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RESEARCH ARTICLE

Preparation and Thermal and Morphological Characterization of Nanocomposite Based on Phenol Formaldehyde – Nylon Thermoset IPN

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Abstract

Interpenetrated network (IPN) of Phenol formaldehyde (PF) and nylon was prepared using sequential IPN preparation method. The Concentration of Nylon was varied in the IPN from 5%, 10% to 15% concentration level with respect to the phenol used. Scanning electron microscopy (SEM) results showed a uniform dispersion of nylon phase in the PF network. Nanoclay was added at 4% concentration level with respect to the phenol to all the IPN compositions and also to the pure PF. SEM studies confirmed the uniform dispersion of the nanoclay in the IPN matrix. Differential Scanning Calorimetry (DSC) studies have also been done. Addition of clay showed improvement in the thermal stability of the IPNs.

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INTRODUCTION

Phenol formaldehyde resins are well known polymeric resins. This resin has a wide range of applications, starting from the molded articles to laminations to adhesives. Between the two types of PF resins, novolac has been used for blending with various polymers and resins. Among them the most common are the blends with epoxy resin and polypropylene, ethylene vinyl resin etc. [1-7]. The thermal, mechanical and morphological properties of these blends have also been studied. The other PF resin i.e. resol is blended with a number of polymers like, epoxy, novolac and polyvinyl chloride [8-10]. In the present study, resol is further modified with polyamide (nylon 66). Polyamide itself is a high performance polymer with flexibility. Interpenetrating network (IPN) is a type of blend where two polymers are in network structure and crosslinked. In this type of structures, both the polymers are mixed at the molecular level. For the present work, sequential IPN preparation method has been followed. Thus nylon 66 is dissolved in phenol and then the phenol is used for resin preparation with formaldehyde and sodium hydroxide (NaOH). This blend is then cured to get a sheet in which the resol is in interpenetrated network structure with the nylon 66.

The first nanocomposite have been prepared with nylon6 using nanoclay by Toyota [12]. Since then nanoclays are in use to improve the mechanical, thermal and barrier properties of a number of polymers. Hence in the present work, the blend of resol and nylon 66 is mixed with 4% nanoclay, to see the effect of nanoclay on the properties of the blend.

In this paper, we have studied the effect of blending with nylon 66 on PF, as well as the effect of nanoclay on the morphological and thermal properties.

2. Experimental:

2.1. Materials:
2.1.1. Nylon 66: Nylon 66 is procured from local market. The MFI of the nylon 66 used is 50g/10min (275^{o}C, 2.16 kg)
2.1.2. Phenol: The phenol used is analytical grade reagent supplied by Loba Chemie Ltd.
2.1.3. Formaldehyde: The formaldehyde used for the experiment is supplied by Loba chemie Ltd. The concentration is 37%.
2.1.4. Sodium Hydroxide (NaOH): A 10% solution of pure sodium Hydroxide pellet is used for the experiment.
2.1.5. Cloisite 30B: Nanoclay Cloisite 30B is generously supplied by Southern Clay Products.

2.2. Instruments Used:
2.2.1. Scanning Electron Microscopy: Morphologies of the blends and the composites have been studied using scanning electron microscopy. The data is collected over the surface area approximately 11mm in width and magnification ranging from 250X to 30,000X.

2.2.2. Differential scanning calorimeter: The crystallization exotherms and melting endotherms of samples have been recorded on a Perkin Elmer differential scanning calorimeter both at cooling and heating rates of 10^{o}C/min in nitrogen atmosphere. Powered samples of about 3 mg are used for this study. All the samples are heated to 400^{o}C and then cooled to 30^{o}C.

2.3. Preparation of PF Resin, PF-PA66 blend and nanoclay composite: In a beaker 30 gram of phenol is taken. An 37% aqueous solution of formaldehyde is weighed at a mole ratio of phenol: formaldehyde equal to 1:1.8 and kept. Separately in a beaker sodium hydroxide (NaOH) pellets weighing 2.5% by weight of phenol is taken. The ingredients are mixed in a single-neck round bottom flask (RB). The mouth of the RB should be attached to a condenser. The mixture is then continued to be heated at a boiling condition for 2.5 hours. By 2.5 hours the formation of a viscous white material takes place inside the RB which is known as the B-stage resin named as resitol. The instance when the white material forms, is known as cloud point. The aqueous water formed at this point may be easily decanted out to separate the white resinous layer. The viscous white material is then cured in an open mold in an oven at 70^{o}C for 10 hours. After 10 hours a reddish- brown cured resin is obtained.
For the preparation of PF-PA66 blend the PA66 granules are solubilised in phenol at 5% and 10% by weight ratio of phenol. These solutions are then mixed with required amount of formaldehyde and NaOH. These mixtures are heated to the boiling condition to form PF-PA66 thermosetting blend following the above mentioned procedure.
For the preparation of nano-composite of the above blend, nanoclay Cloisite 30B is mixed at a weight ratio of 4% of the phenol during the preparation and stirred. Rest of the process remains same.

Abbreviations Used:

Name	Symbol
Phenol formaldehyde resin	PF
Nylon 66	PA66
Phenol formaldehyde+5w%Nylon 66	PF-PA6605
Phenol formaldehyde+10w%Nylon 66	PF-PA6610
Phenol formaldehyde+15w%Nylon 66	PF-PA6615
Phenol formaldehyde resin+nanoclay 4%	PFC4
Phenol formaldehyde+5w%Nylon 66+nanoclay 4%	PFPA6605C4
Phenolformaldehyde+10w%Nylon 66+nanoclay 4%	PFPA6610C4
Phenol formaldehyde+15w%Nylon 66+nanoclay 4%	PFPA6615C4

3. Results and Discussions

Scanning Electron Microscopy (SEM):

PF is blended with Nylon 66 at various weight ratios like 5%, 10% and 15%. When the blends are compared with the unblended PF, the morphology studies reveal that the two phases are mixed thoroughly. The SEM pictures of PF, PFPA6605 and PFPA6610 respectively are given below [Fig. 1, 2, 3]. Fig. 1 shows the surface of PF. Fig. 2 and Fig.3 are the blends of PF with nylon at 5% and 10% level respectively, where we can see no major phase separation or phase difference in the blends.

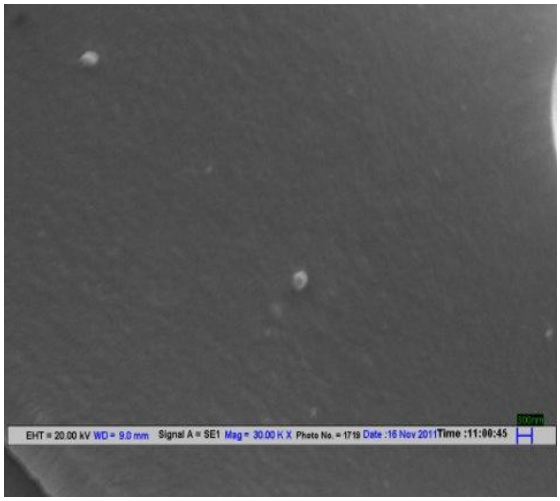


Figure 1: SEM photograph of PF

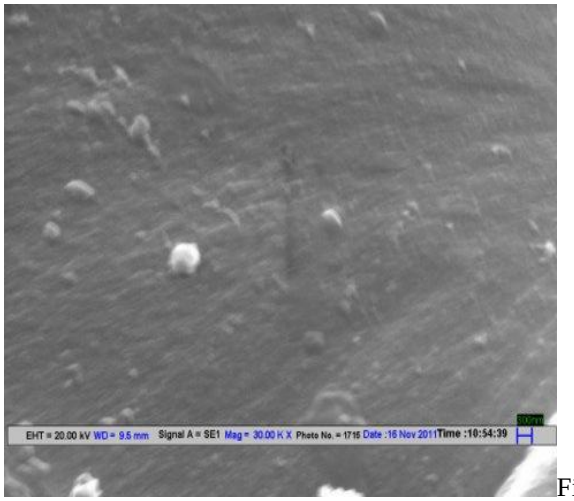


Figure 2: SEM photograph of PFPA6605

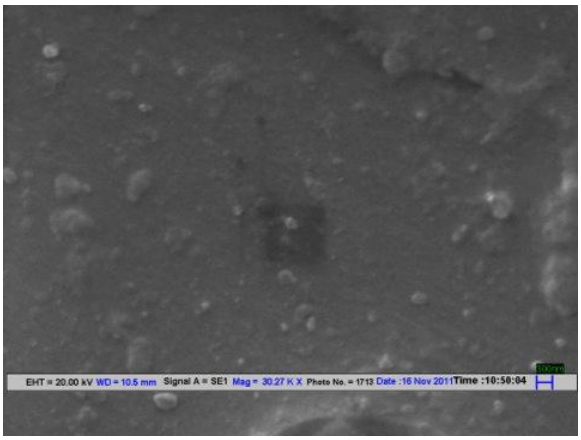


Figure 3: SEM photograph of PFPA6610

There are minor irregularities on the surface because of the unevenness. Since, the nylon is first solubilised in phenol and subsequently the phenol was used for PF preparation, the nylon chains are mixed with the PF network at the molecular level. This is the reason that no phase separation is observed. Rather the whole blend is seen as one single entity.

SEM photos of the nanoclay filled PF and its nylon composites are also investigated. The Fig. 4, 5, and 6 are the representative pictures of the PFC4, PFPA6610C4 and PFPA6605C4 respectively. The photos show that the nanoclays are well dispersed at nanometer levels in the matrix of the polymeric blend. In all the three pictures the average thickness of the nanoclays dispersed in the matrix is around 10 nm with the average aspect ratio of 10. The nanoclay Cloisite 30B® is polar in nature. Hence the polar polymers like nylon and PF could easily intercalate into the interlayer gap to exfoliate the nanolayers of the clays. Thus the SEM photos indicate that the extents of intercalation in the clay interlayer are equally good in pure PF as well as in case of its blends with nylon. Thus we can conclude that PF is polar enough for the intercalation in the given nanoclay. Blending of nylon with PF has very little effect on the extent of intercalation and nanocomposite formation.

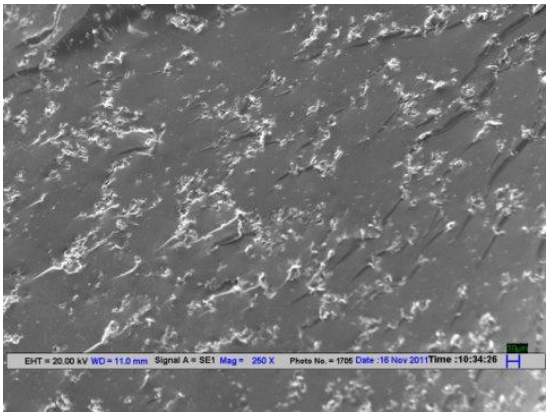


Figure 4: SEM picture of PFC4

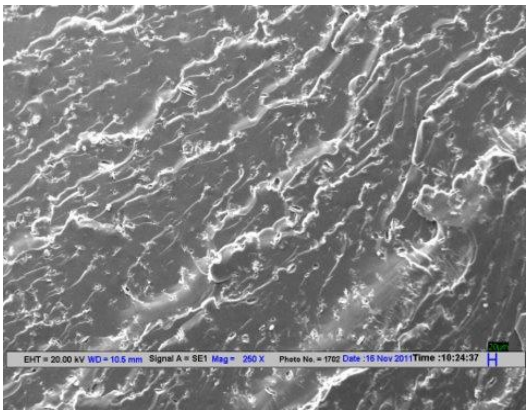


Figure 5: SEM picture of PFPA6610C4

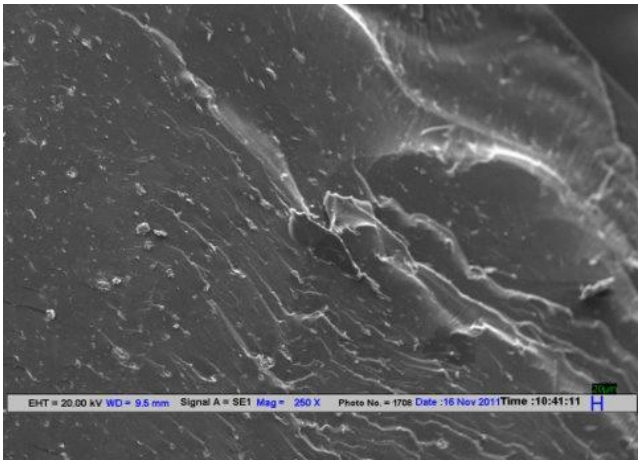
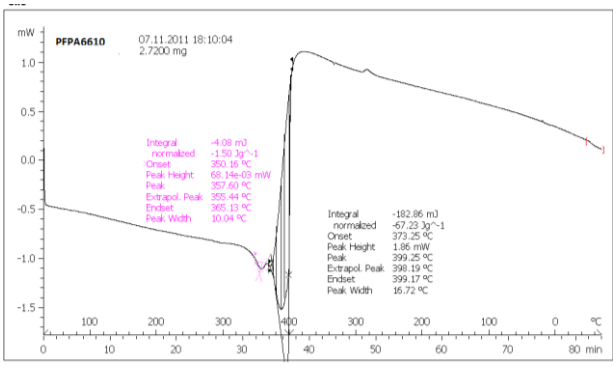


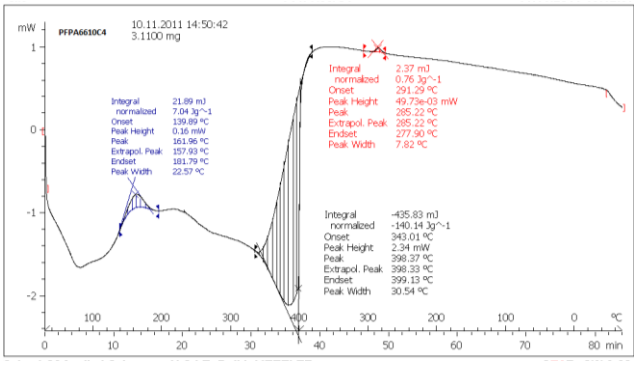
Figure 6: SEM picture of PFPA6605C4

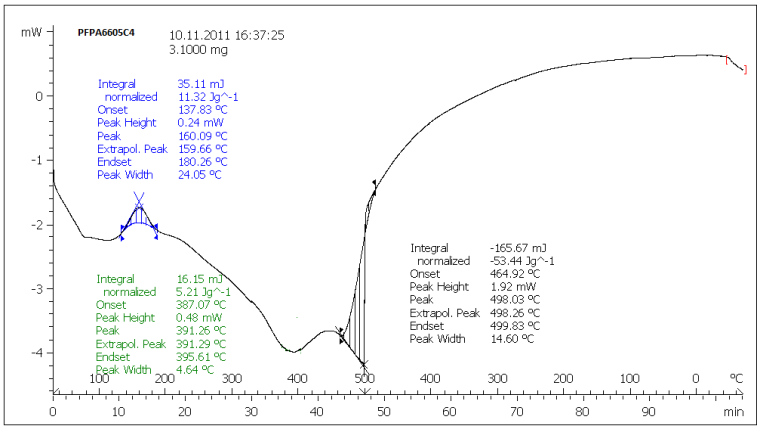
Differential Scanning Calorimetry (DSC): The DSC studies of the representative samples of PFPA66 blends and their nanocomposites have been carried out. The results may be explained with the help of the DSC plots of PFPA6610, PFPA6610C4 and PFPA665C4 [Picture 7, 8 and 9 respectively]. The studies reveal that the pure PF-nylon66 blend undergo two-step degradation. The DSC curve of PFPA6610 shows that between the two degradation peaks, the 1st degradation occurs at 357^0C and the 2nd step at 399^0C. The 2nd step is the major degradation path. The amounts of energies absorbed in each of the exothermic transitions are 4.08 mJ and 182.86 mJ for the 1st and 2nd steps respectively. There is no crystallization or any other peak in the DSC curve of this sample. In the DSC curve of

Picture 7: DSC curve of PFPA6610



Picture 8: DSC curve of PFPA6610C4





Picture 9: DSC curve of PFPA6605C4

PFPA6610C4 sample, one single degradation peak appears at 398.37^{0}C along with a crystallization peak at 161.96^{0}C. DSC of PFPA6605C4 also shows the crytallisation peak at 160^{0}C and the degradation peak at 498^{0}C. In both the nanocomposites the degradations occur in single step. Incase of 5% nylon filled nano-composite PFPA665C4, the thermal stability is almost 100^{0}C higher than that of the 10% nylon added (PFPA6610C4) sample. The degradation pattern of both the nanoclay filled samples although remains the same. Addition of 4% nano clay have not influenced the thermal stability much in case of PFPA6610C4 compared to PFPA6610. The noticeable effect of nano clay is the removal of the 1st degradation peak at 357^{0}C appeared in case of PFPA6610. Both the clay filled samples show crystallization peaks which are absent in unfilled blend indicating that the crytallisation peak is appearing because of the clay structure but not for the polymeric structures. If the energy absorption in the main degradation steps of the clay filled and unfilled samples are compared, it can be noticed that the energy absorption is maximum in PFPA6610C4 (435.83mJ), followed by PFPA6610 (182.86 mJ) and PFPA6605C4 (165.67 mJ).

4. **Conclusions**: In this paper the blend of PF resin and nylon 66 at various ratio have been prepared. The structure and morphology of the blends are studied using SEM. The results of SEM indicate the formation of interpenetrating miscible blend. There is no phase separation between the two polymers. Nanocomposites of the various PFPA66 blends have also been studied using SEM. Here the SEM results show uniform distribution of exfoliated nanoclays in the pure PF matrix and also in the blends.

The thermal properties have been studied using DSC, which shows best thermal stability in case of the 5% nylon added clay nano composite (PFPA665C4). Presence of nano clay have not affected the thermal stability much in case of PFPA6610C4 compared to PFPA6610C4. Thus we can conclude that PF and Nylon 66 form a miscible interpenetrating network. Addition of Cloisite 30B to the PF and the blends result in the formation of nanocomposites. The nanometer level dispersion of the clays is confirmed by SEM. Thermal studies also show best thermal stability in case of 10% loading of nylon in PF with 4% nano clay.

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