

Thermal, mechanical and electrical properties of polyaniline based ceramic nano-composites

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Abstract. Micro/nanohybrid materials have vast applications due to their great potentialities in the field of nanoscience and nanotechnology. Herein we report an investigation on the fabrication and physicochemical characterization of ceramic ($\text{Fe}_{0.01}\text{La}_{0.01}\text{Al}_{0.5}\text{Zn}_{0.98}\text{O}$) and hybrid ceramic-polyaniline nano-composites. Ceramic nano-particles were prepared by sol-gel technique while optimizing the molar ratios of the constituent's metal nitrates. The prepared inorganic particles were then embedded in the polymer matrix via one-pot blending method. The prepared ceramic particles and their composites with polyaniline were analysed under FT-IR, SEM and TGA. The presence of some chemical species was observed at the interface of the compositing materials. TGA analysis showed the thermal stability of the composite material. Frequency dependent dielectric properties were analysed and it was found that conducting polyaniline has an additional effect on the electrical behaviour of the composite. Rheology study showed enhanced mechanical properties of composite material as compared to their constituting counterparts.

1. Introduction

Nanotechnology is the study of the science of nano-structured materials having dimensions in the range from 1 to 100 nm. Various physical properties of these nano-structured materials vary from those of the corresponding bulk materials due to their small dimensions. In this context, extensive research has been done on organic-inorganic nano-composites due to their promised potential application in the last two decades [1-3]. Nano-composites is a class of advanced materials due to their distinctive properties that cannot be found in macrocomposites [4]. Material scientists, chemists, physicist and biologists are trying to fully exploit functional nano-composites so as to produce smart materials. Functional (organic-inorganic) nano-composites are generally composed of inorganic nano-particles embedded in the organic polymer matrix. These hybrid composites combine the benefits of both organic polymer (i.e. process ability, flexibility, ductility, dielectric and mechanical) and inorganic counterpart (i.e. thermal stability, rigidity) [5]. An important characteristic of organic-inorganic nano-composites is that inorganic fillers with nano-dimensions enhance the interfacial area in these composites as compared to traditional composites [6, 7]. Not only for academics but in most of the applied areas such as ionics, electronics, optics, energy, environment, medicine and biology, nano-composites represent new materials. Applications comprise functional smart coatings, smart membranes, fuel cells, sensors, photocatalysts, photovoltaic, nanophotonics, therapeutics, innovative cosmetics, microelectronics, imaging, drug release, packing industries and automobiles etc. [8-10]. In



recent years, significant efforts have been made to devise and control the synthesis of hybrid composites with tailored morphologies.

Numerous organic-inorganic nano-composites have been prepared while adding a wide variety of nano fillers e.g. magnetic nano-particles, semiconductors and carbon nanotubes. A number of polymer's significant properties such as light weight, anti-corrosiveness, mechanical strength and dielectric behavior are used to fabricate these nano-composites [11]. Polyaniline (PANI) is an intrinsic conducting polymer widely used due to its facile synthesis, good environmental stability and process ability [12]. PANI based hybrid nano-composites have adopted a revolutionary progress. PANI has exceptional electrical properties that can be controlled significantly by protonation and charge-transfer doping. However, processing of such conducting polymers generally utilizes a large amount of organic solvents which are noxious to the environment.

Our synthesized ceramic-PANI composite is one of the types of hybrid nano-composites that combine the advantages of conducting polymer along with doping transition metal ions (ceramic). PANI in this composite also acts as a sensitizer that improves light absorption. Instead of strong organic solvents, aqueous media was used throughout the preparation process so as to make it a green pathway. Different physicochemical characteristics of the prepared nano-composites have been analyzed for its possible applications.

2. Experimental

2.1. Materials

All the chemicals applied in the preparation of ceramic nano-particles and composite were of analytical grade. Zinc nitrate, ferric nitrate, sulphuric acid (Scharlu, Spain), lanthanum nitrate (Merck, PAK), aniline (Acros Organics, USA), citric acid (Daejung, Korea) and potassium permanganate, potassium nitrate (BDH, England) were used as received.

2.2. Preparation of ceramic nano-particles

Sol-gel technique was used for the synthesis $\text{Fe}_{0.01}\text{La}_{0.01}\text{Al}_{0.5}\text{Zn}_{0.98}\text{O}$ ceramic particles. In a typical experiment, $\text{Fe}_2(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.073g), $\text{Al}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ (1.242g), $\text{La}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.162g) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (11.552g) were dissolved together in 100 ml double distilled (DD) under stirring with the slow addition of citric acid (5g) to this mixture. Liquid ammonia was used for keeping the environment of the solution neutral. The solution was then kept in an oven for drying at 80°C . A light bluish gel was obtained which was then grinded and sintered for 3 hours at 600°C . The diffused material was ground properly and particles in micro to nano dimensions were obtained.

2.3. Nano-composite synthesis

The *in-situ* free radical polymerization technique was used for composite formation. In 100 ml DD water, 250mg ceramic particles were dispersed. Then 25 ml of aniline solution (10% in 1 M HCl) and 25 ml of ammonium persulphate (0.1 M in 1 M HCl) were added to this suspension drop wise. The reaction mixture was then stirred for 3 hours at 5°C with subsequent overnight digestion. For removing soluble impurities and side products, the sample was centrifuged for 10 minutes twice at 4000 rpm and was dried in an oven at 70°C .

2.4. Characterization

Physicochemical analysis was done via FT-IR spectroscopy (IR Prestige-21 Japan), SEM (JEOL JSM-6700F Japan) and TG/DTA (Diamond, Perkin Elmer USA). Mechanical characteristics were studied using Anton Paar Rheometer (Physica MCR 301 Germany). Dielectric properties were analysed using RF Impedance/Material Analyzer (Agilent E4 997 A USA).

3. Results and discussion

3.1. Functional group determination

The formation of ceramic particles (C) and their compositing with PANI (C-PANI) was determined by FT-IR spectroscopy. Peak at about 3370 cm^{-1} denotes O-H stretching vibration in the particles. The same characteristic peak is shown in the composite at 3506 cm^{-1} . Zn-O stretching in ceramic particles is represented by the starting narrow peak at 430 cm^{-1} [13]. All other peaks in the composite curve show the corresponding IR modes for C-C, C-H, C-N and C=O groups. The narrowing and absence of certain peaks in the composite curve represent the successful dispersion of ceramic particles in PANI matrix. FT-IR results confirm the synthesis of particles and their insertion in the polymer matrix.

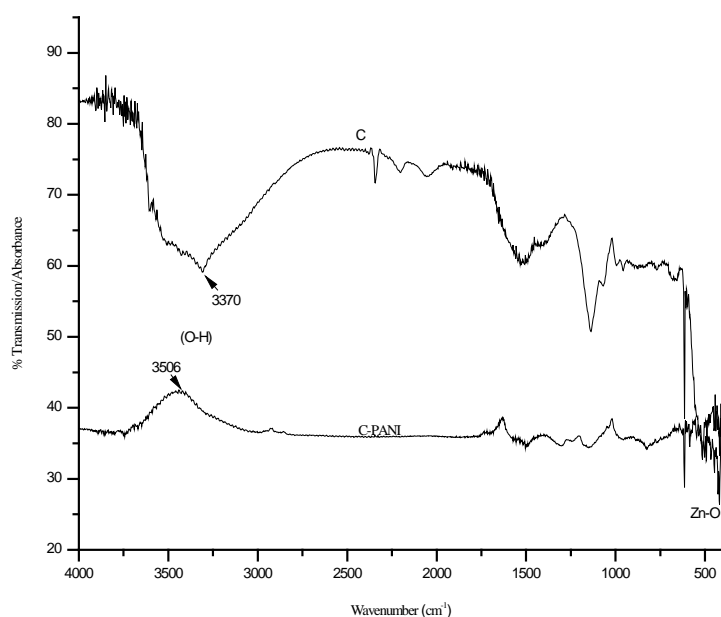


Figure 1. FT-IR spectra of ceramic particles (C) and composite (C-PANI)

3.2. Morphology

Spherical, cylindrical and triangular crystallites of the ceramic nano-particles are shown in Figure 2 (a). The particle size is in the range from nm to μm . A slight agglomeration and small pores are also observed that may be due to sintering process. The micrograph of the C-PANI composite indicates a smooth morphology which is due the immobilization of ceramic particles in the polymer matrix. PANI matrix keep the particles disperse and thus prevent them from aggregation. This property of the composite makes it suitable for its application in nanotechnologies.

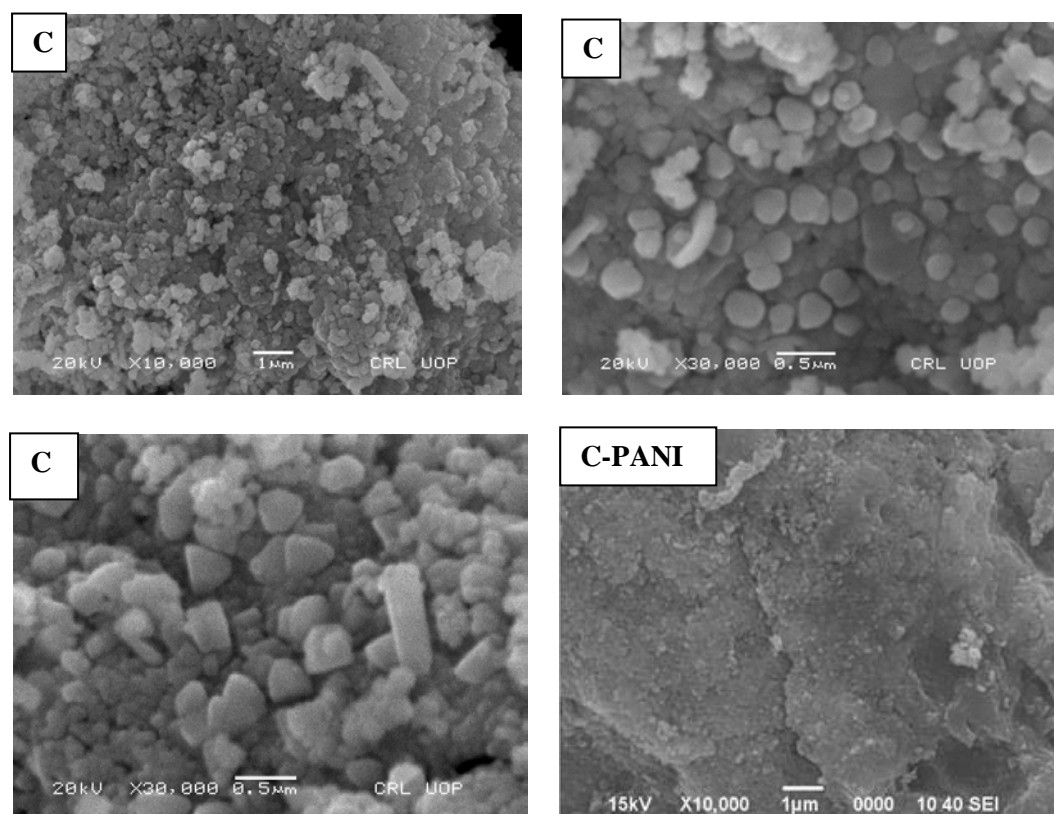


Figure 2. SEM micrographs of the ceramic particles and their composite with PANI

3.3. Thermal properties

Thermal properties were analysed under N_2 atmosphere in the temperature range from 30-700 °C. As shown in Figure 3, ceramic particles are thermally stable up to 600°C and do not show any apparent weight loss. At about 115°C, water molecules evaporate from the particles. The second drop at 600°C (4% weight loss) reveals the creation of metal oxide phase in the ceramic material. TGA curve of C-PANI composite shows three main degradation steps. In the first step at 85°C, water and other volatile gases evaporate from the sample. In the 2nd step at 300°C, PANI chains degradation begins and completely decomposes at 520°C. In the third step at 600°C, destabilization of ceramic particles occurs and thus the composite loses its stability at this stage completely. As a whole, ceramic particles increase the thermal stability of the PANI in the composite due to their tough nature [13].

3.4. Dielectric properties

Frequency dependent dielectric properties were analysed in the range from 1 MHz to 3 GHz at ambient temperature. For both inorganic particles and their composite with PANI, dielectric constant (ϵ') and loss tangent ($\tan \delta$) are strongly dependent on frequency as shown in Figures 4 and 5. With increasing frequency ϵ' and $\tan \delta$ indicate a sharp decrease initially up to 1.70 GHz. This shows the unusual dielectric dispersion. Resonance type behaviour occurs at high frequency (2 GHz) which may be due to the lack of matching between the polarization of applied electric frequency and induced electric moments.

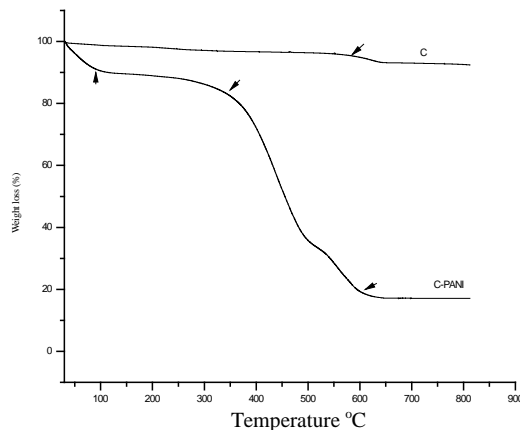


Figure 3. Thermal (TGA) analysis of the prepared materials C and C-PANI

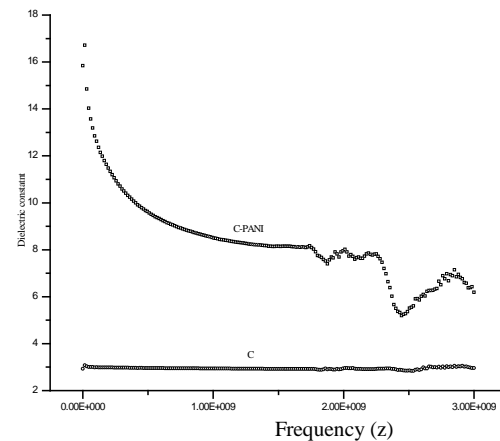


Figure 4. Frequency dependence dielectric constant of C and C-PANI composite

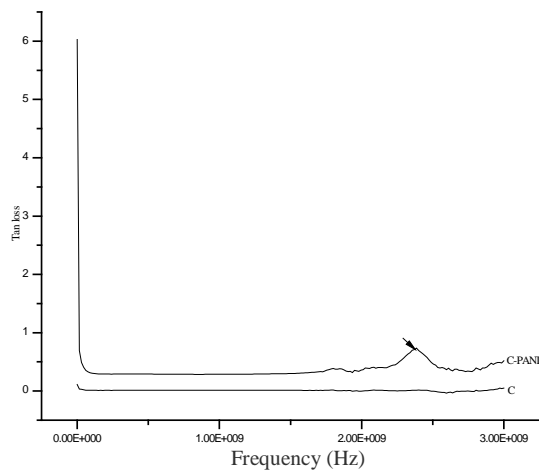


Figure 5. Frequency dependence Tan loss at 300K for C and C-PANI

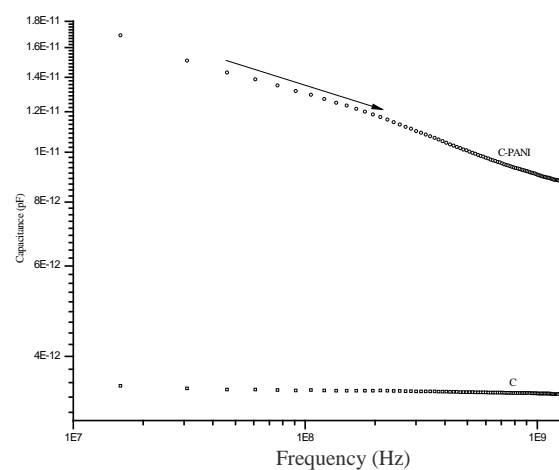


Figure 7. Frequency versus capacitance plot for C and C-PANI composite

Capacitance (Figure 7) of both the materials also shows higher value at low frequency region due to decrease in space charge region at the electrode surfaces. The decrease in capacitance with increase in frequency might be due to moderately blocked charge carriers adjacent to the electrodes [14].

Frequency dependent AC conductivity was found using relation (1);

$$\sigma_{ac} = \omega \epsilon' \epsilon' \tan \delta \quad (1)$$

Where ω is angular frequency, ϵ' is the permittivity of free space, ϵ' is dielectric constant and $\tan \delta$ is the loss tangent. ($\omega = 2\pi\nu$)

From the Figure 8, it is clear that the AC conductivity of the composite increases with the addition of PANI due to its intrinsic conducting property. This also signifies that hopping of electrons conducting mechanism is dominant for which a friction of energy is needed.

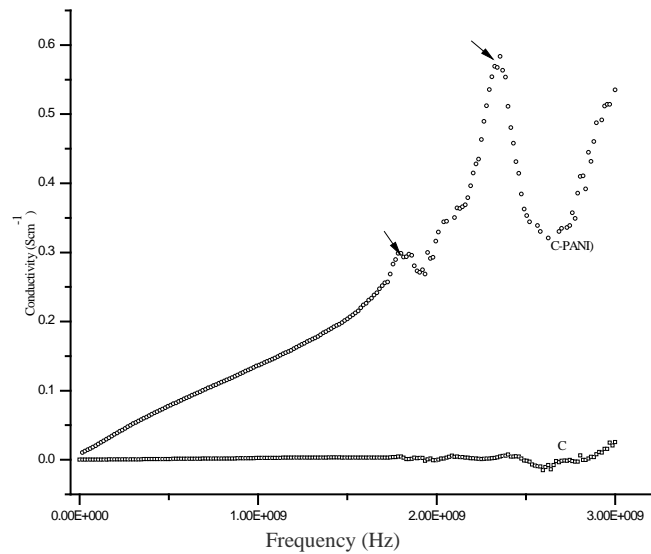


Figure 8. AC conductivity of C and C-PANI as a function of frequency at 313K

3.5. Mechanical behaviour

Rheological properties were measured in order to investigate the mechanical effects of ceramic particles and polymer on the properties of the composite. Shear stress and viscosity of the ceramic particles and their composite with PANI were determined as a function of shear rate at 30, 40 and 50 °C. The shear stress of ceramic particles decreases with increasing shear rate at all temperatures and exhibit equilibrium at high shear rate values [15]. However, this property for the composite first decreases and then increase at high shear rate values as shown in Figure 8 a and b. Particles attraction leads to their aggregation. Shear stress dismisses such aggregates via rising shear rate which is known as shear thinning. The variation of viscosity with shear rate is shown in Figure 9 (a, b). It is clear from these plots that at low shear rate, the viscosity is high and then it drops at high shear rate values at all the three temperatures for both the particles and composite. It shows that in low shear rate region, each system exhibits a strong tendency of shear thinning and Newtonian behaviour. It is accredited to the fact that low shear rate is unable to disturb the metal ions in the ceramic particles and the complex composite system. As the shear rate increases, the structures break down occurs and thus the viscosity of the system decreases. The noticed increase in shear stress and decrease in viscosity of the composite shows the pseudo- plastic nature of ceramic-polymer system.

Figure 10 (a, b) shows that the behaviour C-PANI nano-composite confirms well to the Bingham model [15]. In this model, the shear stress is represented by $\tau = \tau_0 + \eta_0\gamma$, where τ is the shear stress, τ_0 denotes yield stress; η_0 is the zero field viscosity while γ is the shear rate. Both the particles and the composite display Bingham fluid behaviour in the low shear rate region at various temperatures.

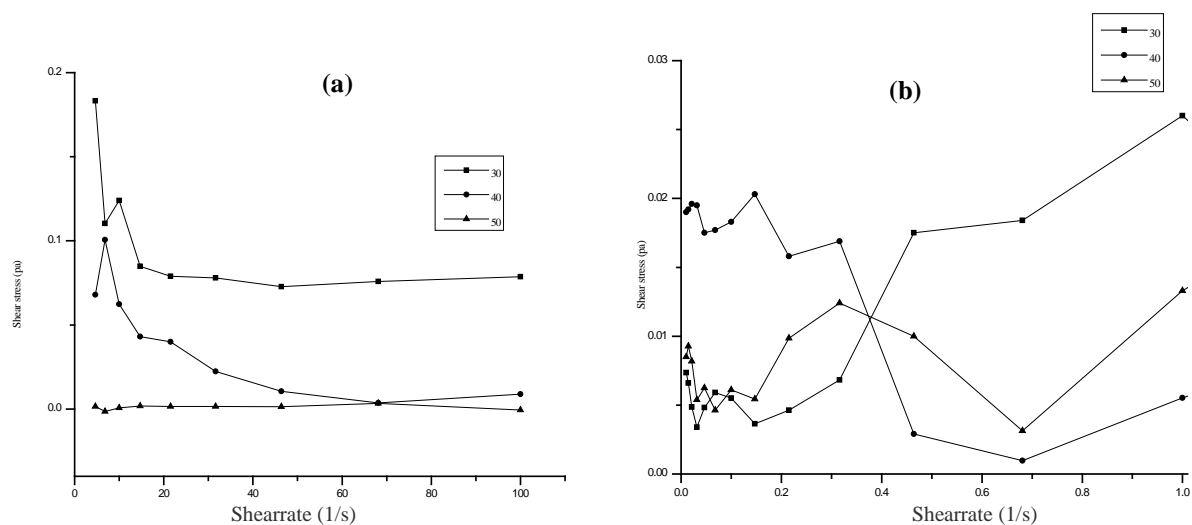


Figure 9. Shear rate versus shear stress plot for (a) ceramic particles and (b) composite with PANI

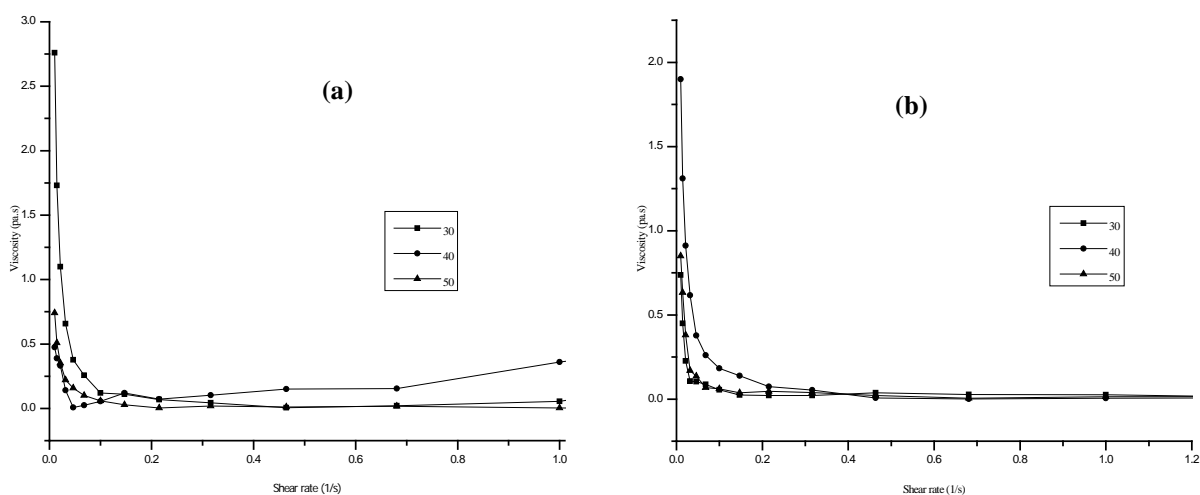


Figure 10. Shear rate versus viscosity plots (a) C and (b) C-PANI composite

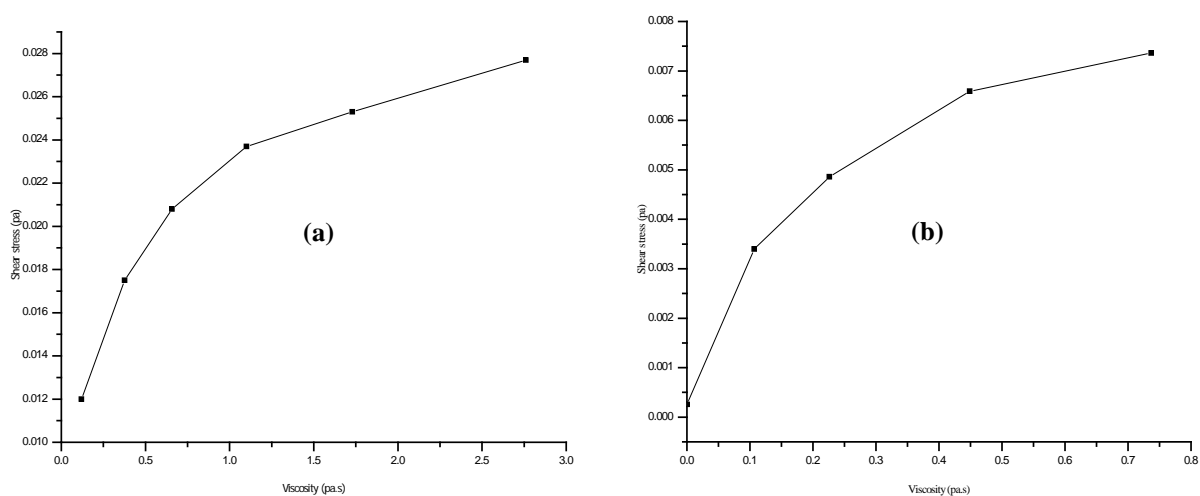


Figure 11. Bingham fluid behaviour of (a) C and (b) C-PANI composite

4. Conclusions

Inorganic ceramic particles were synthesized by sol-gel technique. The prepared particles were successfully incorporated in PANI matrix via *in-situ* free radical polymerization pathway. The composites were characterized by different physicochemical techniques. FT-IR confirmed the synthesis of the particles and composites. SEM showed that the particle are in range nm- μ m and have dispersed well in the polymer matrix. Dielectric properties of the ceramic have been enhanced by the PANI. Particles and composites also showed good rheological properties. It is proposed that the prepared material can be used in embedded capacitors, switching windows and electromagnetic shutters.

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6. References

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