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## POLYURETHANE/FERRITE NANOCOMPOSITES: PREPARATION AND PHYSICAL PROPERTIES

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### ABSTRACT

In the present study, polyurethane/ferrite composites (PU-NFs) were prepared using silver ferrite, copper ferrite and zinc ferrite (1 wt.%) by *in situ* two-step polymerization in solution. PU-NFs based on poly(dimethylsiloxane) as soft segment and hyperbranched polyester of the second pseudo generation/4,4'-methylenediphenyl diisocyanate as the hard segment were prepared with constant soft segment content (60 wt.%). The prepared PU-NFs and PU network (sample without nanoferrites) were characterized by FTIR, DSC and TG analyses. The glass transition of the hard segment ( $T_{gHS}$ ) of PU-NFs was similar to  $T_{gHS}$  value of the unfilled PU network. The results showed that PU-NFs had better thermal stability than pure PU network.

### INTRODUCTION

Polyurethanes (PUs) with poly(dimethylsiloxane) (PDMS) as a soft segment play important role in special technical and medical applications because of many unique properties of PDMS, including low glass transition temperature, low surface energy, good biocompatibility, excellent thermal stability, ultraviolet resistance and high permeability to many gases. The use of dendritic polymers (dendrimers and hyperbranched polymers) as a crosslinking agent in the synthesis of polyurethanes attracted a great deal of interest in recent years, due to their specific properties compared to analogue linear polymers [1,2]. Hyperbranched polymers have similar structure and performance as the dendrimers, and could be synthesized easily, so they have been paid more attention. Nanoparticles (nanotubes, nanospheres, nanofillers nanoflaks, nanorods and nanoplatelets) can make a

drastic change in physio-chemical properties of polyurethanes. The combination effect of nanofillers and polymer matrix has created a great interest towards researchers. Biocompatible magnetic nanoparticles, i.e. ferrites possess some unique characteristics, such as uniform size distribution, less agglomeration and stability in the biological medium. Nanocomposite materials based on PU and ferrite are important in the field of biomaterials due to their good mechanical and biocompatible properties. In this work, the influence of the different type of ferrites (content 1 wt.%) on the structure and thermal properties of prepared materials, was investigated.

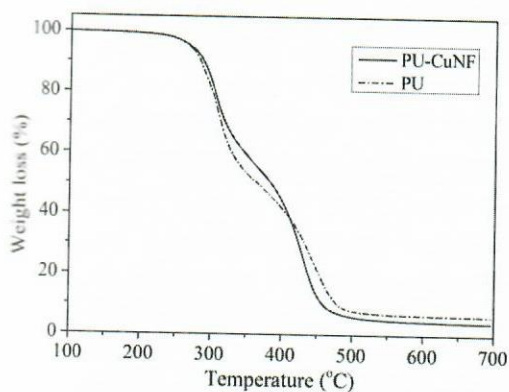
## EXPERIMENTAL

The polyurethane/ferrite nanocomposites were prepared by *in situ* two-step polymerization in solution (NMP/THF) using  $\alpha,\omega$ -dihydroxy-ethylene oxide-poly(dimethylsiloxane)-ethylene oxide (PDMS; ABCR;  $M_n = 1000$  g/mol), 4,4'-methylenediphenyl diisocyanate (MDI; Sigma-Aldrich) as monomers and hyperbranched polyester of the second pseudo generation (BH-20; Boltorn<sup>®</sup>) Polymer Factory;  $M_n = 1780$  g/mol, functionality  $f_{nOH} = 16$ ) as crosslinking agent. For comparison purposes, polyurethane network without ferrite was also synthesized using the same procedure. Complete preparation procedure of the PU-NF films are described in our previous papers [1,2]. Nano ferrites ( $MFe_2O_4$ ;  $M = Zn, Cu$  and  $Cu_{0.5}Zn_{0.5}$ ) were prepared by co-precipitation with microwave-hydrothermal method. FTIR spectra were recorded on ATR Nicolet 380 spectrometer. Differential scanning calorimetry (DSC) was carried out on a DSC Q1000V9.0 Build 275 thermal analyzer. The DSC scans were recorded under a dynamic nitrogen atmosphere ( $50\text{ cm}^3/\text{min}$ ), in the temperature range from  $-90$  to  $230$  °C, at a heating and cooling rate of  $10$  and  $5$  °C/min, respectively (two scans were run for each sample) using the so-called triple cycle of heating-cooling-heating to determine the glass transition temperature. The thermal stability of the PU-NFs and pure PU was determined by thermogravimetric (TG) analysis, using TGA Q500 V6.3 Build 189 instrument, at heating rate of  $10$  °C/min under a nitrogen atmosphere.

## RESULTS AND DISCUSSION

The present study made an attempt to prepare polyurethane/ferrite nanocomposites. The prepared nanocomposites and pure PU network were characterized by FTIR for structural confirmation. The characteristic stretching frequencies of the prepared PU-NFs and pure PU network appeared at  $3320\text{--}3450\text{ cm}^{-1}$  ( $\nu_{N-H}$ ),  $2960$ ,  $2945$ , and  $2865\text{ cm}^{-1}$  ( $\nu_{sym}$  and  $\nu_{asym}$  of C-H),  $1645\text{--}1735\text{ cm}^{-1}$  ( $\nu_{C=O}$ ),  $1535$  and  $1260\text{ cm}^{-1}$  ( $\nu_{C-N} + \delta_{N-H}$ ).

i.e., amide II and amide III bands), 1016 and 1080  $\text{cm}^{-1}$  ( $\nu_{\text{Si-O-Si}}$  and  $\nu_{\text{C-O-C}}$ ), 1597 and 1415  $\text{cm}^{-1}$  ( $\nu_{\text{C=C}}^{\text{arom}}$ ), and 790  $\text{cm}^{-1}$  ( $\rho_{\text{C-H}}$  in  $\text{SiCH}_3$ ). The absorption bands belonging to the isocyanate (2270  $\text{cm}^{-1}$ ) and hydroxyl groups (3300  $\text{cm}^{-1}$ ) were not detected in the FTIR spectra of the prepared PU-NFs and pure PU network, indicating their complete conversion during the reaction. In FTIR spectra of PU-NFs, the peaks at 490 and 580  $\text{cm}^{-1}$  are due to the stretching vibration of M-O band in the tetrahedral and octahedral sites, respectively. The peak at 490  $\text{cm}^{-1}$  can be assigned to the Zn-O, Cu-O or  $\text{Cu}_{0.5}\text{Zn}_{0.5}$ -O band, while 534  $\text{cm}^{-1}$  is related to the Fe-O band. Based on DSC measurements in the investigated temperature region, only the glass transition temperature of hard segments ( $T_{\text{gHS}}$ ) was observed. The  $T_{\text{gHS}}$  value was in the range from 20.8 to 21.58  $^{\circ}\text{C}$  and for pure PU it was 21.20  $^{\circ}\text{C}$  (Table 1). The results showed that addition of ferrite to the PU matrix have no influence on  $T_{\text{gHS}}$  value of prepared nanocomposites.  $T_{\text{gHS}}$  value was higher for pure PU and its nanocomposites as compared to BH-20 ( $T_{\text{g}}$  4.6  $^{\circ}\text{C}$ ). This is attributed to the presence chemical cross-linking that restricts the molecular motion of the polymer chains and leads to the increase in  $T_{\text{gHS}}$ .



**Figure 1.** TG curves of PU-CuNF and pure PU

Fig. 1 presented the typical TG curves of pure PU and selected PU-CuNF film, while in Table 1 characteristic temperatures of thermal degradation and temperatures of derivative TG (DTG) peaks are listed. The  $T_{10\%}$  value is considered to represent the beginning of degradation of

the PU-NFs and pure PU. Thermal degradation of PU-NFs starts between 283 and 285  $^{\circ}\text{C}$ , while that for pure PU sample starts at 279  $^{\circ}\text{C}$ . Thermal stability of the prepared PU-NFs was improved with addition of the nanoferrites as compared to pure PU network. The results showed that thermal stability for all PU-NFs was similar. DTG curves (Table 1) of PU-NFs and PU sample displayed four degradation stages. The first weigh loss stage, from 300 to 309  $^{\circ}\text{C}$  for PU-NFs, is possibly attributed to the degradation of urethane bonds in the hard segment of the PU matrix. The second, third and fourth weigh losses occurred from 304 to 376  $^{\circ}\text{C}$  and from 389 to 399  $^{\circ}\text{C}$ , and from 428 to 445  $^{\circ}\text{C}$ , respectively, which is due to the degradation of the ester, the ether and the PDMS components of the PU.

**Table 1.** The soft segments content (SSC), glass transition temperature of the hard segment ( $T_{gHS}$ ), determined by DSC, and characteristic temperatures of thermal degradation of PU-NFs and pure PU

Sample	SSC, wt. %	$T_{10}$ , °C	$T_{50}$ , °C	$T_{max}$ , °C	$T_{gHS}$ , °C
PU-CuNF	60	285	365	309/376/399/445	21.6
PU-ZnNF	60	284	368	300/304/390/440	20.8
PU- Cu <sub>0.5</sub> Zn <sub>0.5</sub> NF	60	283	368	306/325/389/428	21.8
PU	60	279	360	293/364/402/432	21.2

## CONCLUSION

Novel PU/ferrite nanocomposites based on PDMS as the soft segment and MDI/BH-20 as the hard segment with different types of ferrites and small content of ferrites (1 wt.%) were prepared by *in situ* two-stage polymerization reaction. The PU-NFs formation was confirmed by FTIR. DSC results showed that glass transition of the hard segment in PU-NFs was similar to the pure PU network. TG results indicated that addition of ferrites led to increase in thermal stability of the prepared PU-NFs compared to pure PU network. In future study, the formulation of the PU-NFs needs to be evaluated for its cytotoxicity and antimicrobial properties as well as microstructure-mechanical property relationship, so that it can be further optimized to develop organic-inorganic hybrid nanocomposites showing desired biological activity.

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