of Polyaniline

Polyaniline was synthesized by an alternate method in the presence of perchloric acid. HClO_4 , 3 ml (0.03 mol), was added to 50 ml of methanol solution contained in a 250 ml three-necked, round bottom flask fitted with a condenser, nitrogen inlet tube and magnetic stirrer. Aniline, 9.4 ml (0.1 mol), along with cupric chloride (0.01 mol) oxidant dissolved in 20 ml methanol was added dropwise to the acidic solution while maintaining the temperature at $60 \pm 5^\circ\text{C}$ under a nitrogen atmosphere. The reaction was carried out for 4–6 h. After completion of the reaction, the brown powder thus obtained was isolated from the reaction mixture by filtration and was washed several times with distilled water and methanol to remove the impurities. The dopant was removed from the polymer by using a 1 M aqueous ammonia solution, followed by drying under vacuum at $55\text{--}60^\circ\text{C}$ for 72 h. Doping of the polyaniline powder was then carried out by immersion in 1 M HClO_4 solution for 24 h. Polyaniline obtained by this procedure exhibited maximum conductivity of 10^{-4} S/cm. The doped polyaniline powders were found to be soluble in xylene up to 8 wt%.

The N,N,bis(2-hydroxy ethyl)coconut oil fatty amide(HECA) and coconut oil polyesteramide (CPEA) were synthesized after a reported method (18).

Preparation of (CPEAU)

CPEA (0.0047 mol), dissolved in 50 ml xylene, was added to a three-necked round bottom flask fitted with a Dean Stark trap, nitrogen inlet tube, thermometer and mechanical stirrer. TDI (0.002 mol) (TDI:PEA 2 : 1 mol ratio) along with 2–3 drops of DBTL as a catalyst, was added to the reaction mixture for a period of half an hour while maintaining the temperature at $120^{\circ}\text{C} \pm 5^{\circ}\text{C}$. The reaction was monitored by TLC, the color change and acid value. The reaction mixture was further refluxed for half an hour. On completion of the reaction, a brown viscous solution was obtained. The product was taken from the reaction flask and the excess xylene was removed under reduced pressure, using a rotary vacuum evaporator to obtain the CPEAU.

Preparation of Films of PANI/CPEAU Composites

A conventional solution casting method was adopted to prepare the PANI/CPEAU composites. The composites were prepared by mixing the appropriate amount of polyaniline with 10 wt% CPEAU solution in xylene to obtain different loadings of polyaniline in the composite, with loading varying from 2–8 wt%. Polyaniline was found to be soluble in xylene up to 8 wt%, beyond which it was found to be only partially soluble. Hence, loading of PANI above 8 wt% in CPEAU leads to phase separation in the composite.

After continuous stirring for 4–6 h at 50°C , free standing films of the composites were cast on transparency sheets. Drying of the films was carried out for 2–3 days to ensure the complete removal of the solvent. The films were further dried in a vacuum oven at 60°C for 48 h.

Characterization

Refractive index and specific gravity of CPEA, CPEAU, and PANI/CPEAU composites were determined by the reported standard methods (17). UV-visible spectra were taken on Perkin-Elmer Lambda EZ-221. FT-IR spectra of the films were obtained on a spectrometer model IMPACT 410 NICOLET USA. DSC thermograms were obtained using differential scanning calorimeter model DSC-10 (TA Instruments, USA), at a heating of $10^{\circ}\text{C}/\text{min}$. TGA was recorded on a model TGA51 thermogravimetric analyzer (TA Instruments, USA), after annealing the samples for 24 h at 100°C . X-ray diffractograms were recorded on an X-ray diffractometer (Philips model PW3710), using copper $K\alpha$ radiation. Microcrystalline parameters were calculated by a method reported in the literature (3). Conductivity was measured using Keithley multimeter model (DMM 2001) by the standard four-probe method at 30°C . Scanning electron micrographs of the films of various compositions were taken on JEOL(JSM840) scanning electron microscope under gold film.

Results and Discussion

Film Characteristics

CPEAU showed the consistency of a doughy material and was found to be flexible, and transparent below 25°C . 2-PANI/CPEAU films (with polyaniline loading of 2 wt%)

were lustrous and fairly stiff. 4-PANI/CPEAU films were found to be nonlustrous with lower stiffness, while the films of 8-PANI/CPEAU were dull, flexible, and stiff. It can be concluded that the loading of polyaniline in CPEAU imparts stiffness to the PANI/CPEAU composite, due to reinforcement via closer packing of the polyaniline chains. The decrease in luster can be attributed to the increasing concentration of aromatic rings in the composite.

Physical Characteristics of CPEAU and PANI/CPEAU Composites

The refractive index and specific gravity, Table 1, shows an increase from CPEAU to 8-PANI/CPEAU, which indicates that with the increase in the loading of PANI the structure of the composite becomes more packed. This is also consistent with the SEM micrographs of the composite.

SEM Studies

The SEM micrograph of pure CPEAU, Figure 1(a), shows a predominantly fibrillar structure, which conforms with its linear molecular structure. The SEM micrographs of the film of 2-PANI/CPEAU, Figures 1 (b) and (c), shows homogeneously distributed polyaniline grains in the well-formed CPEAU phase. A film of this composition was well formed and fairly tough in nature, which matches its granular microstructure. The CPEAU phase intervenes the polyaniline grains, which causes interference in PANI-PANI contact leading to lower conductivity of this composite.

The 8-PANI/CPEAU composite, Figure 1(d), consists of a heterogeneous structure, wherein polyaniline particles are distributed into the polyurethane matrix, making intimate contact with each other. The micrograph predicts good conductivity of this composite as the mutual PANI-PANI contacts of polyaniline grains provide a pathway for the conductance of the current. The microstructure also allows for fair mechanical strength of the film prepared from this composite.

Spectral Analysis

The UV-visible spectra, Figure 2, of the 8-PANI/CPEAU composite in xylene shows an absorption maxima at 380 nm and small shoulder around 490 nm. The presence of the peaks around 380 nm and 490 nm indicate the doped state of PANI in CPEAU (18). The FT-IR spectra of CPEAU shows the characteristic peaks of NH (3425.4 cm^{-1}), NHCOO (2361 cm^{-1}) C-O-C (1383) CN (1069 cm^{-1}), Table 2. Composites of PANI/CPEAU with 2 wt% and 4 wt% polyaniline showed no noticeable shift in any of the

Table 1
Characterization of CPEAU and PANI/CPEAU composites

Characteristics	CPEAU	2-PANI/CPEAU	4-PANI/CPEAU	8-PANI/CPEAU
Refractive index	1.455	1.465	1.562	1.580
Specific gravity	0.6615	0.7018	0.7395	0.7409
Conductivity (S cm^{-1})	—	4.5×10^{-5}	2.8×10^{-4}	5.7×10^{-4}

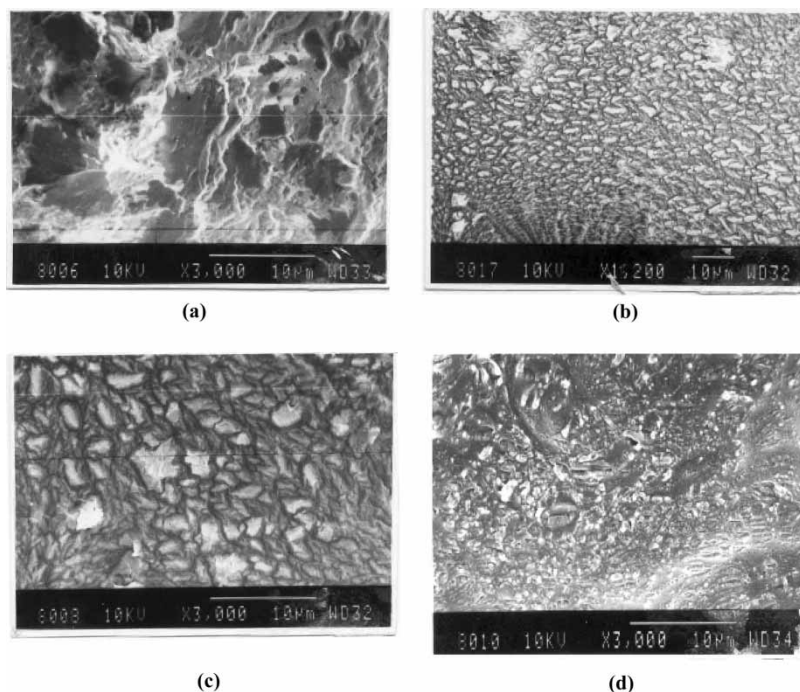


Figure 1. SEM micrographs of (a) CPEAU mag 1200 \times , (b) 2-PANI/CPEAU mag 1200 \times , (c) 2-PANI/CPEAU mag 3000 \times , (d) 8-PANI/CPEAU mag 1200 \times .

NH, NHCOO, C-O-C, CN peaks, which indicates insignificant interaction of polyaniline with CPEAU at lower loading as polyaniline behaves like a filler at low loading. However, at 8 wt% loading of polyaniline, the spectra of 8-PANI/CPEAU showed a shift in NH vibration peak, C-O-C peak and CN peak by 5 cm^{-1} , 7 cm^{-1} and 3 cm^{-1} . Minor shifting of peaks of C-O-C, CN, as well as NH peaks, in the FT-IR spectra of the composite confirms weak hydrogen bonding interaction of polyaniline with CPEAU. This analysis also confirms that interaction between PANI and CPEAU is noticeable up to 8 wt% loading in CPEAU.

Thermogravimetric Analysis

The TGA thermogram of pure CPEAU, 2-PANI/CPEAU, 4-PANI/CPEAU, and 8-PANI/CPEAU, Figure 3, shows a sluggish decomposition curve with 10% wt loss at 240°C , and 235°C , respectively. Polyaniline loading in CPEAU therefore, does not bring about any marked improvement in thermal stability of the composites.

The DSC thermogram of pure CPEAU, Figure 4, shows an endothermic event which lies in the temperature range 110°C – 175°C and an exothermic event between 180°C – 300°C . The endothermic peak centered at 130°C is due to the melting of CPEAU as no decomposition is indicated in the TGA thermogram of the same in this temperature range. We have visually observed that the doughy like mass of CPEAU liquifies around this temperature. 2-PANI/CPEAU gives the endothermic peak in the temperature range 95°C – 160°C (centered at 125°C), which is lower than that of pure CPEAU. In 4-PANI/CPEAU, the endothermic event is noticed between 108°C – 160°C , with the

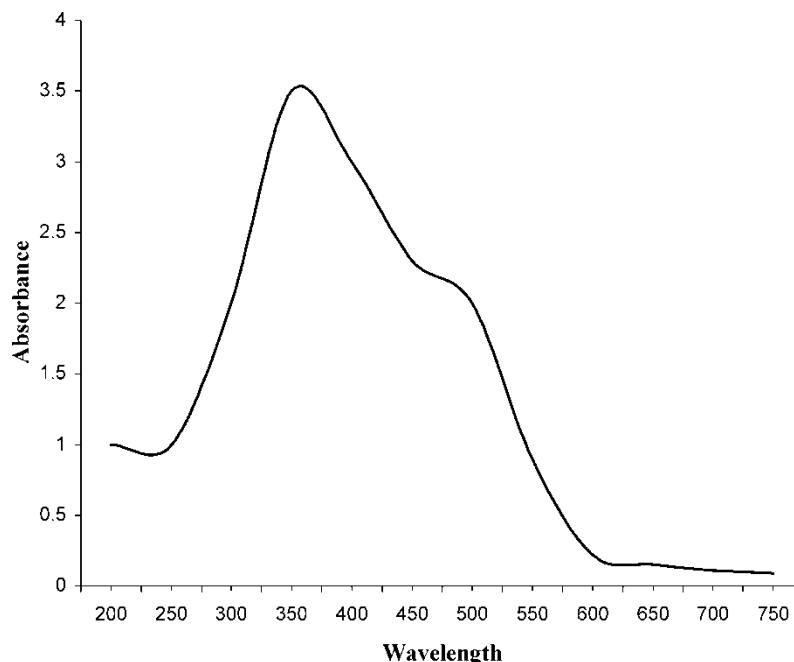


Figure 2. UV-visible spectra of 8-PANI/CPEAU composite in xylene.

endothermic peak centered at 135°C. The 8-PANI/CPEAU thermogram exhibits the endothermic event in the temperature range of 113°C–175°C, with the endothermic peak shifting to 145°C. The increase in the melting point in this case results from some specific interactions through hydrogen bonding between polyaniline and CPEAU as has been previously observed from the FT-IR.

XRD Analysis

The XRD profile of CPEAU, (Figure 5) shows a broad hump centered at 20.7750°. In addition to this, 4 crystalline peaks are observed at 2θ values equal to 9.4450°, 26.5700°, 28.6200°, and 68.7650°, respectively. It can be inferred that CPEAU is partially crystalline in nature with some CPEAU chains packed in an ordered manner between wide amorphous

Table 2
FT-IR spectra of CPEAU and PANI/CPEAU composites

Functional group	CPEAU (cm ⁻¹)	2-PANI/CPEAU (cm ⁻¹)	4-PANI/CPEAU (cm ⁻¹)	8-PANI/CPEAU (cm ⁻¹)
NH	3425.4	3426.8	3426.9	3430.0
NHCOO	2361.0	2361.1	2361.1	2361.1
C=O (amide)	1631.0	1628.1	1628.3	1630
C-O-C	1383.0	1383.2	1383.9	1384.0
CN	1069.5	1069.6	1069.8	1072.1
Aromatic ring	670.0	669.7	669.5	670.0

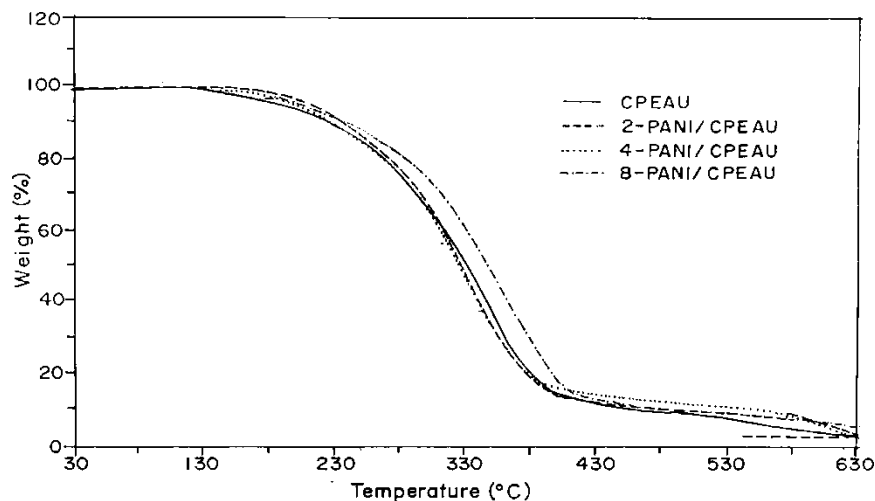


Figure 3. TGA thermograms of CPEAU and PANI/CPEAU composites.

regions. The diffractogram of composites shows minor shifting of peaks due to molecular organization reorganization in the composite upon loading of polyaniline.

Table 3 shows the microcrystalline parameters-interchain distance(r'), interplanar distance(d_{hkl}), and lattice strain(g). It is observed that the interchain distance, as well as the lattice strain, increases from CPEAU to 8-PANI/CPEAU. The microcrystalline

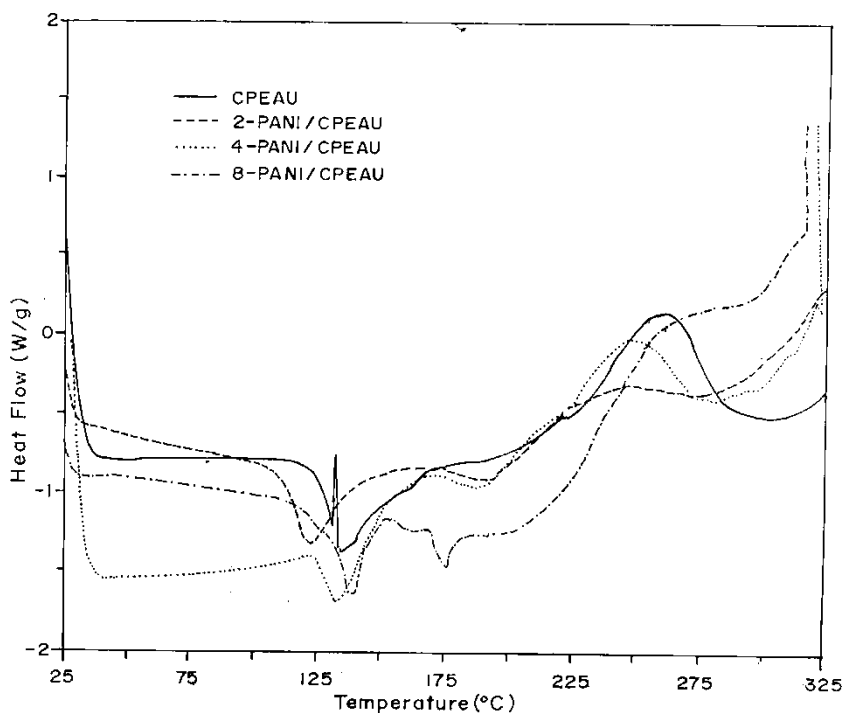


Figure 4. DSC thermograms of CPEAU and PANI/CPEAU composites.

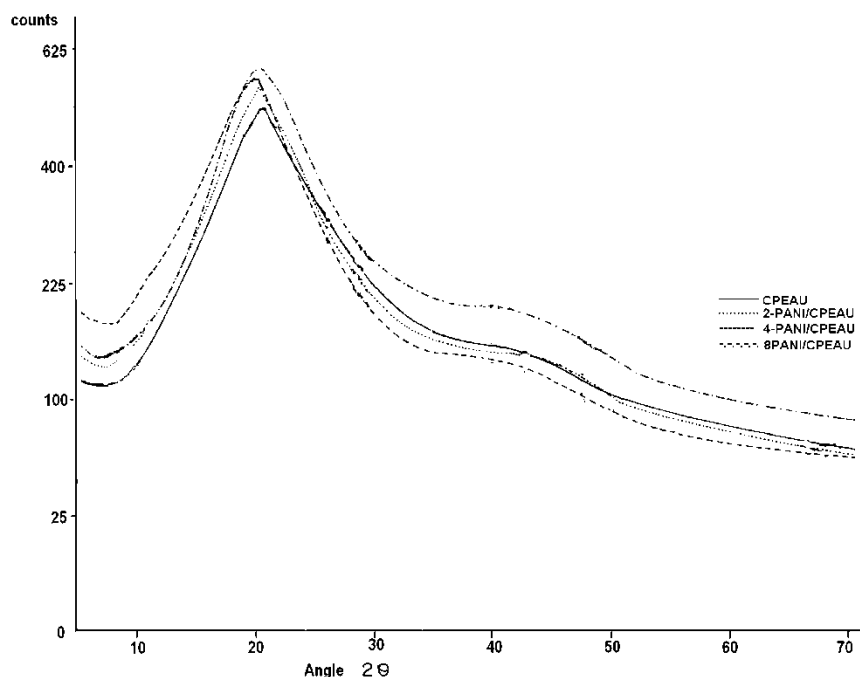


Figure 5. XRD Spectra of CPEAU and PANI/CPEAU composites.

parameters show very little change in the molecular organization, which indicates that if any interactions between CPEAU and polyaniline exist at all, they are weak.

Conductivity Studies

The effect of polyaniline content on the electrical conductivity of PANI/CPEAU composite is shown in Table 1. Conductivity of around $10^{-2} \text{ S cm}^{-1}$ was obtained in the case of castor oil based PU/PANI blends synthesized by Malmonge (18), as well as with castor oil based PU-PMMA IPNs with 12.5 wt% loading of PANI synthesized by Siddaramiah (17).

The conductivity was found to increase in our case with the increase in the loading of polyaniline in the composite and a maximum of $5.4 \times 10^{-4} \text{ S/cm}^{-1}$ at 8 wt% loading which shows the percolation effect as the CPEAU matrix is a perfect insulator in which

Table 3
Microcrystalline parameters of CPEAU and PANI/CPEAU composites

PANI/CPEAU (wt/wt%)	2θ (degrees)	R' (Å)	D_{hkl} (Å)	g(%)
CPEAU	20.7	5.47	4.36	13.00
2-PANI/CPEAU	20.2	5.59	4.46	13.37
4-PANI/CPEAU	20.4	5.53	4.42	13.21
8-PANI/CPEAU	21.0	5.50	4.30	12.8

polyaniline is dispersed as the conducting phase. FT-IR, DSC, TGA all conform to the heterogeneous nature of the composite.

Conclusions

The polymer from a sustainable resource-coconut polyesteramide urethane (CPEAU) can be used to form a conducting composite with PANI as an alternative to petroleum resource based commercial polymers.

CPEAU is a practically unusable doughy like substance, which is transformed into a flexible and tough material upon loading of polyaniline.

A maximum of 8 wt% PANI loading is achieved beyond which no stable composite is obtained and a maximum conductivity of 5.7×10^{-4} is also achieved at this loading.

FT-IR, DSC, TGA, XRD, and SEM studies rule out any miscibility of PANI with the CPEAU. A weak interaction between PANI and CPEAU occurs at 8 wt% loading as indicated by FT-IR.

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