

EFFECT OF CUS NANOPARTICLES AS FILLER ON THE THERMAL STABILITY ABS

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ABSTRACT

Copper sulfide nanoparticles was synthesized via a simple hydrothermal reaction between $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and thioglycolic acid (TG). Then CuS nanoparticles were added to Acrylonitrile-Butadiene-Styrene (ABS) copolymer. The thermal stability behavior and the flammability properties of ABS filled with copper sulfide nanoparticles, at various copper sulfide amounts: 2.5, 5 and 10 wt%, were studied by thermogravimetric analysis (TGA) and cone calorimetry measurements. Nanoparticles and nanocomposite were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectra and atomic force microscopy (AFM).

Key words: Copper sulfide; Nanostructures; Hydrothermal.

INTRODUCTION

Acrylonitrile-butadiene-styrene copolymer (ABS) is widely used as an important engineering thermoplastic because of its desirable properties, which include good mechanical properties, chemical resistance and good processing characteristics. ABS is composed of a styrene-acrylonitrile copolymer (SAN) matrix phase, with grafted polybutadiene particles whose composition, (ABS) has a good balance among various physical properties such as processability of styrene, toughness and chemical resistance of acrylonitrile, impact resistance of butadiene and excellent appearance of its moulded products [1]. However, ABS is extremely flammable and is known as one of the most difficult polymers to flame retard by employing halogen free flame retardant. There are already various methods of improving fire retardancy of ABS for safety consideration and the flame retardant ABS is mainly achieved by halogen antimony synergism [2]. Nanocomposites are very attractive due to the fact that small amount of nanostructure can lead to great improvement in many properties, such as mechanical and thermal property. Very different methods have done for improving ABS fire resistance, such as ABS/clay, ABS/halogenated flame retardant (FR), ABS/phosphorous FR, ABS/intumescent FR, nitrogen-phosphorus

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(FR), ABS zinc stannate, ABS/ferric chloride, synergistic agent, ABS/CNT [3]. We were interested in the synthesis of Bi_2S_3 , SnS, CdS and other [4,5] nanostructures, using thioglycolic acid, via hydrothermal method for a few years. In this work, we have used the thioglycolic acid assisted hydrothermal process to successfully synthesize CuS nanoparticles. Then this metal sulfide was incorporated in ABS copolymer in order to increase thermal stability.

METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

ABS (1 g) was dissolved in 15 mL dichloromethane and copper sulfide was dispersed in 15 mL of dichloromethane with ultrasonic waves. Then dispersion of copper sulfide was added slowly to polymer solution. The solution was mixed under stirring for 5 h. After stirring Product was casted on a glass plate after around 1 h of solvent evaporation, the nanocomposite was placed in the vacuum oven for another 4 h for the removal of residual traces of solvent.

RESULTS AND DISCUSSION

The XRD patterns of pure ABS, CuS nanoparticles and ABS/CuS nanocomposite are shown in *Fig. 1*. *Fig 1a* shows the XRD pattern of pure ABS from Aldrich Company. In *Fig 1b* the XRD pattern of as-prepared copper sulfide nanoparticles was indexed as a pure hexagonal phase which is completely close to the values in the literature (JSPDS No.06-0464).

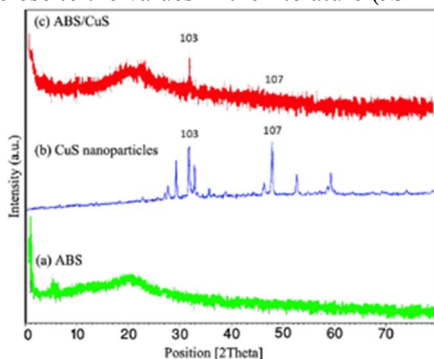


Fig. 1 – XRD patterns of: (a) pure ABS polymer, (b) CuS nanoparticles and (c) ABS/CuS nanocomposite filled with CuS content 10 wt% of CuS_{NP}

In *Fig 1c* XRD pattern of ABS/CuS nanocomposite filled with CuS content 10 wt% of copper sulfide is shown that peaks of CuS in XRD pattern of nanocomposite confirmed existence of copper sulfide in polymeric matrix.

Fig. 2a shows SEM image of CuS nanoparticles obtained at 160 °C. From the image, it was observed that the nanoparticles were formed, and the particles were quasi spherical in shape. The size of nanocrystals obtained from the XRD diffraction patterns are about 30–45 nm. Figs. 2(b–d) are images of ABS filled with different contents of copper sulfide (2.5 wt%, 5 wt% and 10 wt%, respectively) that obviously confirmed presence of CuS in polymeric matrix. In *Fig.2d* CuS nanoparticles attractively constitute flower like structure in polymeric matrix. The thermal stabilities of pure ABS and ABS/CuS nanocomposite filled with CuS contents

of 2.5 wt%, 5 wt%, and 10 wt% at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in N_2 atmosphere were investigated by TGA.

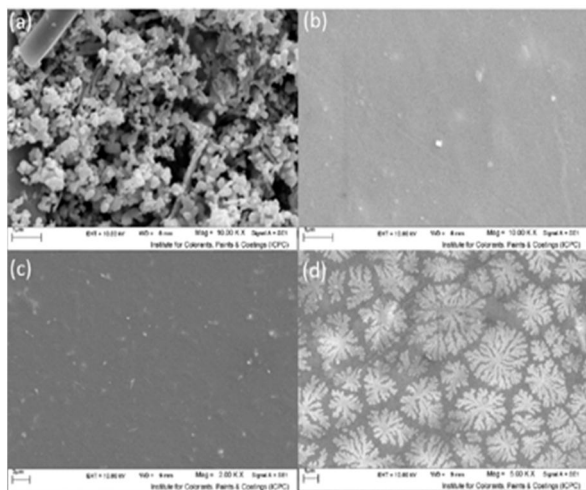


Fig. 2 – SEM images of (a) as synthesized CuS nanoparticles, (b) ABS/CuS nanocomposite filled with CuS content 2.5 wt% of CuS_{NP} , (c) ABS/CuS nanocomposite filled with CuS content 5 wt% of CuS_{NP} and (d) ABS/CuS nanocomposite filled with CuS content 10 wt% of CuS_{NP}

There is one big weight loss for all samples with increasing the temperature from $350\text{ }^{\circ}\text{C}$ to $650\text{ }^{\circ}\text{C}$ due to the decomposition of ABS. Whereas, after $650\text{ }^{\circ}\text{C}$, the weight of samples is basically unchanged. The nanocomposite residue from the TGA curves increases with increasing CuS content. Moreover, the measured residue amounts are in good accordance with the calculated values of pure CuS in the nanocomposites [6]. The thermal decomposition of the ABS shifted towards higher temperature in the presence of the CuS nanoparticles. Improved thermal stability of composites with respect to the pure ABS can be assigned to partially alter molecular mobility of the polymer chains due to their adsorption on the surface of the filler particles [7]. Also, exfoliated CuS filler particles have significant barrier effect to slow down product volatilization and thermal transport during the decomposition of the polymer, which improves thermal stability of nanocomposite. Simultaneously, adsorption of polymer chains onto the surface of CuS filler particles results in restriction of segmental mobility and serves to suppress redistribution and chain transfer reactions [8]. Polymer adsorption on the surface of filler particles is a crucial step for explanation of changed thermal stability of ABS/copper sulfide composites, as was stated earlier [9] there is a delay of weight loss that can be attributed to the CuS which acts as an impervious barrier retarding the diffusion of the volatile products from the polymer bulk to the gas. With regard to the residues left after decomposition, ABS was almost completely decomposed at $500\text{ }^{\circ}\text{C}$, but the residue amounts for ABS/CuS remained stable [10].

CONCLUSIONS

CuS nanoparticles were prepared by TG assisted with hydrothermal process at relatively low temperature. CuS nanostructures were added to acrylonitrile-butadiene-styrene copolymer. The influence of copper sulfide on the thermal properties of ABS matrix was studied using thermogravimetry analysis. The thermal decomposition of the ABS shifted towards higher temperature in the presence of the CuS nanoparticles. Improved thermal stability of composites with respect to the pure ABS can be assigned to partially alerting molecular mobility of the polymer chains due to their adsorption on the surface of the filler particles. Also, exfoliated CuS filler particles have significant barrier effect to slow down product volatilisation and thermal transport during decomposition of the polymer.

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