STUDIES ON MELT PROCESSABLE α,ω–ALKANEDISULFONIC ACID DOPED POLYANILINE AND ITS THERMOPLASTIC COMPOSITES

by

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Submitted

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Dedicated to my Mother
Suresh Bala

CERTIFICATE

*This is to certify that the thesis entitled, "**Studies on Melt Processable α,ω–Alkanedisulfonic Acid Doped Polyaniline and its Thermoplastic Composites**" submitted by **Mrs. Sneh Bharti** to the Indian Institute of Technology Delhi, for the fulfillment of award of the degree, Doctor of Philosophy, is a record of bonafide research work carried out by her under our supervision and guidance. This thesis has been prepared in conformity with the rules and regulations of the Indian Institute of Technology Delhi, New Delhi.*

The thesis, in our opinion, is worthy of consideration for award of the degree of Doctor of Philosophy in accordance with the regulations of the Institute. To the best of our knowledge, the results embodied in the thesis have not been submitted to any other University or Institute for the award of any other Degree or Diploma.

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ABSTRACT

Polyaniline (PANi) has advantages over other conducting polymers because of its ease of synthesis, electrical conductivity and environmental stability but it possesses poor processability due to limited solubility and thermal stability. Melt blending of PANi with thermoplastics can be used as a method to make it processable. Different acids have been used as dopants to increase the thermal stability of PANi. However, only a few acids were reported which showed thermal stability above 275 ºC. Increase in thermal stability of polyaniline is important for better processability using conventional processing technology

In first section of this work, the use of α,ω-alkanedisulfonic acid, $HO_3S(CH_2)_nSO_3H$ (n = 1, 4, 6 and 12), as a dopant for polyaniline was investigated. A series of disulfonic acids with varying chain lengths was synthesized and used in the doping of polyaniline. The doped polymers showed conductivity in the range of 10^{-2} to 10^{-1} Scm^{-1}. Thermal studies showed that the doped polymers, depending on the chain length of α,ω-alkanedisulfonic acid were stable up to ~ 312 ˚C, as per the 5% weight loss criteria and the thermal stability decreased with increasing dopants chain length. Among all doped samples methanedisulfonic acid doped polyaniline showed maximum thermal stability. The thermal stability of α,ω-alkanedisulfonic acid doped PANi was higher than that of alkanesulfonic acid-doped PANi which typically degrades around 250 ˚C, suggesting a moderately broader processing window for α,ω-alkanedisulfonic acid doped PANi for blending with other thermoplastics.

In next section of this work, methanedisulfonic acid doped PANi (PANi-MDSA) with 2:1 ratio of the dopant per repeating unit of EB was used as conductive filler for the linear low density polyethylene (LLDPE) based conducting composites. Melt processed LLDPE/PANi-MDSA composites were prepared with varying PANi-MDSA content from 0-50 phr in micro-compounder. The effect of PANi-MDSA on the electrical conductivity, thermal, mechanical, morphological and rheological properties of composites was investigated. The

percolation threshold of the conducting composites was observed at 0.064 volume fractions of PANi-MDSA. The DSC analysis showed that PANi-MDSA acts as a nucleating agent in composites resulting in increased crystallization rate in composite without affecting percentage crystallinity of LLDPE. The scanning electron microscopy images indicated that PANi was dispersed uniformly in LLDPE matrix and also the existence of weak interaction between them. The Young's modulus of composites showed gradual enhancement in its value on increasing PANi-MDSA content. The dynamic rheological behavior of composite indicated that complex viscosity (η*), elastic modulus (G') and loss modulus (G") decreased with increase in PANi-MDSA content, which suggested that PANi-MDSA may act as a lubricating agent. Loss tangent (tan δ) curves showed that incorporation of PANi-MDSA in LLDPE increases solid like behavior and indicated presence of 3-dimensional structure in polymer melt. In composites, PANi-MDSA has negligible effect on relaxation behavior of LLDPE.

LLDPE/PANi-MDSA composite films with PANi-MDSA content varying from 0.5 to 4 phr were prepared by melt blending in twin-screw extruder followed by film blowing. Melting and non-isothermal crystallization behaviors of LLDPE/PANi-MDSA composites were analyzed by differential scanning calorimeter (DSC). The DSC endotherms results show that PANi-MDSA has no effect on the melting temperature of LLDPE and acts as nucleating agent in these composites. By using optical microscopy, it was observed that the distribution of PANi-MDSA particles was uniform in blown films of composites. Agglomerates of PANi-MDSA were observed at higher content of PANi-MDSA. Blown films of composites were prepared at two different nip-roller speed and characterized for their tensile properties, film thickness, lay flat width, blow-up ratio and draw-down ratio. Further, charge decay studies were conducted to evaluate the antistatic studies of prepared blown films. The results showed

that incorporation of electrically conducting PANi-MDSA improved the antistatic property of films without affecting the mechanical properties of LLDPE films significantly.

Immiscible blends were used to increase the electrical conductivity of composites at low percentages of conducting filler. In the last section, by varying the concentration of ethylene vinyl acetate (EVA) from 0 - 50 wt%, LLDPE/EVA blends were prepared in micro-compounder. The mechanical, morphological and rheological properties of LLDPE/EVA blends have been determined and analyzed as a function of EVA content. Scanning electron microscopy images of blends showed two phase morphology. The result of rheological studies showed positive deviation in the plots of G' and η* versus blend composition which demonstrated that the blends were immiscible. Further, blends showed more solid like behavior compared to that of their neat component. Mechanical properties such as Young's modulus, tensile strength and elongation at break have also been evaluated. Thermal stability of the blends was found to be less than that of LLDPE which can be attributed to the presence of less thermally stable EVA.

Conducting composites of LLDPE/EVA/PANi-MDSA were prepared by melt processing method in a micro-compounder. The effect of EVA and PANi-MDSA content on electrical conductivity of composites was measured. The electrical conductivity of composites was found to be increased in LLDPE/EVA/PANi-MDSA compare to that of LLDPE/PANi-MDSA composites. Significant increment was observed at 10 wt% EVA in composites. Effect of EVA was found to be more pronounced with less amount of PANi-MDSA. Mechanical properties of composites were investigated. Linear decrease in Young's modulus, tensile strength and strain at break were observed with addition of EVA in composite. DSC analysis was used as a tool to estimate the preferable interaction of PANi-MDSA between LLDPE and EVA phase. Complex viscosity, G' and G" of composites were found to decrease with increase in EVA content. Two phase morphology was observed in etched samples of

LLDPE/EVA/PANi-MDSA composites by scanning electron microscopy. On incorporation of PANi-MDSA, no discernable change in morphology of blends was observed. A hypothetical model for the distribution state of PANi-MDSA particles in the blend was also proposed.

TABLE OF CONTENTS