

Thermal, Mechanical and Electrical Studies of Novel Shape Memory Polyurethane/Polyaniline Blends*

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Abstract Shape memory polymer (SMP) blends based on polyurethane (PU) and polyaniline (PANI) were prepared *via* chemical *in situ* polymerization process. The thermal, mechanical, electrical and shape memory properties were investigated. The structural characterization and morphology of the polymer blends were inspected by Fourier transform infrared (FTIR) and scanning electron microscopy (SEM), respectively. The 1 wt% of PANI loading enhanced the thermal stability of the system up to 339 °C. According to differential scanning calorimetry (DSC), the glass transition temperature (T_g) and melting temperature (T_m) of PU/PANI blends increased with the polyaniline loading (0.1 wt%–1 wt%). Improved mechanical properties such as tensile strength and Young's modulus of PU matrix were also observed with PANI. Moreover, the electrical conductivity of PU/PANI blends was also found to be a function of PANI loading. Remarkable recoverability of thermally triggered shape memory (SM) behavior to the extent of 96% was achieved for 1 wt% PANI blend.

Keywords: Shape memory; Polyurethane; Polyaniline; Blends; Conductivity.

INTRODUCTION

Shape memory polymers (SMPs) have been recognized as a class of stimuli-responsive materials having relevance in numerous technical fields such as smart actuators, aerospace engineering, textile engineering and biomedical applications^[1, 2]. SMPs have aptitude of fixing in one or multiple temporary shapes. They are also capable of finally regaining their original shape when induced by external stimuli such as heat^[3], electricity^[4], light^[5], magnetic field^[6], or solution^[7]. Thermally induced SMPs (triggered by heat) have been the most widely studied group so far^[8]. SMPs are multi-block phase-segregated copolymers in which the flexible or soft phase become reversible and can be elastically deformed. On the other hand, the hard segment memorizes the original shape^[9]. Polyurethane (PU)-based shape memory (SM) has gained much importance due to the inexpensive and less dense materials showing exceptional shape memory capability and flexibility^[10]. SM actuations in PU mostly depend on thermal transition of the soft segment phase. For shape memory PU with amorphous and crystalline soft segments, a glass transition (T_g) or melting temperature (T_m) can be tailored as transition temperature (T_{trans}) for shape memorization^[11–13]. The versatility of the PU can be further improved either through composite or blend formation.

In recent studies, more emphasis has been given to blends containing conductive polymers and an inert polymer matrix. The blends with conducting polymer can be potentially used in electro-optical devices, actuators, batteries, packaging, and gasket materials, as rollers in electrostatic imaging, cables and

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chemical/biological sensors^[14–16]. Among the conducting polymers, polyaniline (PANI) has been frequently explored due to its low cost, ease of synthesis, and environmental stability. The blending of PANI with other insulating polymer may result in blends with improved mechanical and electrical properties^[17]. The blend films having conductivity between 10^{-7} and 10^{-5} S·cm⁻¹ have been used in antistatic applications^[18]. Ho and coworkers^[19] reported that the stronger hydrogen bonding in the PU/PANI blend resulted in better miscibility, higher strength and conductivity. Vicentini *et al.*^[20] also synthesized the PANI/DBSA/PU blends with improved electrical conductivity. Similarly, Rangel-Vázquez^[21] described the preparation of PU/PANI with fine mechanical properties.

In this contribution, we have reported the synthesis of novel PU/PANI blends and discussed the structural, thermal and mechanical properties of the prepared blend films. The segmented block PU was fabricated using two polyether polyols, polyethylene oxide, and poly(propylene glycol)-block-poly(ethylene glycol)-block-poly(propylene glycol). The PU was then blended with varying contents of PANI. The electrical conductivity and shape recovery behavior of the prepared blends were also investigated.

EXPERIMENTAL

Chemicals

Polyethylene oxide (PEO, $M_w \sim 100000$), poly(propylene glycol)-block-poly(ethylene glycol)-block-poly(propylene glycol) (PPG-*b*-PEG-*b*-PPG, $M_w \sim 2000$), and 2,4-toluene diisocyanate (TDI, 99%) were purchased from Aldrich and were degassed at 80 °C before use. Aniline (99%), potassium dichromate (K₂Cr₂O₇, 99.99%), and hydrochloric acid (HCl, 37%) were also procured from Aldrich and used as received. Tetrahydrofuran (THF, 99.5%) was purchased from Merck.

Characterizations

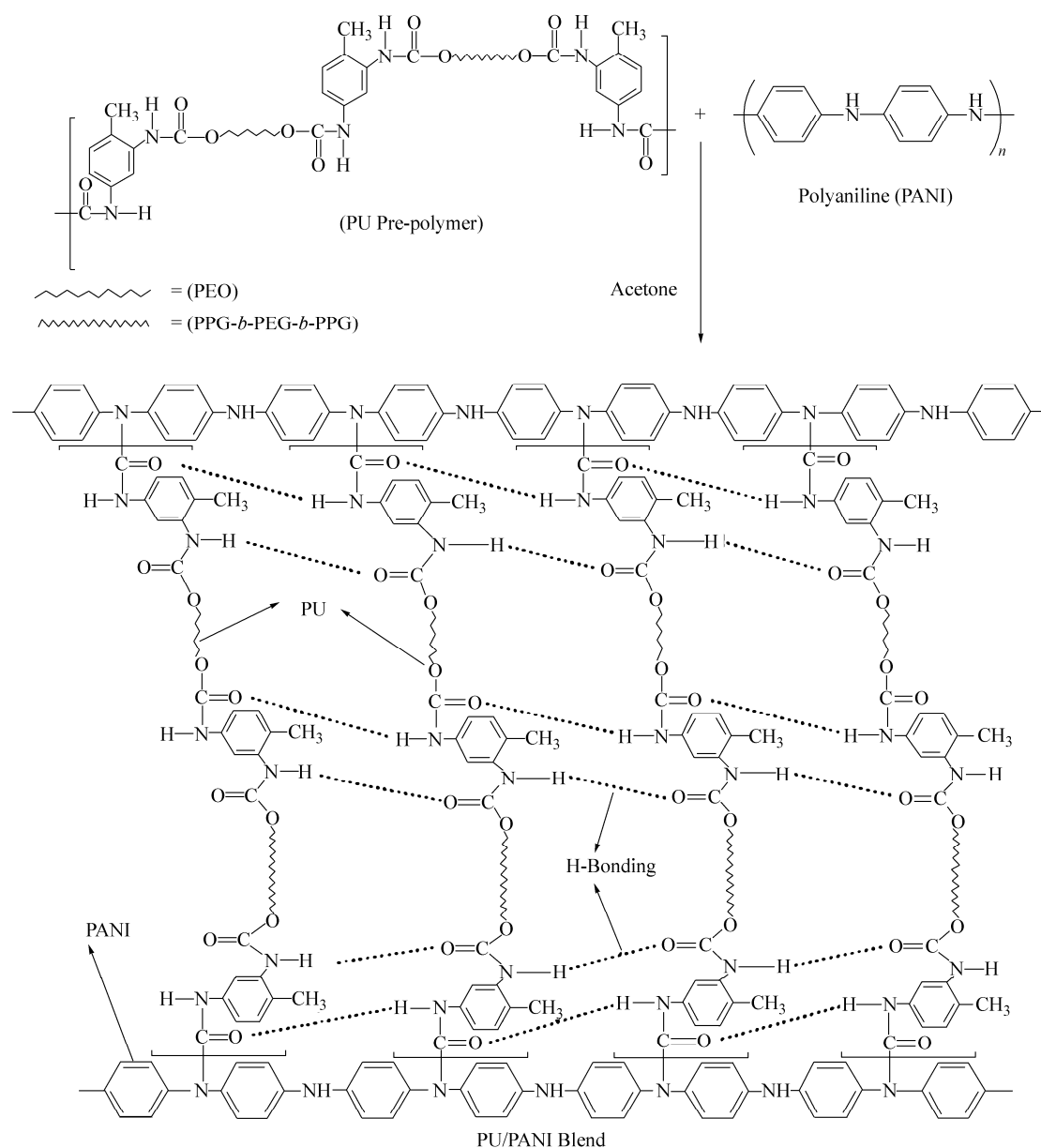
Infrared (IR) spectra were recorded using a Nexus 870 FTIR spectrometer in transmission mode. The range for the scans was selected from 4000 cm⁻¹ to 450 cm⁻¹. The recorded spectra were analyzed for the structural determination of the prepared samples. The scanning electron microscopic (SEM) analysis of the fractured samples was performed using a Hitachi S-4800 microscope to observe the morphology of the prepared blends. The samples were fractured under liquid nitrogen, and then the fractured surfaces were vacuum-coated with a thin gold layer prior to observation. The thermogravimetric analysis (TGA) of blend films was performed with a NETZSCH STA 449 C thermal analyzer to determine the thermal stability. The test was carried out in the temperature range of 25–700 °C under N₂ atmosphere using 7–10 mg of sample in Al₂O₃ crucible (20 K/min). A differential scanning calorimeter (DSC), Perkin-Elmer Pyris 1 DSC (Boston, MA, USA), was used for the analysis of phase transition temperature of the synthesized samples under an argon flow of 20 mL/min. For this analysis 5–7 mg of samples at a heating rate of 10 K/min in the range of –50 °C to 100 °C were used. The stress-strain behavior of samples was examined using a universal testing machine Instron 4466 with a strain rate of 5 mm/min at 23 °C (ASTM D638 standard method). For this purpose, sample specimens of dimensions 40 mm × 10 mm × (1 ± 0.05) mm and a crosshead speed of 20 mm/min were used during the test. The electrical conductivity of thin blend films was measured at room temperature using the four-point method (Keithley 2401). The samples of rectangular geometry with dimensions of 35 mm × 10 mm × (1 ± 0.05) mm were used for conductivity measurements. The shape-memory effect of rectangular strips with dimension 35 mm × 10 mm × (1 ± 0.05) mm was observed by heating the samples at 60 °C, while monitoring the shape recovery (SR) by using a video camera. The shape recovery was calculated using Eq. (1).

$$SR(\%) = \left\{ \frac{90 - \theta}{90} \right\} \times 100 \quad (1)$$

where θ in degree symbolizes the angle between the tangential line at the midpoint of the sample and the line joining the midpoint and the end of the curved samples.

Preparation of Polyaniline

The polymerization of aniline was carried out using 0.1 mol/L $K_2Cr_2O_7$ solution in HCl as an oxidizing agent. 200 mL solution of 0.04 mol/L aniline in HCl was taken in a 500 mL round-bottom flask and same volume of $K_2Cr_2O_7$ oxidant was added drop wise with constant stirring. The reaction was allowed to proceed at 4–6 °C for 4 h. The reaction mixture turned green indicating the formation of PANI. After that the mixture was kept unagitated for 24 h so that PANI precipitates may settle down. The final product was filtered, washed several times with distilled water, and dried at 60 °C for 12 h. The synthesized polyaniline was finally grinded to obtain fine green powder.



Scheme 1 The structural representation of blend formation between PU and polyaniline (PANI)

Synthesis of Polyurethane/Polyaniline Blends

The PU/PANI blend was prepared by *in situ* polymerization method. A polyurethane block copolymer was synthesized from its monomers, polyethylene oxide (PEO), and poly(propylene glycol)-block-poly(ethylene glycol)-block-poly(propylene glycol) (PPG-*b*-PEG-*b*-PPG) as soft segment and 2,4-toluene diisocyanate (TDI) as hard segment (NCO/OH = 1.07) using THF solvent. Firstly, PEO and PPG-*b*-PEG-*b*-PPG (0.1:0.9) were dissolved into a three necked round bottom flask using THF solvent. The mixture was allowed to stir for 1 h at 40 °C. Then TDI was added drop wise to the above mixture and refluxed at 60 °C for 3 h to obtain PU. Thereafter, PANI (preparation mentioned in previous section) dispersed in THF was added to PU solution and polymerization reaction was allowed to proceed for 12 h at 40 °C. At the end, the PU/PANI blend film was cast in glass Petri dish and dried at 60 °C. Four PU/PANI blend films with the varying polyaniline contents (0.1 wt%, 0.3 wt%, 0.5 wt% and 1 wt%) were prepared in the same manner. Thickness of dried PU/PANI blend films was measured as (1 ± 0.05) mm. Scheme 1 shows the blend formation between PU and polyaniline.

RESULTS AND DISCUSSION

Spectroscopic Analysis

The assigned infrared spectrum of polyaniline (PANI) is shown in the Fig. 1(a). A broad intense band around 3327 cm^{-1} is responsible for the N—H stretching vibration of polyaniline. A peak at 3062 cm^{-1} appeared due to the OH stretching vibration of water molecules physisorbed to the PANI backbone^[22] in association with aromatic C—H stretching vibration. The vibrations at 1592 and 1513 cm^{-1} appeared due to the characteristic C=C—C stretch of aromatic nuclei of polyaniline. The peak at 1560 cm^{-1} reflected the N—H bending vibration. Moreover, the peaks observed at 1448 cm^{-1} and 1308 cm^{-1} were assigned to the —C—N stretching vibration of aromatic ring. The several peaks of varying intensities in the region of $1200\text{--}1000\text{ cm}^{-1}$ appeared due to the C—H in-plane bending vibrations. The band at 826 cm^{-1} depicted the characteristics of mono-substituted benzene. The peaks at 913 cm^{-1} and 694 cm^{-1} were the evidence for C—H out-of-plane deformation. A sharp peak at 526 cm^{-1} was due to the ring deformation vibration of PANI. The presences of all distinctive peaks in the FTIR spectrum of polyaniline substantiated that the polymer was successfully prepared from the chemical oxidation polymerization method.

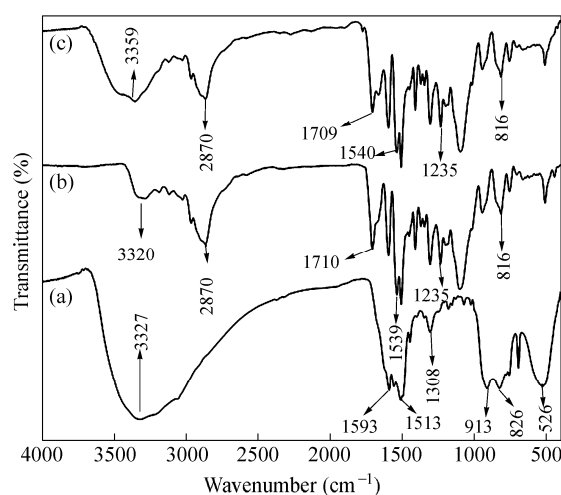


Fig. 1 Fourier transform infrared (FTIR) spectra of: (a) polyaniline (PANI); (b) PU and (c) PU/PANI blend

Figure 1(b) displays the FTIR spectrum of the synthesized PU. The peaks appeared at 3320 cm^{-1} for the N—H stretching vibration, 1710 cm^{-1} for the C=O stretching vibration, 1235 cm^{-1} for the C—N stretching vibration and 1102 cm^{-1} for the C—O—C stretching vibration as the characteristic bands of the urethane

group^[23]. The peaks emerging at 2870 cm^{-1} was assigned to the C—H stretching of $-\text{CH}_2$ and $-\text{CH}_3$ groups. The substituted aromatic ring of TDI was detected at 816 and 757 cm^{-1} . The FTIR spectrum of the synthesized blend is presented in Fig. 1(c). The peak assignments enlisted in Table 1 give the information about the successful synthesis of PU/PANI blend. An intense N—H stretching vibration was found at 3359 cm^{-1} in the blend spectrum indicating the interaction between PU and PANI. The high intensity suggested that the more extensive interaction (between N—H from PANI and C=O from PU) was not only due to the addition of PANI but also because of the increased crosslinking responsible for hydrogen bonding in blends. The peaks at 1709 cm^{-1} and 1668 cm^{-1} indicated the free and hydrogen bonded carbonyl (C=O) stretching vibrations, respectively. The appearance of hydrogen bonded carbonyl stretching vibration at 1668 cm^{-1} reflected the formation of hydrogen bonding and urea linkages in the PU/PANI blend. Rodrigues *et al.*^[24] also observed the peak for carbonyl groups due to urea-type linkages between PANI and PU, without the interference of the urethane carbonyl group. The bands present at 1540 cm^{-1} and 1235 cm^{-1} were associated to the N—H bending and C—N stretching vibration modes, respectively. The peaks of higher intensity at 1598 cm^{-1} and 1510 cm^{-1} reflecting the C=C—C stretching vibrations in aromatic rings were also observed indicating the aromatic structure of polyaniline along with the TDI structure in the blend. The intensity of absorption peak at 816 cm^{-1} concerning the substitution of benzene ring was also relatively higher for the blend spectrum due to the presence of PANI.

Table 1. FTIR peaks assignment for PANI, PU and PU/PANI blend

Assignments	Wavenumber (cm^{-1})		
	PANI	PU	PU/PANI
$\nu\text{N—H}$	3327	3320	3359
$\nu\text{C—H}$ (aromatic)	3062	3029	3029
$\nu_{\text{as}}\text{C—H}$	—	2969	2968
$\nu_{\text{sym}}\text{C—H}$	—	2870	2870
$\nu\text{C=O}$ (Free)	—	1710	1709
$\nu\text{C=O}$ (H-bonded)	—	—	1668
$\nu\text{C=C—C}$ (aromatic)	1592, 1513	1597, 1509	1598, 1510
$\delta\text{N—H}$	1560	1539	1540
$\delta_{\text{as}}\text{C—H}$	—	1454	1452
δCH_2 & CH_3	—	1411	1411
$\delta_{\text{sym}}\text{C—H}$	—	1373, 1348	1373, 1347
$\nu\text{C—O}$	—	1308	1308
$\nu\text{C—N}$	1448, 1308	1235	1235
$\delta\text{C—H}$ (aromatic)	1200–1000	1200	1200
$\nu\text{C—O—C}$	—	1102	1097
$\nu\text{C—C}$	—	946	946
Subst aromatic ring	826	816, 757	816, 757
$\omega\text{C—H}$ (aromatic)	913, 694	730–550	707, 664
Ring deformation	526	510	511

ν = stretch, δ = in-plane bending, ω = out-of-plane bending, sym = symmetric, as = asymmetric, subst = substituted

Scanning Electron Microscopy

The morphology of the synthesized PANI, PU and their blends containing 0.1 wt% and 0.5 wt% of conducting polymer at different magnifications was recorded using SEM (Fig. 2). The SEM image of PANI (Fig. 2a) showed the formation of the spherical structure due to agglomerated particles^[25]. From the SEM image in Fig. 2(b), the homogeneous surface for pure PU was observed and characterized as a smooth fracture^[25]. Figures 2(c) and 2(d) show the morphology of PU/PANI blend with 0.1 wt% PANI at two different resolutions. The surface morphology reflected a smooth continuous surface, representing homogeneous network formation of PANI in polyurethane matrix. The hydrogen bonding between PANI and polyurethane at lower PANI content resulted in better compatibility between the two polymers, leading to homogeneous dispersion in the matrix. The

interaction between the carboxyl groups of PU and imine groups of PANI has been reported by the researchers^[18, 24, 26], which was believed to be responsible for a certain degree of phase mixing/miscibility in PU/PANI blends. However, the appearance of irregular surface in the micrograph revealed the fractured portion of the polymer. When the PANI content was increased to 0.5 wt%, the well distinct large granular structure of the PANI was observed as shown in Figs. 2(e, f). The agglomerated structure signified the formation of more conductive pathway in the insulating matrix. At higher PANI contents, the extensive hydrogen bonding and crosslinking between two polymers resulted in phase separation and consequently heterogeneous morphology was observed. The continuous phase, represented by the darker region was related to the PU matrix, and the dispersive spherical-like domains associated with the phase rich in PANI were observed.

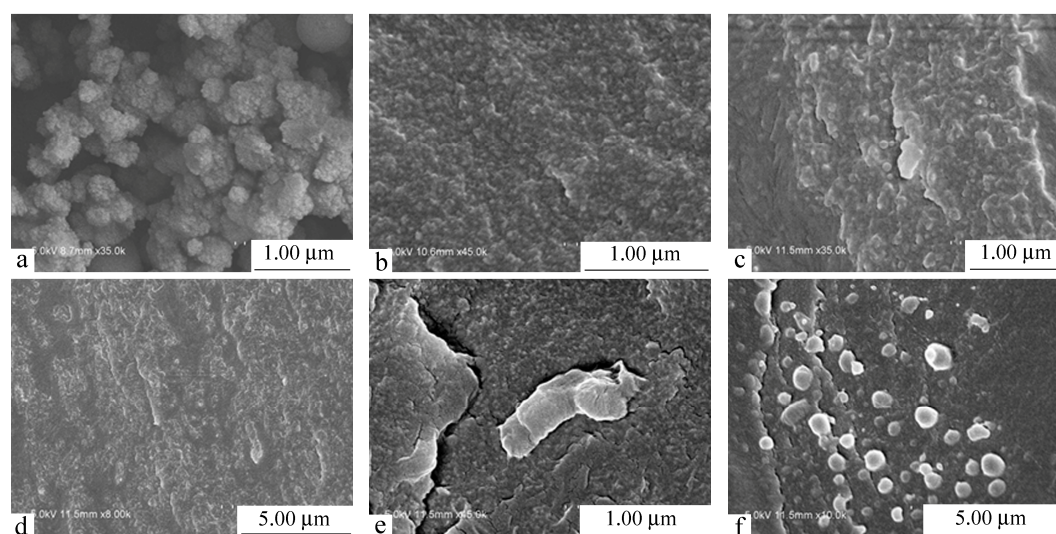


Fig. 2 Field emission scanning electron microscopy (FESEM) images of: (a) PANI, (b) PU, (c) and (d) PU/0.1% PANI of different magnifications, (e) and (f) PU/0.5% PANI of different magnifications

Thermogravimetric Analysis

The thermal stability for the neat PU and polyurethane/polyaniline blends in nitrogen atmosphere is illustrated in Fig. 3. All TGA curves of blends as well as neat PU showed two stages of degradation. The first degradation step was attributed to the degradation of TDI and PANI hard-segments followed with the degradation of soft-segments of polyurethane comprising of polyols in second step^[27]. The on-set, the end-set and maximum degradation temperatures were observed (Table 2). The thermal stability of all blends increased with the increase in PANI content in PU matrix. For the neat PU, the initial weight loss for the first stage was observed starting at around 320 °C and the second one at about 429 °C. The addition of 1 wt% PANI resulted in the increase of initial degradation temperature of first and second stages (19 K and 21 K respectively). Actually, in the sequential polymerization of PU/PANI blends, the PANI segments with amine groups used to form the urea linkages with the isocyanate groups of TDI and contributed as the hard-segment of PU. Consequently, the increase in PANI content increased the number of urea linkages which were thermally more stable than the urethane linkages and were responsible for the enhanced thermal stability of the blends. The maximum decomposition rates for the first and second stage of neat PU were around 410 and 482 °C, while those of PU/1% PANI blend were at 424 and 499 °C. This increase for blend was because of the interaction between the PU and PANI chains^[28] and the formation of urea linkages. In addition, it was also found that the char residue increased with the PANI content. As for the char residue, many results demonstrate that enhanced char formation reflects the improved thermal stability of a system^[29, 30]. It is obvious that the higher char yield was produced by the higher weight percent of PANI in the blend due to its improved thermal stability^[27] representing that the aromatic rings with stable bonds in the PANI chains are not completely decomposed at high temperatures in inert atmosphere^[31].

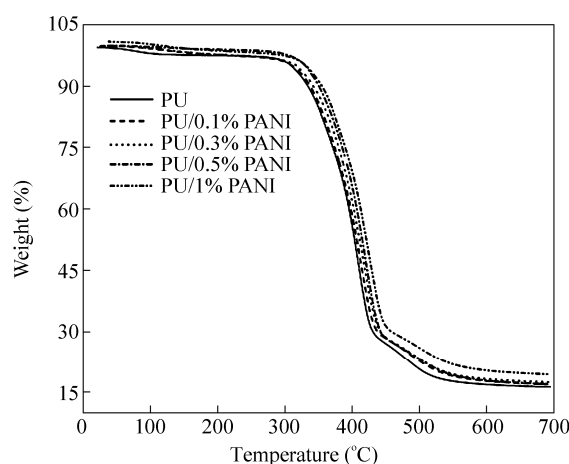


Fig. 3 Thermogravimetric analysis (TGA) curves for PU and PU/PANI blend films

Table 2. TGA data of decomposition of PU and PU/PANI blend films

Sample composition	First step degradation			Second step degradation			Y_c at 700 °C (wt%)
	T_o (°C)	T_e (°C)	T_{max} (°C)	T_o (°C)	T_e (°C)	T_{max} (°C)	
PU	320.71	429.28	409.77	429.28	534.83	482.20	16.73
PU/0.1% PANI	323.75	433.63	415.23	433.63	551.96	485.16	17.18
PU/0.3% PANI	325.60	441.37	419.66	441.37	561.68	491.66	17.42
PU/0.5% PANI	333.34	443.22	422.11	443.22	561.68	497.52	16.92
PU/1% PANI	339.06	451.80	423.75	451.80	563.70	499.15	19.35

T_o : On-set decomposition temperature; T_e : End-set decomposition temperature; T_{max} : Maximum decomposition temperature; Y_c : Char yield at 700 °C

Differential Scanning Calorimetry

The glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c), heat of melting (ΔH_m), and heat of crystallization (ΔH_c) obtained from DSC studies are summarized in Table 3. Figures 4(a) and 4(b) demonstrate the effect of PANI content on the melting and crystallization temperature of PU/PANI blends respectively. It was apparent that the higher melting and crystallization temperatures as well as the higher values for heat of melting and crystallization occurred due to the incorporation of higher content of PANI in PU. The increase of PANI content up to 1 wt% in PU matrix resulted in rise of only about 4 K in melting temperature as compared to neat PU. Furthermore, the melt enthalpy was also enhanced to some extent but a significant shift observed for crystallization behavior. For neat PU the peak for crystallization appeared at around 18 °C, while for the PU/PANI blend with 1 wt% PANI, this peak moved to higher temperature at around 42 °C. Such a significant increase was attributed to the presence of higher degree of hydrogen bonding and formation of urea linkages with higher PANI content. The polymer chain crosslinking, both physical (hydrogen bonding) and most important chemical (urea linkages), could be the key factor for enhanced melting and crystallization temperatures. As crosslinking reduced the chains flexibility and also hindered the motions of polymer chains, so thermal transitions occurred at higher temperatures. These findings indicated that the increase in chain rigidity was due to the introduction of relatively stiff benzene containing groups in PU. The cross linking was also responsible for an increase in T_g as displayed in Fig. 4(c). Higher PANI content may increase the phase mixing between the hard and soft segments due to the increase of hydrogen bonding and is responsible for the higher glass transition temperature^[27].

Table 3. DSC data of decomposition of PU and PU/PANI blend films

Sample composition	T_g (°C)	T_m (°C)	ΔH_m (J·g ⁻¹)	T_c (°C)	ΔH_c (J·g ⁻¹)
PU	5.28	56.94	3.97	17.58	3.44
PU/0.1% PANI	7.46	59.29	4.24	35.59	3.57
PU/0.3% PANI	7.48	60.45	3.57	37.93	3.32
PU/0.5% PANI	7.78	60.64	3.61	40.93	3.16
PU/1% PANI	8.31	61.23	5.54	41.98	5.18

T_g : Glass transition temperature; T_m : Melting temperature; ΔH_m : Heat of melting; T_c : Crystallization temperature; ΔH_c : Heat of crystallization

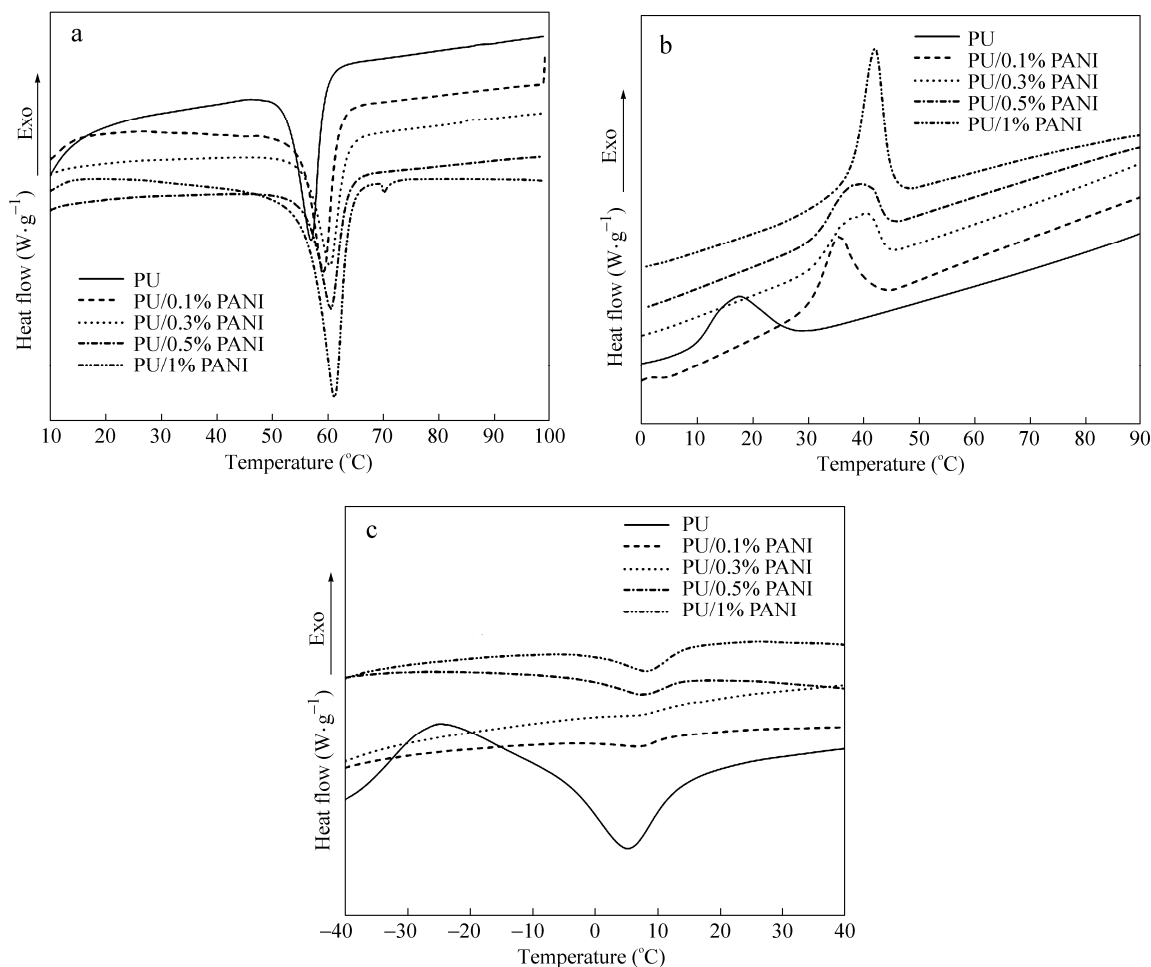


Fig. 4 Differential scanning calorimetry (DSC) thermograms for PU and PU/PANI blends on heating (a), on cooling (b) and in low temperature region (c)

Mechanical Properties

The mechanical response (stress-strain curves) for neat PU and all prepared polyurethane blends with PANI is plotted in Fig. 5. The mechanical properties for pure PU film were poor due to the presence of entangled polyol soft segments. For the blend (Table 4), the tensile strength and Young's modulus at 1 wt% PANI loading reached 24.50 MPa and 427.87 MPa respectively (higher than those of neat PU). It was noticed that the higher PANI content has increased the values of Young's modulus and tensile strength (Fig. 6). Luo *et al.*^[32] reported that the presence of second dispersed phase in a PU matrix may affect the mechanical properties of the blends, depending on the nature and concentration of the disperse phase, surface characteristics, distribution pattern, domain size and the degree of compatibility. Ho and coworkers^[19] also presented that the tensile strength showed

monotonical increase with PANI loading for the PU/PANI blends with higher degree of hydrogen bonding. However, a monotonical drop was observed for the blends with lower degree of hydrogen bonding. Therefore, the improved mechanical performance of PU/PANI blends with PANI loading may be the result of good confinement of PANI chains in the blend network. The interaction between N—H groups of PANI backbone and C=O groups of PU matrix (Scheme 1) was also responsible for the improved properties. On the contrary, for all blend films, the elongation at break was lower with higher PANI content. This was due to the presence of stiffed aromatic structure of PANI backbone rendering PU blends more rigid and brittle. High PANI loadings may increase the cross-linking density leading to enhancement in the rigidity of the blends. Therefore, decrease in the elongation at break with increasing PANI loadings was observed.

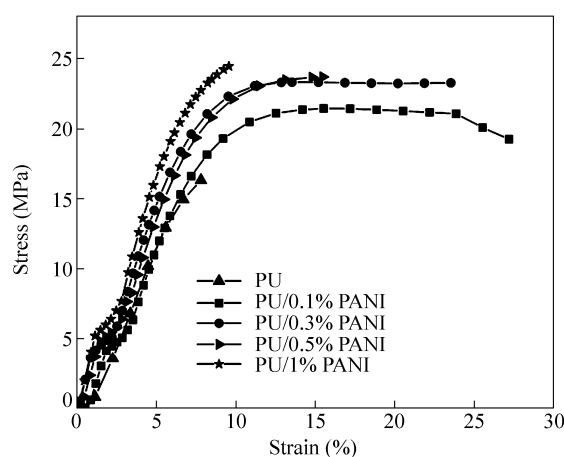


Fig. 5 Stress-Strain curves for PU and PU/PANI blend films

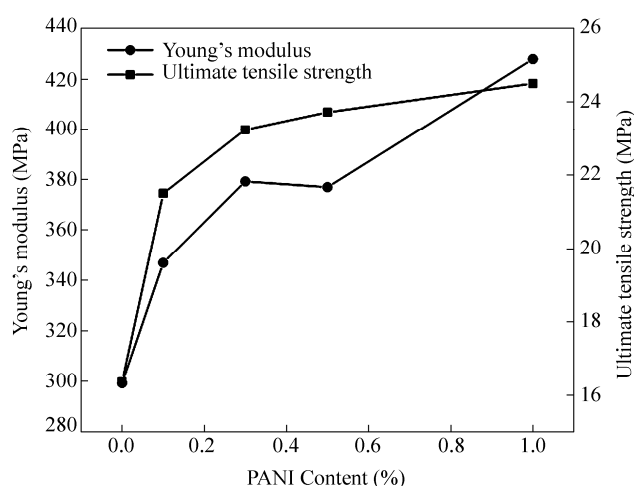


Fig. 6 Effect of PANI content on Young's modulus and ultimate tensile strength for PU/PANI blend films

Table 4. Mechanical properties of PU and PU/PANI blend films

Sample composition	Ultimate tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
PU	16.36	7.93	299.29
PU/0.1% PANI	21.50	27.27	346.97
PU/0.3% PANI	23.24	24.85	379.31
PU/0.5% PANI	23.72	15.80	376.98
PU/1% PANI	24.50	9.75	427.87

Electrical Conductivity Measurement

Figure 7 shows the conductivity as a function of the content of the conductive component *i.e.* PANI in PU blends. The electrical conductivity results for neat PU and PU/PANI blends are summarized in Table 5. For the polyurethane matrix alone, the electrical conductivity was in the order of 10^{-7} S·cm⁻¹, and it increased to 10^{-6} S·cm⁻¹ by addition of 0.1 wt%–1 wt% PANI. Fan and coworkers^[31] presented the increasing trend for the electrical conductivities of PU/PANI blends with the rise in PANI content. The synthesized blends, in this study, owned conductivity in the range of 1.29 – 6.94×10^{-6} S·cm⁻¹. These values were comparable to the literature values established by other researchers^[18, 20, 33, 34]. Ultimately, these values in the range of 10^{-6} S·cm⁻¹ might meet the requirement for the antistatic materials^[18]. The conductivity results led to the conclusion that the PANI chains were inter-mixed in the PU matrix to form conductive phase^[26], which could be responsible for the enhanced conductivity with higher PANI loading^[35]. The stronger hydrogen bonding between PU and PANI in the blend added better miscibility and contributed to higher conductivity is also reported^[19].

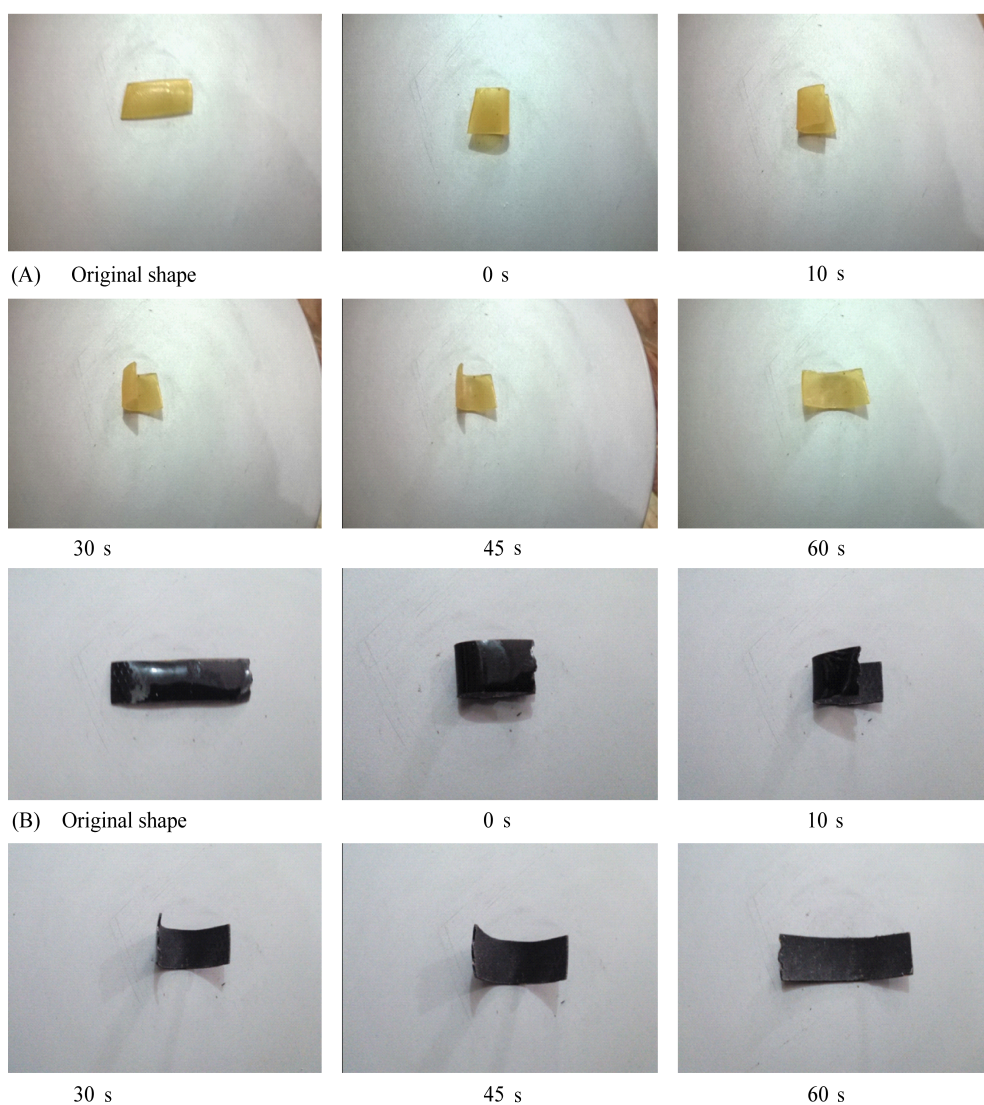
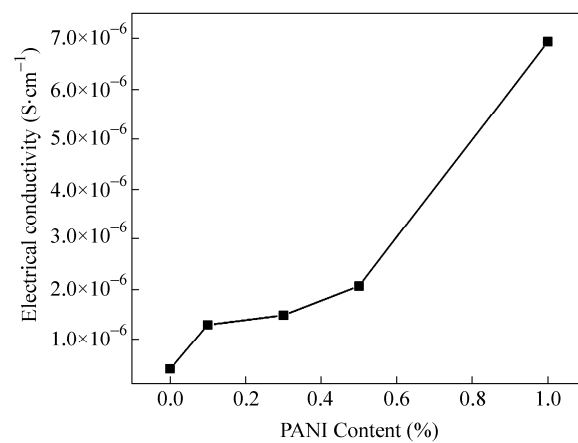


Fig. 8 Shape memory recovery of (A) PU and (B) PU/1% PANI blend films heated at 60 °C

Table 5. Electrical conductivity and shape recovery of PU and PU/PANI blend films

Composition	Electrical conductivity (S·cm ⁻¹)	Shape recovery (%)
PU	4.06×10^{-7}	84
PU/0.1% PANI	1.29×10^{-6}	89
PU/0.3% PANI	1.48×10^{-6}	90
PU/0.5% PANI	2.06×10^{-6}	92
PU/1% PANI	6.94×10^{-6}	96

Shape Memory Study

The shape memory property was observed by bending the samples at transition temperature (T_{trans}) followed by cooling at room temperature (20 °C) to obtain temporary shape and finally reheating the sample. The value of T_{trans} for SM polyurethane blends was around 60 °C representing the T_m obtained from DSC studies. This shape memory PU belongs to T_m -type, because the glass transition temperature is low and hard to control the temperature around T_g ^[36, 37]. The shape recovery was studied on a hot plate with a surface temperature of 60 °C. The PU and PU/PANI blends displayed a prompt response, recovering to their original shape within 60 s as enlisted in the Table 5. For neat PU, 84% shape recovery was observed while maximum value of shape memory recovery of 96% appeared for blend with 1 wt% PANI as shown in Fig. 8. It was obvious that the incorporation of PANI directed to a noticeable enhancement in shape recovery. The fact was attributed to polyaniline that acted as the hard phase in PU matrix and strengthened the polymer networks *via* hydrogen bonding and formation of urea linkages. The physical and chemical interaction of PANI with PU chains was responsible for maintaining the permanent shape of the sample. Hydrogen bonding together with dipole-dipole interaction fixed the hard segments to form a hard domain which acted as key factor in recovering the original shape above T_m ^[38].

CONCLUSIONS

We have successfully synthesized the PU/PANI blends with varying PANI contents through chemical *in situ* polymerization method. It was found that the hydrogen bonding between the PU segments and formation of urea linkages (reaction N—H of PANI and —NCO of PU) were responsible for the compatibility between the two polymers. The chemical and physical interactions resulted in improved tensile strength and Young's modulus. The degradation temperature of the blends was shifted to higher values with the increase in PANI content. The DSC analysis revealed that the addition of PANI up to 1 wt% increased the T_g , T_m and T_c owing to crosslinking and chain rigidity. Addition of PANI also enhanced the electrical conductivity values. Good shape memory recovery effect of nearly 96% was observed in the blends with higher PANI content.

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