Thermal Properties of Polyimide Composites with Nanostructured Silicon Carbide

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ABSTRACT

A series of polyimide composites reinforced with different loadings of silicon carbide (SiC) nanoparticles are prepared by in-situ polymerization technique. The polyimide (PI) matrix resin is derived from 4,4'-oxydianiline (4,4'-ODA) and pyromellitic dianhydride (PMDA). The dispersions of SiC nanoparticles are prepared via ultrasonic irradiation or mechanical homogenization. In this method, the SiC nanoparticles are dispersed in diamine solution followed by polymerization with dianhydride. The composites obtained under sonication were found to have lower thermal properties than composites prepared under homogenization.

Keywords: Polymer composite, Silicon carbide, Polyimide, Particle-reinforced nanocomposite, Sonication, Mechanical homogenization.

INTRODUCTION

Aromatic polyimides (PIs) are known for their high thermal stability and chemical resistance as well as high mechanical properties[1]. Although there are many high temperature stable polyimides, there is a growing demand for the use of these materials at higher temperatures in oxidizing and corrosive environments. Thus, an oxidation-resistant materials are used to improve the properties of the polyimide composition[2].

Recent research directions have been focused on attempts to combine polymer structure and nanoparticles to obtain materials with high stiffness, strength and tribological properties[3]. This approach is based on the ability to improve and modify the properties of materials by adding nanofillers in a polymer matrix[4–7]. Aeronautics is one of the most promising fields in terms of composite materials consumption. In the aviation industry, metal or ceramic materials are widely replaced by fiber-reinforced polymer composites[8].

The SiC nanoparticles were chosen in this project because of their high chemical resistance, heat resistance, high thermal conductivity and outstanding mechanical properties[9]. According to the literature, there are only one research group working in the field of PI/SiC composites[10, 11]. The poly(triazole-imide)/SiC nanocomposites were prepared via in-situ polymerization. In comparison with pristine polymer matrix the poly(triazole-imide)/SiC nanocomposites had improved mechanical and thermal properties.

In previous work we introduced results of utilizing nanostructured silicon carbide particles as filler of poly-oxydiphenylene-pyromellitimide matrix[12]. In current paper we study thermal properties of PI composites in dependence of SiC loadings (0,1%, 0,5%, 1%, 2%, 3%, 4% by weight) and dispersion technique (ultrasonic or mechanical homogenizer). In this work we used matrix resin derived from 4,4'-oxydianiline (4,4'-ODA) and pyromellitic dianhydride (PMDA) (see Fig. 1).

EXPERIMENTAL

Materials

Nanostructured silicon carbide (SiC) was purchased from InKhimSintez. The properties of SiC are listed in Table 1.

Pyromellitic dianhydride (PMDA) was synthesized by oxidation of durene with potassium permanganate in pyridine followed by anhydridization with diphenyl ether according to the literature[13].

Table 1: The properties of the SiC nanoparticles (according to InKhimSintez)

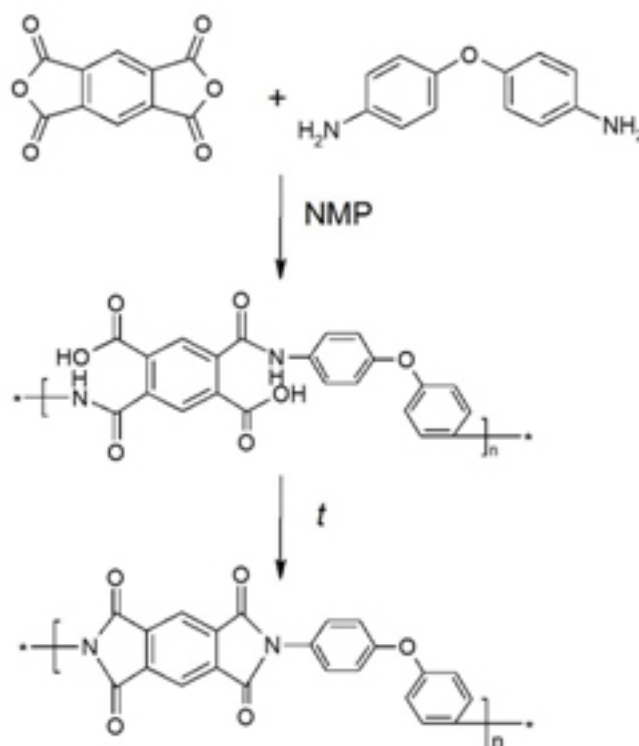|	
Purity	> 97 %
Surface area	$30 - 35$ m^2/g
Color	From light gray to black
Morphology	Nearly spherical
Bulk density	< 0.5 g/cm3

Fig. 1: Synthesis of polyimide matrix

4,4'-Oxydianiline (4,4'-ODA) was purchased from Vekton and was purified prior to use by sublimation (~5 torr at ~155°C).

1-Methyl-2-pyrrolidinone (NMP) was purchased from Component-Reaktiv and purified prior to use by drying over calcium hydride followed by distillation.

Preparation of the nanocomposites

In a three-neck round-bottom flask equipped with a condenser and an argon inlet the mixture of 9,17 g (45,8 mmol) of 4,4'-ODA, SiC nanoparticles and 74 mL of NMP was dispersed by ultrasonic dispersant (at 20kHz upon cooling) or mechanical homogenizer (~4000 rpm) for 15 min. Then dispersant (or homogenizer) was replaced by mechanical stirrer and 10,0 g (45.8 mmol) of PMDA was added with small portions. The mixture was left stirring overnight and was stirred for another 20 hours. The resulting poly(amic acid) solution was cast onto clean and dry ceramic plates by a film applicator with thickness 500 ìm. The films were dried

in a vacuum oven at 80°C for 6 h. Then heating was performed in a programmed manner in the following sequence: one hour at 100°C, one hour at 150°C, one hour at 200°C, one hour at 250ºC, one hour at 300°C and 15 min at 350°C.

Analytical techniques

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis was

Table 2: Viscosities of PAA with different loadings of SiC, Pa·s

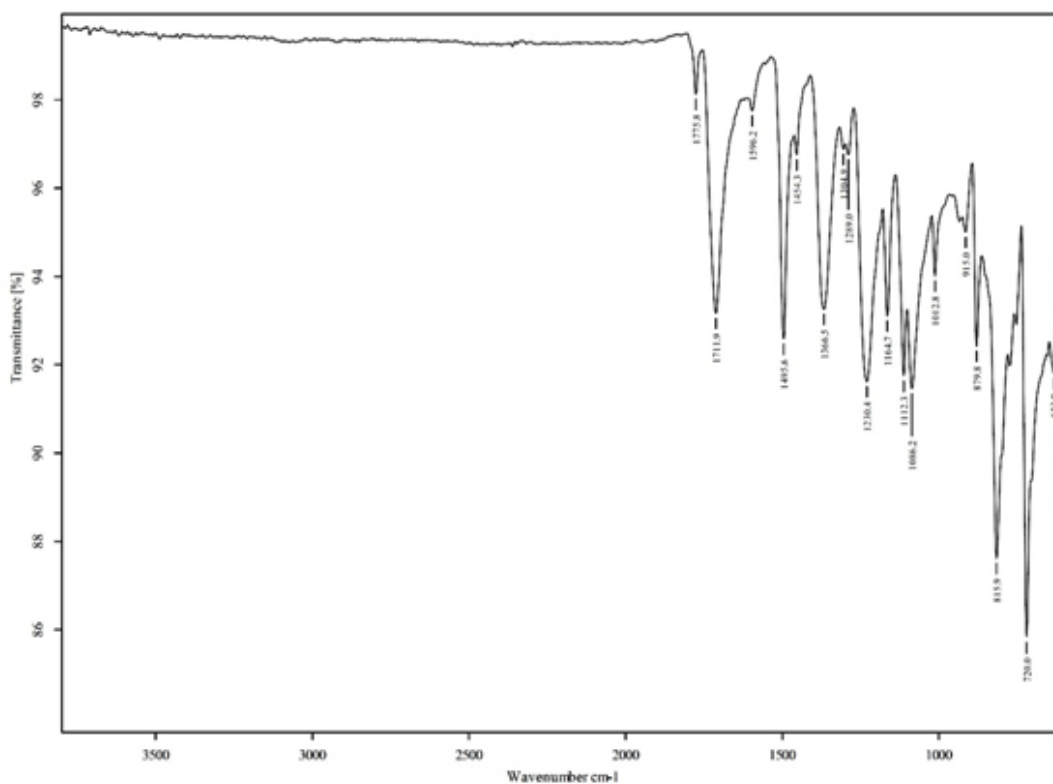| SiC content, wt%	A dispersing method	
	Sonication	Homogenization
0	7,86	5,94
0,1	10,10	4,79
0,5	11,30	4,01
1	2,89	3,97
2	5,24	7,13
3	5,06	6,82
4	4,70	4,19

Fig. 2: The typical FTIR spectrum of the nanocomposite film (with 0,5% loading of SiC)

conducted under atmosphere of argon and air with a heating rate of 10°C/min with a TA Instruments SDT Q600. Scanning electron microscopy (SEM) was recorded with Hitachi SU-1510 VP-SEM under accelerating voltage of 7 kV and working distance of 5.5mm. IR-spectra were obtained on a VERTEX 70 FT-IR, Bruker Optics. Viscosities were measured with rheometer MCR 52, Anton Paar.

RESULTS AND DISCUSSION

Synthesis of nanocomposites

The nanostructured SiC was dispersed in solution of 4,4'-ODA in NMP under sonication or homogenization followed by polymerization with PMDA to give the poly(amic acid)s (PAA) with concentration of 20wt% with viscosities listed in Table 2. The experiments without loading of nanofiller were conducted to study the dependency of the viscosity of PAA solution from SiC content and dispersing method. PAA solutions with lower loadings of SiC and without nanofiller obtained under sonication were more viscous than PAA solutions obtained under homogenization that can be attributed to uniformly dispersed filler and/or greater values of molecular weights.

Thermal imidization consists of casting the poly(amic acid) solution onto a suitable substrate, followed by gradual heating to effect solvent removal and the cyclodehydration reaction to form polyimide. Solid films with color from beige to brown were obtained.

Properties of composites

The infrared spectra of the films (Fig.2) were common for all composites and had absorption peaks specific to imide groups (1775 cm^{-1} (C=O), 1712 cm^{-1} (C=O), 1368 cm^{-1} (C-N), and 721 cm^{-1} (C=O). The absence of absorption band at 1660 cm^{-1} (C=O amide) specific to poly(amic acid) shows complete imidization

The thermal properties of the polyimide nanocomposites were obtained by TGA. The 5% and 10% weight loss temperatures of films in air and inert atmosphere (Ar) are shown in Table 3. TGA/DSC curves of polyimide composites with 0,5%wt. and 4%wt. SiC (obtained under sonication or homogenization of nanofiller in diamine solution) in air are shown in Fig. 3 and Fig. 4. The sonication of monomer solution resulted in decrease of T_{d5} of pristine polyimide in air and inert atmosphere. The composites with 0,1% and 0,5%wt. SiC obtained under sonication also have lower thermal properties than composites prepared under homogenization of SiC in monomer solution.

Table 3: The thermal properties of the polyimide nanocomposites

SiC content, wt%	A dispersing method	Air *Td*/°C5% weight loss	*Td*/°C10% weight loss	Argon *Td*/°C5% weight loss	*Td*/°C10% weight loss
0	Sonication	519	555	504	553
	Homogenization	540	567	566	579
0,1	Sonication	518	557	557	577
	Homogenization	528	566	554	569
0,5	Sonication	518	560	570	585
	Homogenization	539	569	562	576
1	Sonication	557	578	556	573
	Homogenization	521	566	560	582
2	Sonication	524	570	563	585
	Homogenization	531	567	552	573
3	Sonication	496	541	558	577
	Homogenization	536	570	553	572
4	Sonication	541	565	571	587
	Homogenization	513	554	569	585

Solid films were examined by SEM to determine how the particles were distributed in the polymer matrix (see Fig. 5). The nanofiller was uniformly distributed in all concentrations. SEM microphotographs didn't show any differences in composite surface depending on dispersing technique.
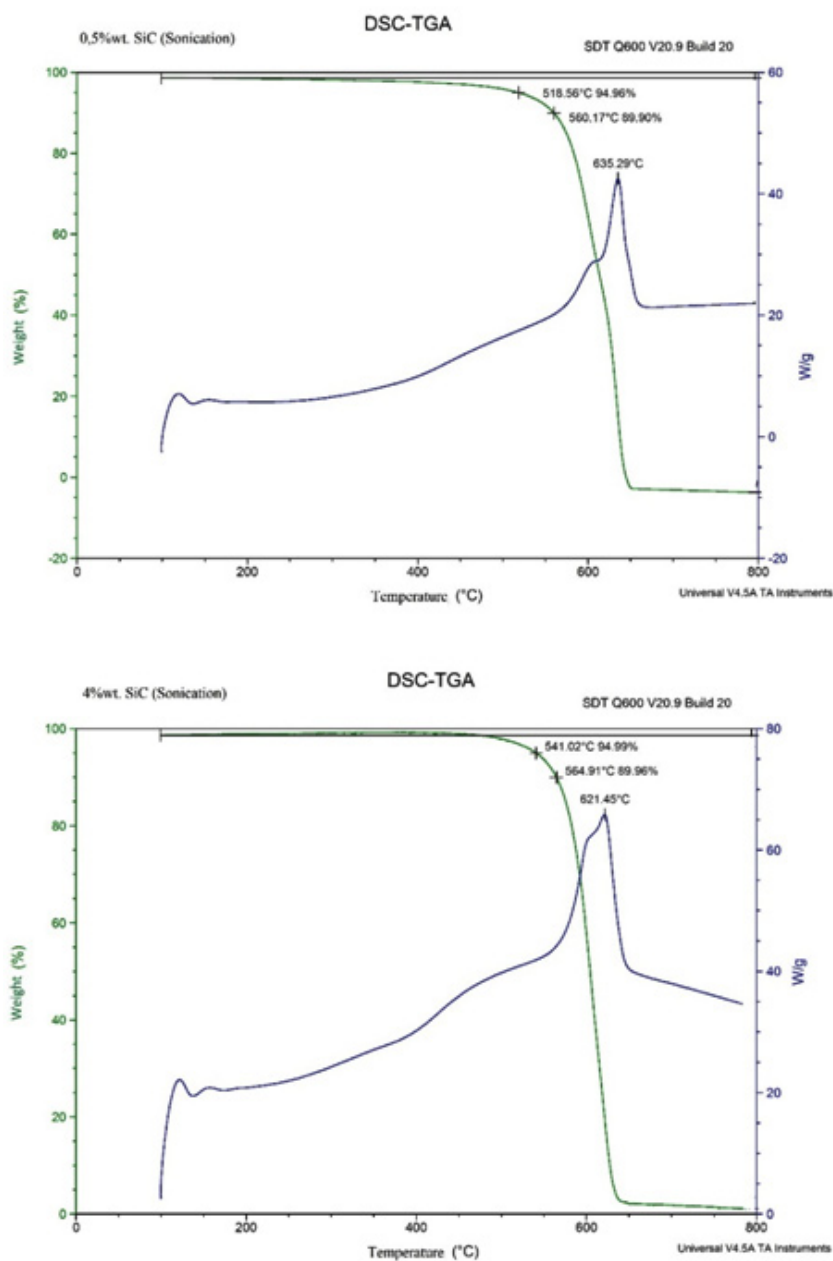

Fig. 3: TGA/DSC curves of PI/0,5%SiC and PI/4%SiC composites (obtained under sonication of nanofiller in diamine solution) in air
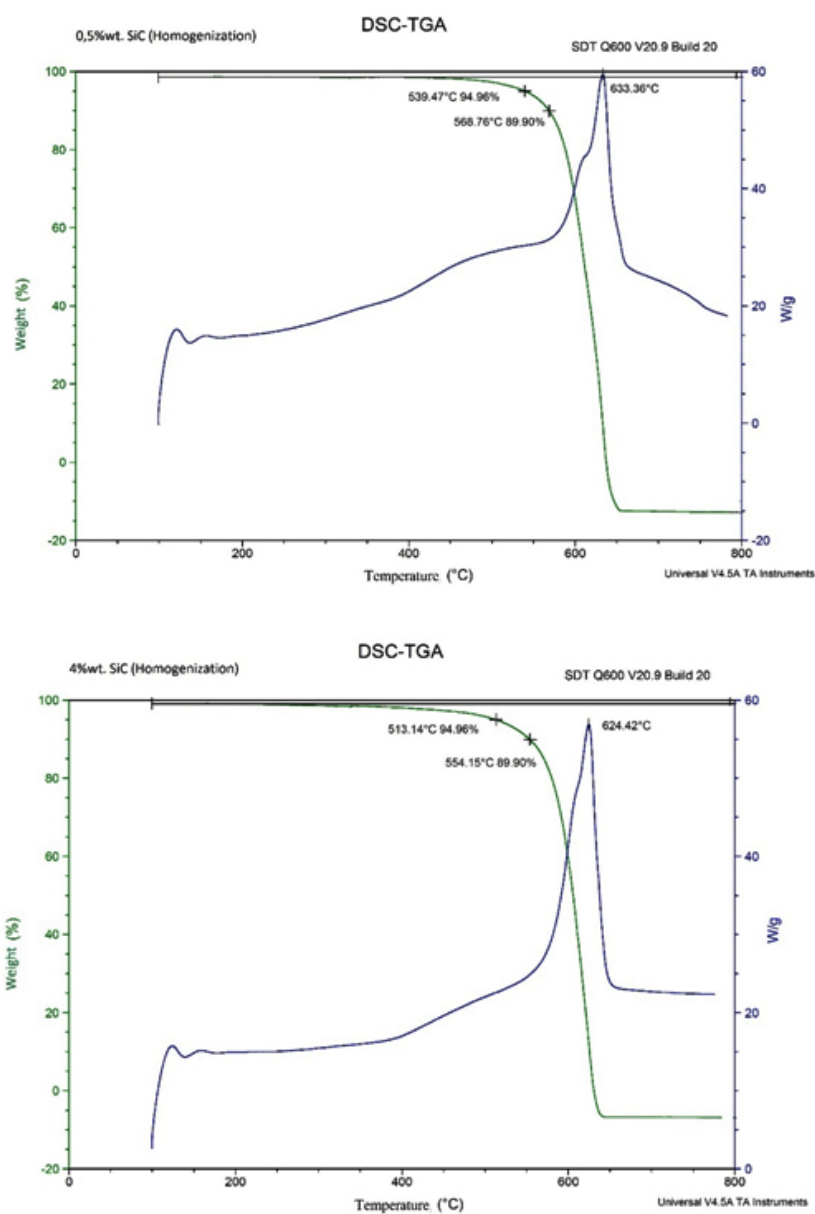
**Fig. 4: TGA/DSC curves of PI/0,5%SiC and PI/4%SiC composites
(obtained under homogenization of nanofiller in diamine solution) in air**

CONCLUSION

A series of polyimide composite materials filled with nanostructured SiC with loadings from 0,1% to 4% wt. has been obtained by in-situ imidization and show good thermal stability. It was found that a method of dispersion of filler (sonication and homogenization) influenced on the thermal properties of composite. Sonication of monomer solution resulted in decrease of T_{d5} of pristine polyimide and PI/SiC composites compared to homogenization. Further research will be conducted
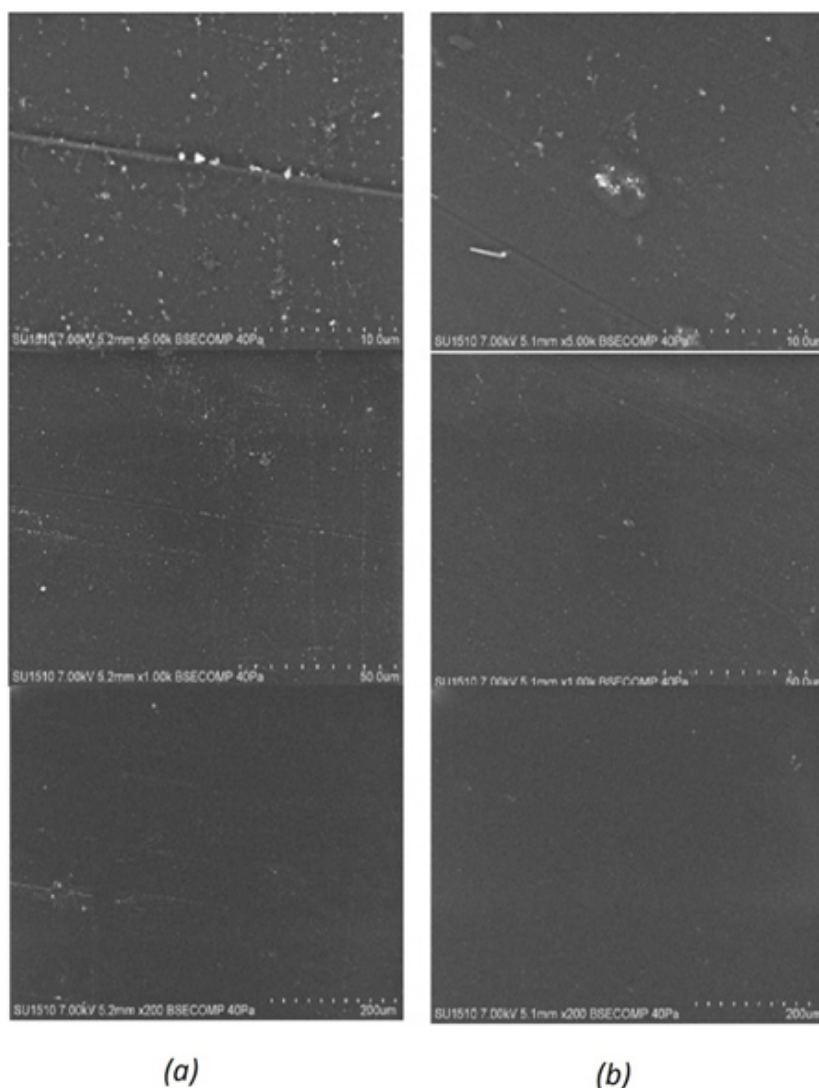
(a)	(b)

Fig. 5: Microphotographs of the nanocomposite surface PI/1%SiC obtained either under sonication *(a)* or homogenization *(b)* of SiC nanoparticles in monomer solution

for the detailed interpretation and understanding of current results. Further work on this project will focus on the production and study of composite materials with a variety of polyimides.

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