Temperature-dependent rigidity and magnetism of polyamide 6 nanocomposites based on nanocrystalline Fe-Ni alloy of various geometries

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Received 21 March 2016; accepted in revised form 22 May 2016

Abstract. The focus of this study is to explore the potential use of Polyamide 6 nanocomposite reinforced with nanocrystalline (nc) Fe₂₀Ni₈₀ alloy (Fe₂₀Ni₈₀/PA6 PNC) in electromagnetic applications and provide understanding of how the alloy particle geometry is controlling the nanocomposite's physical properties. Thermomechanical rigidity, room-temperature soft magnetic performance and thermal soft magnetic stability of Fe₂₀Ni₈₀/PA6 PNCs based on spherical-sea urchin alloy particles (UMB2-SU) and necklace-like alloy chains (UMB2-NC) have been investigated. Both PNCs have considerably superior bulk properties compared to neat PA6 and UMB2-SU exhibits the most remarkable overall performance. Morphological observations disclose two relevant phenomena: i) improved dispersion and distribution of the SU alloy particles than the NC ones within PA6 matrix, leading to stronger filler-matrix interfacial interactions within the UMB2-SU as compared to the UMB2-NC and ii) presence of constraint polymer regions in between alloy segments within the UMB2-SU that provide secondary reinforcing and soft magnetic mechanisms. Such phenomena along with the lower alloy crystallite size and PA6 γ -crystal type content within the UMB2-SU than in the UMB2-NC, are considered the main responsible factors for the distinctive performance of UMB2-SU. Overall, compared to various ferromagnetic nanocrystalline metallic materials, the research proposes the SU nc Fe₂₀Ni₈₀ alloy as a valuable nanofiller in polymers for electromagnetic applications.

Keywords: polymer composites, nanomaterials, reinforcements, thermal properties, industrial applications

1. Introduction

Magnetic nanomaterials are essential components of modern technology in a wide range of applications, including catalysis [1], sensors [2], data storage [3], biotechnology/biomedicine [4], magnetic resonance imaging [5], environmental remediation [6], spintronic [7] and microwave devices [8, 9]. Nanoscale magnetic materials are so attractive because they show

remarkable novel phenomena compared to their bulk counterparts, such as superparamagnetism, ultrahigh magnetic anisotropy and coercive force, and giant magnetoresistance. These phenomena arise from finite size and surface effects that dominate the magnetic behavior of individual nanoparticles [10, 11]. Among magnetic nanomaterials, ferromagnetic nanosized metals, metal alloys and metal oxides are the

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most exploited ones due to their distinctive magnetic properties [12, 13]. However, drawbacks of such materials, including corrosion, high density (weight), and physical rigidity, make alternatives desirable in many technological areas. Incorporation of ferromagnetic metallic nanomaterials into polymer matrices is regarded as a good strategy to overcome their shortcomings. Polymer nanocomposites doped with ferromagnetic metallic nanomaterials (FMNMs-PNCs) retain the key features of polymers such as lightweight, exceptional processability, flexibility and corrosion resistance. Meanwhile, they display new functionalities such as magnetism and electrical conductivity as well as enhanced mechanical and thermal properties as compared to the neat polymer due to metallic inclusions. Therefore, FMNMs-PNCs can emerge as promising alternatives to ferromagnetic metallic nanomaterials in various disciplines [14, 15]. It is well known that, intensive filler-matrix interfacial interactions should dominate the PNC structure, in order to attain a unique combination of constituents' properties. Accordingly, this has become a focal point of significant interest in the design and development of PNCs, by controlling the size, geometry, orientation, dispersion and distribution of nano-sized fillers within polymer matrix and bonding at the filler-matrix interface [15, 16].

Nanocrystalline (nc) Fe-Ni alloy is among the most attractive ferromagnetic metallic nanomaterials for electro-magnetic applications including magnetic-field sensors, read-write heads in magnetic data storage devices, magnetic actuators and motors, electro-magnetic shielding and transformers magnetic cores [17]. The attention to this alloy is attributed to its unique soft magnetic properties, excellent mechanical stiffness, strength and thermal dimensional stability (rigidity) and good electrical properties [17–19]. In particular, nc Fe₂₀Ni₈₀ alloy is known of permalloy anomaly [17, 20]. The potential of using nc Fe-Ni alloy, as a nano-filler in polymers has been explored for the first time by the authors [21]. In that study, the room-temperature mechanical properties of nc Fe-Ni alloy/Polyamide 6 nanocomposites (Fe-Ni/PA6 PNCs) were determined as a function of the compounding technique and nano-filler content. It was concluded that the mechanical stiffness and strength of PA6 were significantly enhanced for low content of nc Fe-Ni alloy (up to 3 wt%) when the Fe-Ni/PA6 PNCs

were prepared by ultrasound-assisted master batch (UMB) technique, indicating the great promise of nc Fe-Ni alloy as a nano-reinforcement to polymers.

In electro-magnetic applications, components are exposed to thermal stresses, thus requiring the material to have good thermal stability in terms of rigidity, magnetism and electrical properties [17]. Accordingly, this study focuses on the investigation of the rigidity and magnetic properties of Fe-Ni/PA6 PNC as function of temperature, in order to explore the potential use of such nanocomposite in electromagnetic applications. The alteration of the nanocomposite microstructure and subsequently thermal stability in terms of rigidity and magnetism due to different alloy geometries, was the focal point of interest throughout the research. 2 wt% Fe-Ni/PA6 PNCs based on nc Fe₂₀Ni₈₀ alloy with two different particle geometries; spherical-sea urchin particles and necklace-like chains, were prepared by compounding via the UMB process followed by injection molding. The morphology, crystalline structure, softening temperature and temperature-dependent coefficient of thermal expansion and magnetic properties of the nanocomposites were investigated.

2. Experimental

2.1. Materials

The polymer used is PA6 pellets (Tecomid® NB40 NL E). It was obtained in a sealed package from Eurotec® Engineering Plastics, Tekirdag, Turkey. Formic acid (HCO₂H, 98%) and ethanol (C₂H₅OH, 96%) used as a solvent and a precipitant for PA6, respectively, were obtained from Chem-Lab NV, Zedelgem, Belgium and VWR, Pennsylvania, USA, respectively.

2.2. Preparation of Fe₂₀Ni₈₀/PA6 PNCs

nc Fe₂₀Ni₈₀ fine particles with two different geometries; spherical-sea urchin particles (SU) and necklace-like chains (NC), were chemically synthesized. Crystal sizes are 16 and 20 nm for the alloy particles with SU and NC geometries, respectively. Detailed information on the synthesis process as well as on the morphology, nanocrystalline structure and magnetic properties of the alloys with the two geometries can be found in Mohamed's prior study [22]. The 2 wt% Fe₂₀Ni₈₀/PA6 PNCs samples were made in a two-step process: i) SU and NC nc Fe₂₀Ni₈₀ particles were separately compounded with PA6 pellets and ii) the com-

pounded material was injection molded into standard Izod bars (ASTM-D256).

The typical compounding process is as follows. nc Fe₂₀Ni₈₀ particles were compounded with half of the PA6 amount via ultrasound-assisted solution mixing (USM) to prepare concentrated USM composite powder containing 4 wt% nc Fe₂₀Ni₈₀. The USM PNCs were then compounded (diluted) with the rest of PA6 pellets via melt mixing to prepare UMB PNCs with 2 wt% nc Fe₂₀Ni₈₀. Specifically, a 15 wt% PA6-formic acid solution was prepared. Then, nc Fe₂₀Ni₈₀ particles were dispersed and sonicated into a second very dilute 1 wt% PA6-formic acid solution for 30 min, using ultrasonic bath. The alloy particles/PA6 ratio was 1:1 wt/wt. The particles suspension was then added to the 15 wt% PA6-formic acid solution, so that the concentration of polymer in the mixture was 10 wt% and the mixture was vigorously stirred for 1 h. Addition of ethanol, with the volumetric ethanol/formic acid ratio being 2:1, initiated the precipitation of PA6 after 30 min and led to formation of the composite powder which was completed within 30 minutes. The composite powder was separated from mixed solvent through filtration and dried in vacuum oven at 80 °C for 48 h.

A DSM Micro 15 cc extruder (vertical, co-rotating twin-screw micro extruder) and 10 cc injection molding machine (Xplore Instruments, Geleen, The Netherlands) were then used for compounding the USM PNCs with the rest of PA6 pellets and fabrication of the UMB PNCs, respectively. The conditions used were: 240 °C as T_{barrel} in the compounder and injection molding machine, screw speed of 150 rpm, residence time of 4 min, T_{mold} of 70 °C and injection pressure of 0.8 MPa. Before compounding, the PA6 pellets were dried in a vacuum oven at 80 °C for 48 h. After molding, the specimens were sealed and placed in a desiccator for a minimum of 24 h prior to testing. The detailed codes of PNCs' samples are listed in Table 1.

Table 1. Nanocomposite samples' codes

Sample	Code
Control PA6	UMB0
2 wt% spherical-sea urchin Fe ₂₀ Ni ₈₀ /PA6 PNC	UMB2-SU
2 wt% necklace-like chains Fe ₂₀ Ni ₈₀ /PA6 PNC	UMB2-NC

2.3. Characterizations

Thermomechanical (TMA) analysis measurements were performed, using a Shimadzu TMA-60H thermomechanical analyzer (Shimadzu Corporation, Tokyo, Japan). Compression and penetration testing modes were employed to determine the coefficient of thermal expansion (CTE, ASTM-D696) and softening temperature, respectively, for neat PA6, UMB2-SU and UMB2-NC PNCs. Samples with dimensions of 5×5×3 mm were cut from the standard Izod bars and heated at a rate of 5 °C/min to 180 °C. Constant loads of 0.05 and 0.3 N were applied during the TMA analysis, when compression and penetration testing modes have been respectively employed. The reported results reflect an average of three measurements.

The magnetic properties of neat PA6, UMB2-SU and UMB2-NC PNCs were measured at room-temperature using a vibrating sample magnetometer (7410-S VSM, Lake Shore Cryotronics Inc, Ohio, USA), with an applied field $-25 \text{ kG} \leq H \leq 25 \text{ kG}$. The magnetic properties of the composite sample with the best room-temperature soft magnetic performance were also characterized as a function of temperature up to 150 °C. For magnetization measurements, thin sheets with dimensions of 10 mm×5 mm×0.5 mm were cut from the central region of the Izod bars and tested along their longitudinal direction.

Morphology of the composites was investigated by scanning electron microscopy (SEM) of the impact fracture surfaces, using a JEOL JSM 6360 LV SEM (JEOL Ltd., Tokyo, Japan) operating at accelerating voltage of 20 kV. The samples were gold coated to avoid charging.

Melting and crystallization behaviors of neat PA6 and PA6 phase in the PNCs were studied using modulated differential scanning calorimeter (MDSC Q200, TA instruments, Delaware, USA). The degree of crystallinity, melting and crystallization temperatures were determined. Slices had a net weight of about 8 mg were cut from the standard Izod bars. The sliced samples were heated from ambient temperature to 270 °C, held at this temperature for 3 min to erase the thermal history and then cooled to 25 °C. All MDSC runs were conducted under nitrogen atmosphere with heating/cooling rates of 5 °C/min. The degree of crystallinity, X_C , was calculated from

the enthalpy evolved during melting based on the heating scans, using Equation (1):

$$X_C = \frac{\Delta H_m}{(1 - \Phi)\Delta H_m^0} \cdot 100 \quad (1)$$

where ΔH_m is the apparent heat of fusion of the sample, ΔH_m^0 is the heat of fusion of the 100% crystalline pure PA6, which is 190 J/g, and Φ is weight fraction of nc Fe₂₀Ni₈₀ in the PNCs [23, 24].

X-ray diffraction (XRD) was employed to determine the relative fraction of α and γ crystalline phases in neat PA6 and PA6 phase within the PNCs. This is important in interpreting the thermomechanical performance of Nylon compounds, because α -phase is much stronger and less ductile than the γ -phase [25, 26]. The average crystallite sizes of nc Fe₂₀Ni₈₀ alloys within the UMB2-SU and UMB2-NC PNCs were also determined, in order to understand the influence of thermal processing on the alloy nanocrystalline structure. XRD patterns were obtained using X'Pert PRO Alfa-1 diffractometer (PANalytical, Almelo, The Netherlands) in reflection mode (45 kV, 40 mA; Cu K α + Ni-filtered radiation, λ = 0.154 nm). The analysis was performed on the Izod specimens, at ambient temperature with a 2θ range between 8 and 80°, at a scanning rate of about 4°/min and a scanning step of 0.016°. Diffraction peaks assigned to PA6 were de-convoluted to peaks corresponding to amorphous phase and crystalline phase, which is composed of α and γ crystal forms, using xPert Pro software. The percentage of γ -phase with respect to the total crystalline PA6 phase was calculated by Equation (2):

$$\gamma [\%] = \frac{A_\gamma}{A_\alpha + A_\gamma} \cdot 100 \quad (2)$$

where A_α is the area under α diffraction peaks and A_γ is the area under γ diffraction peaks [27].

3. Results and discussion

3.1. Thermomechanical behavior of

Fe₂₀Ni₈₀/PA6 PNCs

Figure 1 presents the coefficient of thermal expansion (CTE) of neat PA6, UMB2-SU and UMB2-NC PNCs at different temperature intervals. It is obvious that UMB2-SU and UMB2-NC PNCs possess considerably lower CTE values than that of neat PA6, through the temperature interval of 25–50 °C that is

Figure 1. Coefficient of thermal expansion of neat PA6, UMB2-SU and UMB2-NC PNCs at different temperature intervals

below the T_g of PA6 (~50–60 °C) [28]. This indicates that the interfacial interactions between nc-Fe₂₀Ni₈₀ alloy of either SU or NC geometry and glassy PA6 phase are strong enough to modify the polymer chains dynamics and lead to significantly improved bulk thermal dimensional stability of PNCs relative to that of neat PA6. It is notable that the improvement in thermal dimensional stability is much more pronounced for the case of alloy particles with the SU geometry rather than the NC one as the CTE of UMB2-SU PNC is 43% lower while that of UMB2-NC PNC is only 18% lower, compared to that of neat PA6.

For temperature intervals above the T_g of PA6 and up to 150 °C, although PA6 becomes in the rubbery state, UMB2-SU PNC still exhibits better thermal dimensional stability relative to neat PA6. The CTE UMB2-SU PNC at higher temperatures i.e., 100–125 and 125–150 °C range, is almost the same as that of neat PA6 at lower temperatures i.e., 75–100 °C range, indicating that more energy is required to activate the segmental motion of polymer chains in the presence of SU nc Fe₂₀Ni₈₀ particles. However, the enhancement of PA6 thermal dimensional stability by SU nc Fe₂₀Ni₈₀ particles when the polymer is in the rubbery state is decreased to around half that when it is in the glassy state. This is expected and can be attributed to the increased mobility of polymer molecules in the rubbery state. Such phenomenon counteracts the reinforcing effect of SU nc Fe₂₀Ni₈₀ particles which restricts the PA6 chains mobility, leading to less net improvement in the nanocomposite thermal dimensional stability. On the other hand, the en-

hancement of PA6 thermal dimensional stability by NC nc $\text{Fe}_{20}\text{Ni}_{80}$ particles is highly deteriorated beyond PA6 T_g . Thus, UMB2-NC PNC exhibits slightly improved thermal dimensional stability relative to neat PA6 within temperature range 50–150 °C. The remarkable thermal dimensional stability of UMB2-SU PNC over neat PA6 and UMB2-NC PNC, in both glassy and rubbery states of PA6, implies stronger filler-matrix interfacial interactions within the $\text{Fe}_{20}\text{Ni}_{80}$ /PA6 PNC when alloy particles assume the SU geometry rather than the NC one.

In penetration test, a fixed load of 0.3 N was applied on the sample by a needle and the variation of needle level with increased temperature from ambient to 180 °C was recorded. The plots, demonstrating needle level versus temperature, for PA6, UMB2-SU and UMB2-NC PNCs are displayed in Figure 2. For all the samples, the needle level increases initially with increased temperature until a certain temperature beyond which decreases dramatically. This is due to thermal expansion of samples with heating up until could be penetrated by the needle at a certain temperature that expresses the material softening temperature (T_s). Beyond T_s the penetration depth within sample is increased as the temperature is getting higher due to further material softening. It is clearly obvious that UMB2-SU and UMB2-NC PNCs have significantly higher T_s than neat PA6 and UMB2-SU PNC shows synergistic softening temperature as compared to UMB2-NC one. Thus, the T_s of UMB2-SU and UMB2-NC PNCs are higher by 113 and 63% respectively relative to that of neat PA6. Higher T_s is in good agreement with lower CTE of $\text{Fe}_{20}\text{Ni}_{80}$ /PA6 PNCs compared to neat PA6, confirming pinning of

Figure 2. Thermomechanical penetration behavior of neat PA6, UMB2-SU and UMB2-NC PNCs

polymer chains by nc $\text{Fe}_{20}\text{Ni}_{80}$ particles of either SU or NC morphology leading to restricted molecular segmental motions within nanocomposites under thermomechanical stresses. Further, the highly synergistic T_s agrees well with the significantly suppressed CTE of UMB2-SU PNC as compared to those of UMB2-NC one, indicating remarkable rigidity of UMB2-SU PNC against thermomechanical stresses rather than UMB2-NC PNC does.

3.2. Microstructure of $\text{Fe}_{20}\text{Ni}_{80}$ /PA6 PNCs

3.2.1. Morphology

SEM micrographs of SU and NC nc $\text{Fe}_{20}\text{Ni}_{80}$ particles and their corresponding nanocomposites are presented in Figure 3. SU nc $\text{Fe}_{20}\text{Ni}_{80}$ alloy, Figures 3a–b, exhibits spherical morphology with average particle diameter of about 230 nm. In addition, many sea urchin-like particles are also observed. Such sea urchin-like architecture is composed of several dendrites with average diameter of about 122 nm, growing out from the surface of the spherical core, as clearly seen in the high magnification image (Figure 3b). On the other hand, necklace-like chains with average diameter of about 225 nm dominate the architecture of NC nc $\text{Fe}_{20}\text{Ni}_{80}$ alloy, as shown in Figures 3c–d. Unlike the spherical-sea urchin like particles, the necklace-like chains appear quite smooth and little bit branched, few dendritic branches can be hardly seen at high magnification (Figure 3d). At this point the architecture of SU nc $\text{Fe}_{20}\text{Ni}_{80}$ alloy can be considered quasi-isotropic while that of NC nc $\text{Fe}_{20}\text{Ni}_{80}$ alloy is anisotropic.

Regarding UMB2-SU PNC, Figure 3e illustrates good distribution of submicron aspheric nc $\text{Fe}_{20}\text{Ni}_{80}$ particles within PA6 matrix. In the high magnification SEM image, Figure 3f, spherical and sea-urchin alloy particles, denoted by black and white arrows respectively, can be clearly distinguished within PA6 matrix. The good distribution of SU nc $\text{Fe}_{20}\text{Ni}_{80}$ particles within PA6 matrix along with the highly branched nature of sea-urchin particles allow large filler-matrix interface and therefore extensive interfacial interactions between the two phases, leading to efficient reinforcement of PA6 phase by SU alloy particles. Magnified view of the area within the white square shows constrained polymer regions, with a width in the order of tens nanometer, in between dendrites of alloy sea urchin particles. Often, confinement effect

Figure 3. SEM micrographs of (a–b) SU nc Fe₂₀Ni₈₀ alloy, (c–d) NC nc Fe₂₀Ni₈₀ alloy, (e–f) UMB2-SU PNC and (g–i) UMB2-NC PNC

of SU nc Fe₂₀Ni₈₀ particles on the polymer chains in these narrow constraint regions is much more pronounced than on those in the free volume of UMB2-SU PNC. Therefore, such constrained polymer regions are characterized by dramatically restricted chains mobility rather than polymer segments in the free volume of UMB2-SU PNC. Thus, their abundance within UMB2-SU PNC can enable a secondary reinforcing mechanism which in addition to the primary reinforcing effect of SU nc Fe₂₀Ni₈₀ particles significantly contributes to the macroscopic properties of the nanocomposite, leading to the dramatically enhanced thermomechanical rigidity of UMB2-SU PNC as compared to that of neat PA6.

SEM micrographs of UMB2-NC PNC, Figures 3g–i, at various regions of the specimen reveal the presence of three different forms of NC nc Fe₂₀Ni₈₀ particles within PA6 matrix. Thus, NC nc Fe₂₀Ni₈₀ particles appear either as short dispersed rods, agglomeration of short rods or long dispersed rods within PA6 matrix, as seen in Figures 3g, h and i respectively. Obviously, the short rods, with a length of hundreds nanometers, are considerably shorter than the nc Fe₂₀Ni₈₀ necklace-like chains, which are few microns in length as depicted in Figures 3c–d. On the other hand, the long rods are almost comparable in length to the nc Fe₂₀Ni₈₀ necklace-like chains. This reveals the breaking up of some alloy necklace chains while preparing UMB2-NC PNC, due to the intensive mixing forces applied during the UMB compounding process. Such intensive mixing forces, however, could not homogeneously disperse the nc Fe₂₀Ni₈₀ short rods, originated from breakage of alloy necklace chains, as SU nc Fe₂₀Ni₈₀ particles, leading to some extent of nc Fe₂₀Ni₈₀ agglomeration within UMB2-NC PNC. The worse dispersibility of NC nc Fe₂₀Ni₈₀ particles compared to SU nc Fe₂₀Ni₈₀ particles can be attributed to the substantial increase of the alloy permanent magnetic moment as the degree of particle anisotropy increases. It has been noted that the remanent magnetization value at zero magnetic field (M_r) for the NC nc Fe₂₀Ni₈₀ alloy is 12.3 emu/g as compared to 8.5 emu/g for the SU nc Fe₂₀Ni₈₀ alloy [22]. The crucial role of the magnetic nanofiller's geometry in controlling its particles' dispersion and distribution within PNCs due to changing their magnetic characteristics, can be considered among the most important new findings of this study.

It is possible that few filler agglomerates within UMB2-NC PNC reduce the available interface and therefore the interfacial interactions between NC nc Fe₂₀Ni₈₀ particles and PA6 matrix, limiting thus the reinforcing effect of alloy particles on polymer chains. Further, short and long dispersed rods of NC nc Fe₂₀Ni₈₀ alloy within UMB2-NC PNC appear unbranched, as shown in the inset in Figure 3i, which clearly indicates that the rod surface is entirely smooth and unbranched. This results in absence of constrained polymer regions in between alloy segments which, in turn, eliminates the secondary reinforcing effect within UMB2-NC PNC. The limited reinforcing effect of NC alloy particles as compared to SU alloy particles on PA6 chains along with the absence of the secondary reinforcing effect within UMB2-NC PNC, are mainly responsible for the worse thermomechanical rigidity of UMB2-NC PNC as compared to the UMB2-SU one.

3.2.2. Crystalline structure

The degree of crystallinity (X_c), melting (T_m) and crystallization temperatures (T_c) of neat PA6 and PA6 phase within the nanocomposites have been characterized, using DSC melting and crystallization thermograms. The results, which reflect an average of three measurements, are listed in Table 2. It is noted that the T_m of PA6, dictated by the lamellar thickness of crystals, is insensitive to the presence of nc Fe₂₀Ni₈₀ alloy of either SU or NC particle geometry within polymer matrix. Unlike T_m , clearly the PA6 degrees of crystallinity in UMB2-SU and UMB2-NC PNCs are higher than that of neat PA6. Also, the PNCs exhibit slightly higher T_c of PA6 phase, as compared to neat PA6. This can be because the nc Fe₂₀Ni₈₀ particles act as effective nucleating centers, allowing thus the PA6 crystallization to start earlier and inducing the rate of crystallization leading eventually to increased degree of crystallinity. Figure 4 further supports such hypothesis, as the observed sub- T_m exotherm in the displayed DSC heating scans is more

Table 2. DSC data for neat PA6, UMB2-SU and UMB2-NC PNCs

Sample	X_c [%]	T_m [°C]	T_c [°C]
UMB0	32.3±0.4	222.7±1.2	198.3±0.10
UMB2-SU	37.5±0.9	222.3±0.5	198.9±0.30
UMB2-NC	36.4±0.4	221.7±1.0	199.1±0.07

Figure 4. MDSC heating traces of neat PA6, UMB2-SU and UMB2-NC PNCs

Figure 5. XRD patterns of neat PA6, UMB2-SU and UMB2-NC PNCs

pronounced for UMB2-SU and UMB2-NC PNCs as compared to neat PA6. The enhancement of the sub- T_m exotherm, which is attributed to the recrystallization of PA6 chains prior to melting, upon addition of nc $\text{Fe}_{20}\text{Ni}_{80}$ alloy to PA6 confirms the nucleating action of alloy particles within both PNCs. Although the alloy surface available for nucleation of polymer chains is significantly larger within UMB2-SU PNC than in UMB2-NC one, as evidenced from the SEM micrographs, crystallization of PA6 phase has not been further induced within UMB2-SU PNC; values of the area under the sub- T_m exotherm, T_c and X_C for the PA6 phase are almost comparable within both PNCs. Most probably, this is due to the increased restriction of PA6 chain mobility which, in turn, increasingly hinders the crystallization of PA6 molecules within UMB2-SU PNC as compared to the UMB2-NC one.

It is worth mentioning that the increased degree of crystallinity of PA6 phase in both PNCs is a possible reinforcing mechanism that contributes to the significantly enhanced thermomechanical rigidity of such nanocomposites as compared to neat PA6. However, the parameter doesn't contribute to the considerably improved thermomechanical rigidity of UMB2-SU PNC over UMB2-NC one, as both nanocomposites possess a comparable PA6 degree of crystallinity.

XRD patterns for neat PA6 and the nanocomposites are presented in Figure 5. The peaks around $2\theta \approx 20$ and 23° are assigned to α_1 and α_2 crystal planes of PA6, respectively while those around $2\theta \approx 10$ and 21° are assigned to γ_1 and γ_2 crystal planes of PA6, respectively [24, 29]. The observed peaks at $2\theta =$

44.4 , 51.6 , 76.2° in the XRD patterns of UMB2-SU and UMB2-NC PNCs, are corresponding to the (111), (200) and (220) crystal planes of FCC-Awaruite FeNi_3 , respectively [22].

It is noticed that the nanocomposites exhibit increased relative fraction of γ -form to α -form PA6 crystals, as compared to neat PA6. Thus, the percentage of γ -form crystals with respect to the total crystalline PA6 phase measures 20, 26 and 41% for neat PA6, UMB2-SU and UMB2-NC PNCs, respectively. This indicates that the less ordered γ PA6 crystalline phase is favored in the presence of nc $\text{Fe}_{20}\text{Ni}_{80}$ particles, in particular, when alloy particles assume the NC geometry. This is probably because the nc $\text{Fe}_{20}\text{Ni}_{80}$ particles disturb the PA6 crystals while being formed during the crystallization process. Higher degree of alloy particles agglomeration within the UMB2-NC PNC as compared to the UMB2-SU one, may be responsible for the significantly increased PA6 γ -phase [%] within the former nanocomposite than in the latter one. This is because as the alloy particles are getting larger in size, they further disturb the PA6 crystalline order, leading to the profusion of less ordered PA6 γ -phase crystals in the nanocomposite. The significantly higher PA6 γ -phase [%] within UMB2-NC PNC than in UMB2-SU one, might be one reason for the smaller thermomechanical rigidity of the former nanocomposite as compared to the latter one. The average crystallite sizes of nc $\text{Fe}_{20}\text{Ni}_{80}$ alloys within the UMB2-SU and UMB2-NC PNCs, calculated based on the full width at half maximum of the (111) peak using the Scherrer formula [30], are 27 and 43 nm, respectively. They are significantly larger

than the crystallite sizes of the corresponding as synthesized nc $\text{Fe}_{20}\text{Ni}_{80}$ alloys; which are 16 and 20 nm for the alloy particles with SU and NC geometries, respectively [22]. This indicates some extent of alloy crystal growth during the thermal processing of PNCs, but eventually the nanocrystalline nature of $\text{Fe}_{20}\text{Ni}_{80}$ alloy is still preserved within both nanocomposites. The significantly lower nanocrystallite size of SU nc $\text{Fe}_{20}\text{Ni}_{80}$ alloy versus NC nc $\text{Fe}_{20}\text{Ni}_{80}$ alloy, reveals remarkable thermomechanical rigidity and soft magnetic properties of the alloy within the UMB2-SU PNC as compared to the UMB2-NC one. This contributes to the considerably improved overall performance of UMB2-SU PNC over UMB2-NC one.

3.3. Magnetic properties of $\text{Fe}_{20}\text{Ni}_{80}$ /PA6 PNCs

Figure 6 shows the room-temperature magnetic hysteresis loops, representing the magnetization (M) versus magnetic field (H), for neat PA6, UMB2-SU and UMB2-NC PNCs. Neat PA6 exhibits a weak diamagnetic response to the applied magnetic field; the up-right inset in Figure 6 indicates a very low magnetization of 0.01 emu/g for neat PA6 at the maximum applied magnetic field (≈ 25 kG). Thus, it can be considered a nonmagnetic material. Impressively, UMB2-SU and UMB2-NC PNCs exhibit a ferromagnetic behavior with dramatically higher saturation magnetization (M_s) than the maximum magnetization of neat PA6; M_s equals 0.43 emu/g for UMB2-SU PNC and 0.54 emu/g for UMB2-NC one. It is found elsewhere that PNCs filled with other pristine (not functionalized or surface modified) ferromagnetic nanocrystalline metallic materials such as Fe_3O_4 [31], Fe_2O_3 [32], Ni-Zn ferrite [33], and Ba-ferrite [34] exhibit M_s of about 0.5 emu/g at 5–9 wt% filler content. Herein, $\text{Fe}_{20}\text{Ni}_{80}$ /PA6 PNCs (UMB2-SU and UMB2-NC PNCs) can attain such M_s value at significantly lower filler content, indicating that nc $\text{Fe}_{20}\text{Ni}_{80}$ alloy based PNCs can be of great potential in the electromagnetic applications.

Figure 6. Room temperature magnetic hysteresis loops of neat PA6, UMB2-SU and UMB2-NC PNCs

Important magnetic parameters including initial magnetic susceptibility (χ_{ini}), saturation magnetization (M_s), saturation field (H_s), remanent magnetization (M_r), squareness (M_r/M_s) and coercivity (H_c), have been extracted from the M - H initial curves and hysteresis loops of the UMB2-SU and UMB2-NC PNCs, using IDEAS-VSM4 software. The data are summarized in Table 3. The corresponding magnetic parameters of the as synthesized SU and NC nc $\text{Fe}_{20}\text{Ni}_{80}$ alloys, reported in Mohamed's previous work [22], are also listed in Table 3. χ_{ini} is equal to $(dM/dH)_{H \rightarrow 0}$; it is determined from the initial magnetization curve. M_s is the magnetization value to $(1/H) = 0$, H_s is the magnetization field when $dM/dH \rightarrow 0$, M_r is the remanent material magnetization value at zero field, M_r/M_s is a measure of how square the hysteresis loop is and H_c is the field strength required to bring the material back to zero magnetization. As shown the SU nc $\text{Fe}_{20}\text{Ni}_{80}$ alloy possesses slightly higher χ_{ini} and M_s and lower H_s by 6, 3 and 3% respectively, as compared to the NC nc $\text{Fe}_{20}\text{Ni}_{80}$ alloy. On the other hand, M_r , M_r/M_s and H_c of the SU nc $\text{Fe}_{20}\text{Ni}_{80}$ alloy are significantly smaller than those of the NC nc $\text{Fe}_{20}\text{Ni}_{80}$ alloy by 45, 48 and 26% respectively. Higher χ_{ini} implies greater permeability of alloy particles to the magnetic moment when assuming quasi-iso-

Table 3. Room-temperature magnetic properties of nc $\text{Fe}_{20}\text{Ni}_{80}$ alloys of SU and NC geometries and their PA6 based nanocomposites

Sample	χ_{ini} [emu/g/G]	M_s [emu/g]	H_s [G]	M_r [emu/g]	M_r/M_s	H_c [G]
SU- $\text{Fe}_{20}\text{Ni}_{80}$	0.146	78.820	14 848	8.500	0.108	85.760
UMB2-SU	$0.76 \cdot 10^{-3}$	0.433	6233	0.066	0.153	92.584
NC- $\text{Fe}_{20}\text{Ni}_{80}$	0.138	76.650	15 290	12.300	0.160	108.330
UMB2-NC	$0.63 \cdot 10^{-3}$	0.544	7 500	0.123	0.227	197.980

tropic architecture (SU geometry) rather than anisotropic one (NC geometry). Therefore the SU nc Fe₂₀Ni₈₀ alloy exhibits easier magnetization/demagnetization behavior, evidenced by higher χ_{ini} and M_s along with lower H_s , M_r , M_r/M_s and H_c , i.e. improved soft magnetic character than the NC nc Fe₂₀Ni₈₀ alloy does.

Considering the effect of alloy crystallite size besides the predominant effect of alloy geometrical architecture on the magnetic properties, interprets why M_s is slightly decreased but M_r and H_c are significantly increased as transfer from SU to NC nc Fe₂₀Ni₈₀ alloy. It is known that the M_s of ferromagnetic nanocrystalline metallic materials is suppressed with decreased crystallite size due to the enhanced surface spin disorder which conflicts with the magnetic moment induced by the external applied magnetic field. On the other hand, M_r and H_c are reduced with the decreased crystallite size because the crystal magnetic behavior is getting toward the single-domain behavior. Such single-domain behavior, characterized by M_r and H_c tend to zero, dominates at crystallite size lower than the critical size (d_c). The estimated d_c is about 20–30 nm for ferromagnetic nanocrystalline metallic materials [35]. Thus, the little increase of crystallite size from 16 nm in the SU nc Fe₂₀Ni₈₀ alloy to 20 nm in the NC nc Fe₂₀Ni₈₀ alloy, has resulted in a small increase in the alloy M_s . This counteracted the main decrease in M_s due to the increased anisotropy of alloy architecture. Consequently, a slight net decrease in the M_s value is observed for the NC nc Fe₂₀Ni₈₀ alloy. On contrary, both factors i.e., increased anisotropy of alloy architecture and alloy crystallite size, enhance the M_r and H_c values. Accordingly, NC nc Fe₂₀Ni₈₀ alloy possesses considerably higher M_r and H_c than SU nc Fe₂₀Ni₈₀ alloy.

Regarding the polymer nanocomposites, χ_{ini} of UMB2-SU PNC is higher than that of UMB2-NC PNC by 20%, indicating that the UMB2-SU PNC is significantly more permeable to the magnetic moment than the UMB2-NC one. Therefore, the magnetization/demagnetization of UMB2-SU PNC is considerably facile, as compared to that of UMB2-NC PNC. This is confirmed as H_s of the UMB2-SU PNC is 20% smaller than that of the UMB2-NC one. Moreover, the UMB2-SU PNC possesses almost one-half M_r and H_c and two-third M_r/M_s , compared to the UMB2-NC one. Thus, UMB2-SU PNC with a coer-

civity less than 95 G can be considered a magnetically soft material [36], whereas UMB2-NC PNC with a coercivity of about twice that limit is a hard magnetic material.

Lower M_s of UMB2-SU PNC than that of UMB2-NC PNC by about 20%, doesn't mean difficult magnetization of the former PNC as compared to the latter one. This is because the behavior of other magnetic properties, χ_{ini} , H_s , M_r , M_r/M_s and H_c , contradicts such hypothesis. The magnetic performances of the Fe₂₀Ni₈₀/PA6 PNCs are determined by, in addition to the magnetic properties of the corresponding as synthesized alloys, other three factors: (a) filler-matrix interfacial interactions, (b) presence of narrow constrained polymer regions in between branches of the sea urchin alloy particles within the UMB2-SU PNC and (c) different crystallite sizes of the nc Fe₂₀Ni₈₀ alloys within PNCs as compared to the as synthesized ones. The constrained polymer regions in between alloy segments are often largely influenced by the alloy characteristics rather than polymer segments in the free volume and therefore can enable a secondary soft magnetic effect within the UMB2-SU PNC. Thus, the extensive interfacial interactions between PA6 matrix and SU alloy particles rather than NC ones and the secondary soft magnetic effect present in the UMB2-SU PNC, have made the PA6 matrix within the UMB2-SU PNC less resistive to the magnetic moment than that within the UMB2-NC PNC. Consequently, this lead to considerably easier magnetization/demagnetization of UMB2-SU PNC. The increased gap between crystallite sizes of SU nc Fe₂₀Ni₈₀ alloy (27 nm) and NC nc Fe₂₀Ni₈₀ alloy (43 nm) within PNCs, as compared to the case for the as synthesized alloys, has resulted in two effects. First, it has caused the M_r and H_c of SU alloy to be lower than those of NC alloy within PNCs, by significantly more percentages than those recorded for the as synthesized alloys. This has subsequently contributed to the large gap between the M_r and H_c of UMB2-SU PNC and those of UMB2-NC one. Second, it might cause the M_s to invert its trend i.e. M_s of SU alloy becomes lower than that of NC alloy and this may be the reason for the lower M_s of the UMB2-SU PNC than that of the UMB2-NC one. The UMB2-SU PNC is regarded a better suit for the electromagnetic devices requiring good soft magnetic properties, where the nc Fe₂₀Ni₈₀ alloy has been

Figure 7. Magnetic hysteresis loop of UMB2-SU PNC as a function of temperature

Table 4. Magnetic properties of UMB2-SU PNC at different temperatures

Temperature [°C]	χ_{ini} [emu/g/G]	M_s [emu/g]	M_r [emu/g]	H_s [G]
25	$0.76 \cdot 10^{-3}$	0.433	0.066	92.584
50	$0.76 \cdot 10^{-3}$	0.404	0.064	87.615
100	$0.69 \cdot 10^{-3}$	0.363	0.051	75.145
150	$0.63 \cdot 10^{-3}$	0.305	0.042	66.630

extensively exploited, due to its distinctive morphological features, remarkable thermomechanical rigidity and room-temperature soft magnetic character. Accordingly, the temperature-dependent magnetic behavior has been only investigated for the UMB2-SU PNC, in order to explore its thermal soft magnetic stability.

Figure 7 displays the M - H hysteresis loop of UMB2-SU PNC as a function of temperature up to 150 °C. The corresponding magnetic parameters are listed in Table 4. It is noted that all the magnetic parameters including χ_{ini} , M_s , M_r and H_c are reduced; indicating suppressed ferromagnetic nature of the nanocomposite, with the increased temperature. This is due to the greater thermal activation energy of spins at higher temperature [37]. Interestingly, χ_{ini} and M_s at 100 °C are little lower than those at room temperature by 9 and 16% respectively. This reveals that the ferromagnetic performance of the UMB2-SU PNC is still relatively good at such high temperature, i.e. good thermal soft magnetic stability of the nanocomposite.

4. Conclusions

Results of the study reveal a major role of the nc $\text{Fe}_{20}\text{Ni}_{80}$ alloy geometry in controlling the bulk properties of the 2 wt% $\text{Fe}_{20}\text{Ni}_{80}$ /PA6 PNC. The UMB2-

SU PNC, filled with alloy particles of SU geometry, exhibits remarkable thermomechanical rigidity and room-temperature soft magnetic properties, relative to neat PA6 and to the UMB2-NC PNC, which is filled with alloy particles of NC geometry. Variant nanocomposites' overall performances can be due to the distinctive microstructural differences between them, evidenced from the SEM and XRD analyses. Morphological observations disclose good dispersion and distribution of SU nc $\text{Fe}_{20}\text{Ni}_{80}$ particles within the UMB2-SU PNC while some agglomerates of NC nc $\text{Fe}_{20}\text{Ni}_{80}$ short rods are present in the UMB2-NC PNC. The crucial role of the magnetic nanofiller's geometry in controlling its particles' dispersion and distribution within PNCs is first recognized in this study and attributed to changes in the filler magnetic properties. Thus, improved filler-matrix interfacial interactions dominate the UMB2-SU PNC as compared to the UMB2-NC one. Additionally, the SEM images reveal the presence of narrow constraint polymer regions in between branches of the sea urchin alloy particles within the UMB2-SU PNC. Whereas such phenomenon is absent in the UMB2-NC PNC because NC alloy particles are unbranched. These constrained polymer regions enable secondary reinforcing and soft magnetic effects within the UMB2-SU PNC. Thus, the extensive filler-matrix interfacial interactions and the significantly lower alloy crystallite size within the UMB2-SU PNC as compared to the UMB2-NC one, along with the secondary reinforcing and soft magnetic effects present in the UMB2-SU PNC are the main factors responsible for the superior overall performance of UMB2-SU PNC. The considerably lower PA6 γ -crystal type [%] within the UMB2-SU PNC than in the UMB2-NC one, contributes also to the improved thermomechanical rigidity of the UMB2-SU PNC. The PA6 degree of crystallinity, however, is comparable in both nanocomposites and therefore doesn't contribute to their variant thermomechanical rigidities. On the other hand, the temperature-dependent magnetic behavior of the UMB2-SU PNC indicates that its ferromagnetic performance is quite good up to 100 °C. Overall, the good thermomechanical rigidity and thermal soft magnetic stability of UMB2-SU PNC infer that the material can sustain the thermal stresses present in the electromagnetic applications. Accordingly, the $\text{Fe}_{20}\text{Ni}_{80}$ /PA6 PNCs based on nc $\text{Fe}_{20}\text{Ni}_{80}$ alloy of SU

particle geometry can lead to new promising structural material for electromagnetic applications.

Acknowledgements

Authors deeply appreciate Mr. Mahmoud Darwish, Mrs. Basant Ewida and Ms. Sarah Abdelaziz, Central Lab. Engineers at SRTA City, for performing the SEM imaging and thermo-mechanical analysis. This research received no specific grant from any funding agency. Thus, financial support for this research has been provided by the authors' universities; SRTA City, Egypt and Georgia Tech, USA.

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