



Effect of acyl chloride functionalized carbon black on mechanical and thermal properties of acrylonitrile butadiene styrene/polyaniline blend

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Pristine Carbon Black (CB) has been first oxidised to introduce carboxylic acid functional group on the surface of CB, followed by treating with thionyl chloride. The presence of acyl chloride group in the resultant product has been ascertained by FTIR spectroscopy. The acyl chloride functionalized CB (CB-Ac) has been used as a filler in Acrylonitrile Butadiene Styrene (ABS)/Polyaniline (PANI) blend to improve the mechanical and thermal properties. Further addition of Nanoclay (NC) in the blend has improved the dispersion of fillers in the polymer matrix as confirmed by FESEM images and XRD pattern. The Ultimate Tensile Analysis (UTA) and Dynamic mechanical analysis (DMA) have been studied. The Young modulus has shown increment of 48% and 66% in case of CB-Ac and CB-Ac/NC filled blend, respectively. The ultimate tensile strength has also been found to be increased in CB-Ac and CB-Ac/NC filled blends. DMA has given the insight about the excellent improvement in damping properties of the composites due to filler addition. Thermo gravimetric analysis (TGA) and Differential scanning calorimetry (DSC) has been carried out to ascertain the thermal properties. TGA has revealed the excellent augmentation in the flame retardancy and heat resistance of the composites due to CB-Ac/NC loading. DSC study has further verified the improvement in degree of crystallinity due to interfacial attraction between fillers and polymer matrix.

Keywords: Dynamic mechanical analysis, Nanoclay, Tensile strength, Thermal stability, Thermo gravimetric analysis

1 Introduction

Conductive polymers have attracted attention of researchers from their inception¹. These polymers have found their potential applications in various fields of science and technology such as sensors^{2,3}, light emitting diodes^{4,5}, antistatic devices⁶, batteries^{7,8}, electronic tongues⁹, electrochromic devices^{10,11} etc. Polyaniline (PANI) is one of such important polymer. It has been found to be very useful due to its easy and economic preparation, excellent thermal stability, chemical stability and high conductivity. But its applications have been observed to be limited due to its poor mechanical and dynamic properties, worse processability and solubility¹². So PANI has been used as a blend with some thermoplastic polymers like Poly methyl methacrylate (PMMA), Polystyrene (PS), Acrylonitrile Butadiene Styrene (ABS) etc. ABS has also been extensively used in daily life as it can be machined, injection moulded, extruder moulded and softened by heating to give a desired shape^{13,14}. The

ABS/PANI blend has been studied extensively as it exhibits good electrical properties and transport mechanism but at the cost of its mechanical properties¹⁵⁻¹⁷.

Carbon based materials have shown tendency of agglomeration due to their hydrophobicity. Agglomeration has been possible to be prevented by surface functionalization¹⁸ or chemical modification, thus enhancing the homogeneous dispersion of CB in polymer matrix.

There are several methods of functionalization of CB like oxygen plasma treatment^{19,20}, heat treatment with mineral acids^{21,22}, electrochemical oxidation²³, etc. There are ample of literatures to support that, some functionalization of fillers improves the ability of dispersion and binding efficiency of the thermoplastic polymer matrix. Thus, eventually enhances mechanical and other properties^{24,25}.

Nanoclays (NC) are fine-grained aluminosilicate minerals with well-defined plate like microstructures where the plates are held upon one on another by weak Vander Waals forces. NC minerals have high strength, very large surface area and aspect ratio. NC

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plates readily dissociate and it itself get dispersed and assists dispersion of other fillers in polymer matrix. A single layer of NC has been reported to have Young modulus, ranging between 178 to 265 GPa²⁶. The plates can be split into thin layers along the cleavage planes. NC assisted dispersion of fillers in polymer matrix and subsequent improvement of mechanical properties has been well demonstrated in the literature^{27,28}.

In this paper, the chemical modification of CB has been carried out by two step process. Pristine CB has been first oxidised to introduce carboxylic acid group on the surface of the CB and further treated with thionyl chloride to convert the acidic group to acid chloride. The resultant product has been found to be acid chloride functionalized CB and labelled as CB-Ac. Besides, we have tried to improve some physical properties like mechanical and thermal properties of ABS/PANI blend by the incorporation of chemically modified Carbon Black (CB) and nanoclay (NC). It has simultaneously increased the flame retardancy and the heat withstanding capacity by incorporating CB-Ac and CB-Ac+NC.

2 Materials and Methods

ABS was brought from Bansali Engineering Pvt. Ltd., Mumbai, India and used as received, without any further treatment. The synthesis of PANI was carried out as per our previous work²⁹. Carbon black (P-842) was purchased from Philips Carbon Black Ltd., Kolkata, India. Nanoclay (Cloisite 25[®]) was obtained from Connell Brothers, California, USA. FTIR of CB-Ac was done with the help of FTIR Spectrometer (Thermo Scientific, Nicolet 6700) to determine various functional groups present in the surface of functionalized CB. FESEM was done using FESEM instrument (model Zeiss- Ultra Plus, Gemini Co.) to investigate the surface morphology of the composites. X-ray diffractometer (Bruker AXS Diffractometer D8) equipped with Cu K α radiation ($\lambda=0.1540$ nm) was used to obtain X-ray diffraction (XRD) patterns of composite samples and CB-Ac. Tensile test was carried out on universal tensile testing machine (Instron 5582), at room temperature (25 ± 2 °C). The samples for tensile tests were prepared according to ASTM D638-10. Initial gauge length of specimens was 50 ± 5 mm and crosshead speed was maintained at 2 mm/min. Three samples were tested for each set of parameters and the average properties from tensile tests were reported here.

Dynamic mechanical thermal analysis (DMTA) was carried out on DMA machine (TA Q800, USA). Rectangular specimens of dimensions ($60 \times 12 \times 2$ mm) were prepared on the basis of lateral dimensions required for 3-point bending clamp. Variation of all three fundamental dynamic properties i.e. storage modulus (E'), loss modulus (E'') and damping factor ($\tan \delta$) were studied against temperature (room temperature to 120 °C). Thermal characteristics of all composites were studied with the help of thermogravimetric analysis (TGA) using 'TGA-SII-6300 Exstar' instrument. These tests were carried out in nitrogen atmosphere at a scanning rate 10 °C/min and the temperature range was varied from 32 °C to 700 °C.

2.1 Functionalization of acid functionalized CB (f-CB) from pristine CB

1 g of dried CB was added to 10 mL of conc. HNO₃ under vigorous stirring and the solution was refluxed for about 8 hours at 70-80 °C, under mild stirring. The refluxed solution was diluted with water, filtered and washed with distilled water until the pH of the sample become constant. Finally, f-CB was dried in a vacuum oven at 80 °C for 24 hours.

2.2 Preparation of acid chloride functionalized CB from f-CB

Dried f-CB was grinded finely with gradual drop by drop addition of thionyl chloride (SOCl₂). The success of the reaction was confirmed by the pungent smell of HCl. The residue obtained (CB-Ac) was used without any further treatment.

2.3 Preparation of polyaniline

Polyaniline (PANI) was prepared using most greener, efficient (in terms of energy and time) and convenient method described in literature³⁰. At first 0.25 M ammonium peroxodisulphate was prepared by dissolving 5.71 g of ammonium peroxodisulphate with 50 ml of double distilled water. Again, 0.2 M aniline hydrochloride was prepared by dissolving 2.59 g of aniline hydrochloride with 50 ml double distilled water in a separate beaker. The solutions were kept at room temperature for 1 hour. Both the solutions were mixed slowly with mild stirring and resultant solution was kept for polymerization with continuous stirring. The precipitate of PANI was washed several times with 0.2 M HCl solution followed by acetone. The PANI was dried in vacuum at 60°C for 24 hours and grinded.

2.4 Preparation of nano-composites

Nano-composites were prepared using internal mixer machine (SC Dey & Co. Kolkata, India) and

subsequent processing of composites in compression moulding to achieve desired shapes of the specimens. ABS polymer was heated at 220°C in an internal mixture rotating at 60 rpm. The dried fillers (CB-Ac, PANI, NC) were fed into the semisolid polymer through the hopper and were allowed to mix homogeneously. Composite samples obtained from internal mixer were pressed in hot press machine (compression molding), to obtain samples of desired shapes, under 3 tons of pressure at 150°C for 5 min and were cooled down to room temperature under the same pressure. The details about composition of different composites have been illustrated in Table 1.

3 Results and Discussion

3.1 FTIR

The presence of different functional groups in CB surface were ascertained by FTIR technique and discussed in our previous work. Acyl chloride functionalized CB (CB-Ac) was also tested using FTIR technique and same was shown in the Fig. 1. The spectrum was almost similar to that of pristine CB²⁹ with additional peaks at 1710 cm⁻¹, 644 cm⁻¹, 619 cm⁻¹, 472 cm⁻¹ were also observed. Peak at 1710 cm⁻¹ is due to the presence of C=O stretching band and 644 cm⁻¹, 619 cm⁻¹ peaks may be attributed to C-Cl bond. Some common peaks were observed in both the peaks of CB and CB-Ac i.e. the basic graphitic structure of the CB was not hampered³⁰. Only the modification occurred on the surface.

A broad peak at 3439 cm⁻¹ was due to the presence of alcoholic or phenolic O-H³¹. The peak at 1639 cm⁻¹ may be attributed for C=C stretching present in graphitic layer of CB and 1411 cm⁻¹ for aromatic C-H (C=C-H). A sharp peak at 1018 cm⁻¹ may be due to =C-O bond of Phenolic OH^{32,33}.

FTIR spectrum was evident to the success of the production of CB-Ac from pristine CB via acid functionalized CB. Same was qualitatively determined by the pungent smell of HCl during the reaction.

3.2 XRD

Figure 2 showed the XRD patterns for prepared composite samples. A characteristic peak around

$2\theta = 20^\circ$ was observed corresponding to ABS³⁴. In all the composites this peak was prominent. ABS/PANI blend exhibited its amorphous nature with a broad peak around $2\theta = 20^\circ$. Since no polymer is perfectly crystalline or perfectly amorphous and there is flexibility in polymer molecular chains, there is a scope to improve the degree of crystallinity. Addition of fillers in the polymer matrix remarkably increased the crystallinity of the polymer matrix. This indicated that there was a development of more orderly arrangement of chains. This may be due to interfacial adhesion between fillers and polymer, which was caused by the huge difference in specific surface energy. Interfacial adhesion restricted the molecular chain movement, thereby increasing the more orderly arrangement; hence degree of crystallinity increased.

All the curves exhibited relatively sharp peak at $2\theta = 20^\circ$ other than ABS/PANI indicated some development of crystallinity due to CB-Ac loading. One significant observation was that, NC sharpened the peak. Indicating the homogeneous dispersion and good intercalation of NC in polymer matrix. Another remarkable observation in the support of molecular chain restriction (i.e., crystallinity) was the development of additional peaks around $2\theta = 45^\circ$.

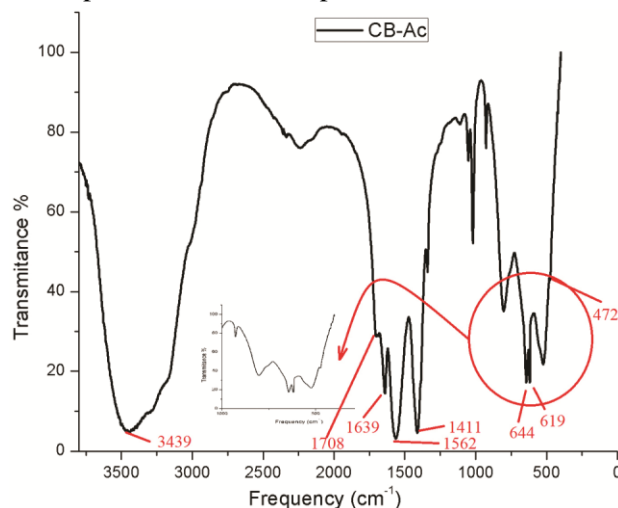


Fig. 1 — FTIR of the acyl chloride modified carbon black.

Table 1 — Composition of different composites

Sample codes	Composition of Elements (wt%)			
	ABS	PANI	Acid (-COOH) functionalized CB	Nanoclay
ABS/ CB-Ac	97	-	3	-
ABS/PANI	97	3	-	-
ABS/PANI/CB-Ac	94	3	3	-
ABS/PANI/CB-Ac/NC	91	3	3	3

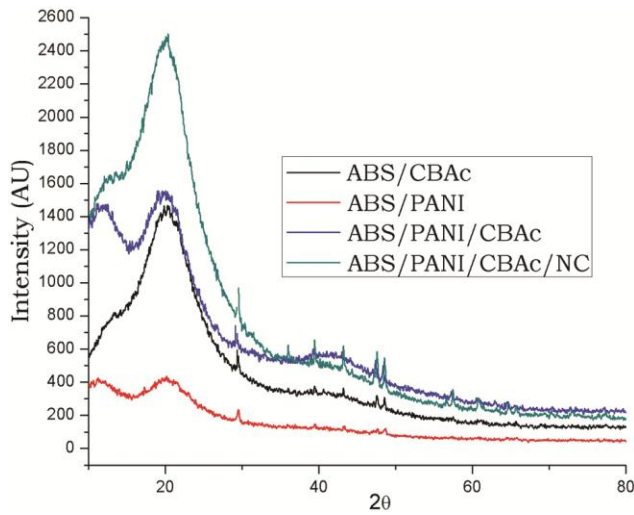


Fig. 2 — XRD-pattern of the nano-composites.

3.3 FESEM

Surface morphology of the prepared composites and fillers were determined by FESEM images and same was shown in Fig. 3(a-f). The figures gave a qualitative idea about the dispersion of fillers and consequent change in surface and other properties. The ABS/PANI interface was clearly visible in Fig. 3(a). Weak interfacial adhesion and consequent poor mechanical properties of said blend can easily be ascertained from this figure. Thermoplastic (ABS) component and the PANI component were distinctly visible in the figure; ABS component can be compared with Fig. 3(e). Low difference of specific surface energy between the polymer matrixes may be the reason behind the weak interfacial adhesion³⁵.

ABS/CB-Ac and blends were shown in Fig. 3(c and d) respectively. In the figures, only thermoplastic component was shown and there was no considerable

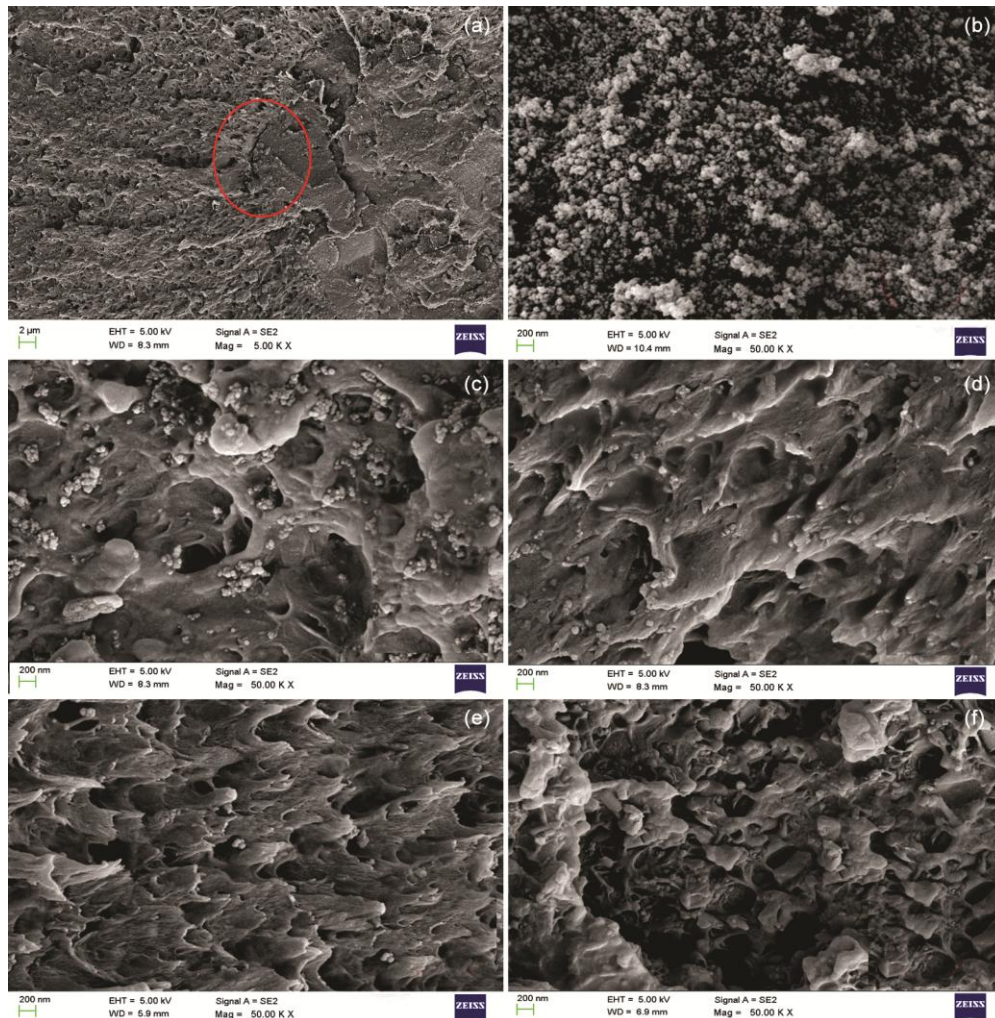


Fig. 3 — FESEM images of nano-composites (a) ABS/PANI interface has been shown in circle, (b) Acid chloride modified CB, CB-Ac, (c) ABS matrix with CB-Ac, (d) ABS matrix with CB-Ac, (e) ABS matrix, (f) ABS/PANI/CB-Ac/NC.

change due to presence of PANI. Fig. 3(f) showed the surface morphology of ABS/PANI/CB-Ac/NC composite. It clearly showed the change in surface morphology due to incorporation of NC. CB-Ac particles were also visible and they were more homogeneously dispersed in the ABS matrix than previous samples. Homogeneous dispersion enhanced mechanical and other properties and discussed earlier.

3.4 Tensile

Tensile properties of the composites were determined and Stress vs. Strain graphs were presented in the Fig. 4; some of the important tensile properties were shown in the Fig. 4 and summarized in Table 2. Both CB-Ac and NC loading in ABS/PANI blend increased the Young modulus of the composites by 65.76% while, only CB-Ac loading increased Young modulus by 47.39%. Same can be observed in case of ABS/CB-Ac composite by 56.33%. That means, the augmentation in young modulus was largely due to the contribution of ABS matrix. Ductility of the composites was also shown in Table 2 and can be visualized from the graph (Fig. 4). NC loaded composite was brittle and less ductile, while other composites showed good extent of elongation hence those were relatively ductile. In the stress vs strain curve, ABS/PANI showed a stress relaxation after

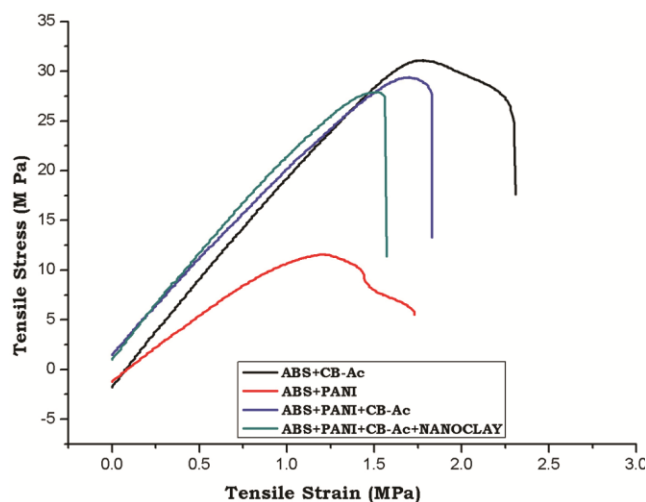


Fig. 4 — Stress vs. Strain curve of nano-composites.

yield point indicating the non-homogeneous mixing of polymers and weak interfacial attraction. Thus ABS component retained its individual property and PANI has less influence on it.

There was no binding site between ABS and PANI and both were organic material, so there was very less difference of specific surface energy, hence no interaction. Since the mechanical properties were increased due to CB-Ac loading, it may be presumed that, there was a development of some filler-matrix interaction that restricted the matrix movement along the interface. The results found here were comparable with the available literature having similar works^{27, 29, 36}.

3.5 DMA

Polymers are composed of long chain molecular structure and often crosslinked among them, due to which it shows a unique property called viscoelastic property, which is a combined characteristic of elastic solid and Newtonian fluid. Applying force on an ideal viscous substance, dissipates the entire applied force in the form of heat and the energy cannot be recovered by removing the external force; again in case of ideal elastic materials external force may be recovered just by releasing the force from the elastic material.

On application of force on viscoelastic materials, some of the force is absorbed by the material and remaining force is dissipated. Storage modulus represents the force which is stored by a viscoelastic material on application of force on it; again loss modulus represents the force which is release by the material. The ratio of the loss modulus and storage modulus is known as $\tan\delta$.

Dynamic mechanical study was carried out with all the prepared composites and shown in Fig. 5. Change of Storage modulus, Loss modulus and $\tan\delta$ with respect to temperature (room temperature to 120°C) was shown in the graphs. Figure 5(a) represented Loss modulus vs. temperature curve. Loss modulus of both ABS/CB-Ac and ABS/PANI/CB-Ac/NC increased from ABS/PANI blend indicating increase in elastic behaviour. Whereas, ABS/PANI/CB-Ac showed decrease in loss modulus. Figure 5(b) showed the

Table 2 — Tensile properties of the composites.

Sample Code	E-Modulus (MPa)	Tensile Stress at Yield (MPa)	Ductility (%)	Tensile Stress at Break (MPa)
ABS/CB-Ac	2134.84	23.72	2.68	31.15
ABS/PANI	1365.21	7.900	1.96	11.56
ABS/PANI/CB-Ac	2012.58	17.054	2.57	29.25
ABS/PANI/CB-Ac/NC	2262.92	13.617	1.72	27.87

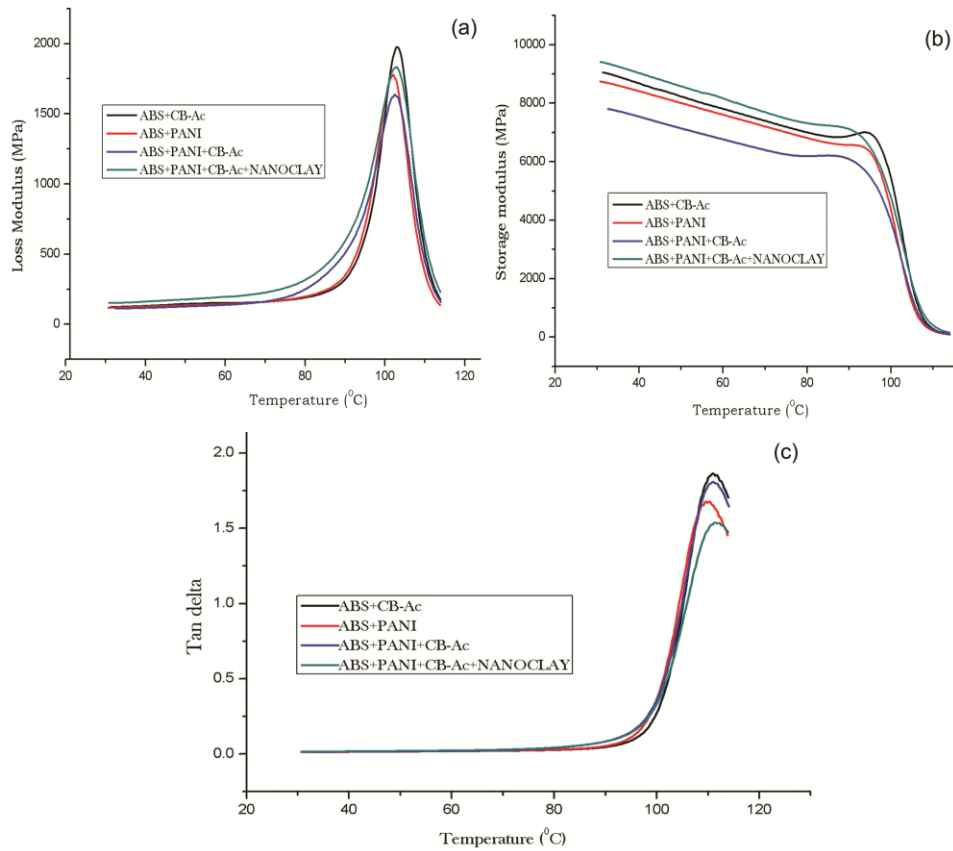


Fig. 5 — Dynamic mechanical analysis of the prepared composites.

Storage modulus vs. Temperature curve of the prepared composites. Storage modulus was increased due to the incorporation of CB-Ac and NC in the ABS/PANI blend. This may be due to development of some cross linking among the polymer chains or between the fillers and polymer matrix. Both Loss and Storage modulus of the ABS/PANI/CB-Ac/NC composite were higher than that of remaining composites, representing better dispersion of fillers in the polymer matrix and also may be due to increased interlayer spacing of the NC and CB-Ac³⁷. ABS/PANI/CB-Ac again showed lesser storage modulus. Figure 5(c) showed the tan delta vs. Temperature curve. Tan delta represents a measure of the viscous portion to the elastic portion³⁸. In all the three graphs, near glass transition (T_g) temperature, the curves showed different behaviour. In this temperature region (the glass transition), molecular segmental motions were activated as the molecular vibrational frequency increases, however the segmental motions were difficult and this is described as molecular friction that dissipates much of the force. Hence the material became less stiff/hard and more

force was dissipated as heat, hence increased the loss modulus. Much less energy was stored since the molecules can move with the force giving a rapid decline in storage modulus.

3.6 TGA

Thermogravimetric analysis was carried out with all the prepared composites. Figure 6 showed the gradual weight loss due to thermal decomposition of the samples with respect to temperature. ABS/PANI blend showed its initial degradation onset at 223°C. There was a tremendous augmentation of initial degradation onset in TGA after addition of CB-Ac and NC. Degradation onset of both ABS/CB-Ac and ABS/PANI/CB-Ac was 351°C. Whereas, NC loading on ABS/PANI/CB-Ac slightly reduced to 320°C. Still it is much higher than that of ABS/PANI blend. That means, initial thermal degradation of ABS/PANI blend was remarkably increased due to filler loading. At 370°C, when the degradation started, weight retention of the composites was significant. The values were shown in Table 3. At this temperature, when ABS/PANI decomposed to 83%, decomposition of other composites still not started significantly.

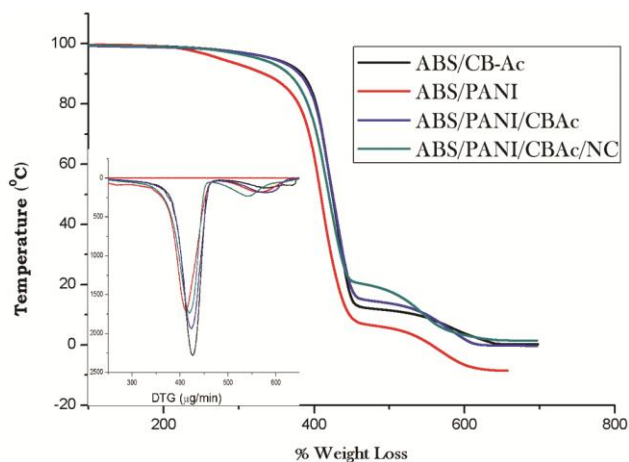


Fig. 6 — TGA curve of nano-composites.

Table 3 — TGA of the nano-composites.

Composites	Residual weight % at 370 (°C)	Residue percentage 10 % at temperature (°C)
ABS/CB-Ac	92	532
ABS/PANI	83	442
ABS/PANI/ CB-Ac	92	546
ABS/PANI/ CB-Ac/NC	89	546

Residue retention upto 10% (assuming complete degradation) was shown in the Table 3. 10% residue remained for ABS/PANI composite at 442°C. Whereas, filler loading extensively increased the temperature for other composites by more than 100°C. That means composites achieved greater thermal resistance and flame retardancy.

3.7 DSC

No polymer is perfectly crystalline or perfectly amorphous, rather there is simultaneous existence of both the phases. In a same polymer there will be some portion where polymer chains exist in well-arranged manner and called crystalline domain again some of the polymer chains are randomly arranged and called as amorphous domain. The extent of crystallinity is expressed by a term called Degree of crystallinity. More value of degree of crystallinity represents, the existence of large number of well-arranged polymer chains. Mixing of fillers in a polymer matrix alters the degree of crystallinity. Crystalline substance shows a sharp phase change on heating while amorphous substance shows phase change in a range of temperature.

Differential scanning calorimetry was carried out with all the prepared composites and heat flow vs Temperature curve was shown in Fig. 7. ABS/PANI blend showed one exothermic phase change at lower

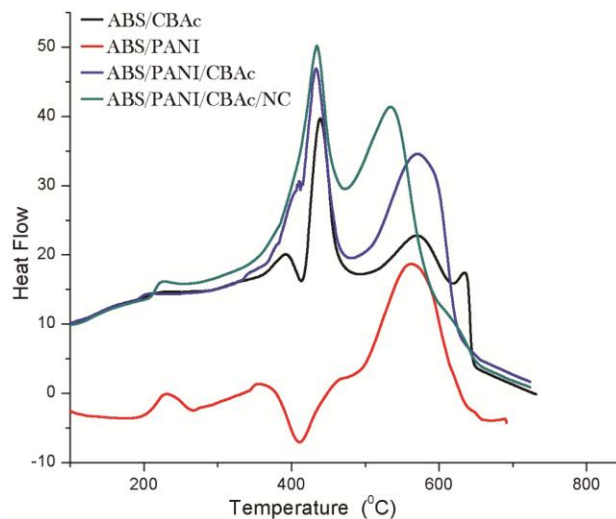


Fig. 7 — DSC of the nano-composites

Table 4 — Enthalpy of phase change of the composites

	Enthalpy of Phase change (-ΔH)
ABS/CB-Ac	348
ABS/PANI	409
ABS/PANI/CB-Ac	433
ABS/PANI/CB-Ac/NC	434

temperature range. Endothermic phase change referred to development of higher orderly arrangement of polymer chains, may be due to development of intermolecular attraction or polymer-polymer interaction. This phase change was shown by ABS matrix only and confirmed by ABS/CB-Ac curve where same phase change was observed without the presence of PANI.

At lower temperature range (439°C), there appeared a relatively sharp peak which was absent in ABS/PANI curve. Sharp peak corresponding to phase change was an indication of crystalline phase. It can be concluded from the DSC curves that, CB-Ac and NC loading in the ABS/PANI blend increased the crystallinity i.e. the polymer molecular chain movement along the filler-matrix interface was restricted due to interfacial attraction and provides rigidity in the matrix. The same observation may be cross verified by obtained XRD analysis.

Area under the curve is a function of enthalpy of phase change. ($\Delta H = kA$ (where, H is the enthalpy of transition, k is the calorimetric constant, and A is the area under the curve). 'A' is calculated by integrating the peak corresponding to a given transition.). Enthalpy values are given in following Table 4.

4 Conclusion

In this paper authors have successfully improved the mechanical and thermal properties of ABS/PANI blend. Authors have studied morphology, crystalline properties, mechanical properties and thermal properties of the ABS/PANI blend, and the blend filled with CB-Ac and CB-Ac+NC. CB surface has been functionalized with acyl chloride group. More electronegative Chlorine atom and oxygen attracts electron density towards them and creates an electron deficient (partially positive) centre at carbon atom. This consequently increases the binding efficiency of filler and matrix. Acyl chloride functionalization has been exhibited and confirmed by the characteristic peaks obtained from FTIR spectroscopy. FESEM images have confirmed the homogeneous dispersion of the fillers and have exhibited the role of NC as compatibilizer. XRD curves have exhibited the crystalline properties of composites. Filler loading has enhanced the crystalline property thereby supporting the fact that, filler loading has restricted the polymer chain movement and enhanced the orderly arrangement of polymer chain. Ultimate tensile properties have been measured. Filler loading has shown excellent enhancement in Young modulus, Ultimate Tensile Strength, Load at break, brittleness. Damping property has also been measured using Dynamic mechanical analysis. Storage modulus and loss modulus has been enhanced by filler loading, may be due to polymer chain movement restriction. TGA study has shown the development of high temperature heat stability and flame retardancy of materials. The observation of XRD has been cross supported by DSC study.

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