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Preparation and characteristic of expandable polyamide-6/graphite composite

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ABSTRACT

Expandable polyamide-6/graphite composite (P-6/GC) is a new composite. Expandable P-6/GC is provided with the exfoliated property while is heated at 300°C. Owing to using an expandable reagent containing graphite carbon, electron transfers property of P-6/GC exfoliated has been strengthened. Infrared spectrum is applied to attest polyamide-6 on graphite worm. Images of scanning electron microscope show worm-like morphology of P-6/GC exfoliated. Comparing the volume resistivity of expandable P-6/GC to P/-6GC exfoliated, the result is that P-6/GC exfoliated has stronger electron transfers than expandable P-6/GC.

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KEYWORDS

Composite;
Covering;
Nylon-6;
Expanded graphite;
Volume resistivity.

INTRODUCTION

Polyamide-6 (Nylon-6) is a very important engineering material and has been applied widely^[1]. For developing polyamide-6 application further, lots of polyamide-6 nanocomposites have been prepared or synthesized as well as. For instance, Fe₂O₃/PA-6 nanocomposite fiber^[2], nano-Al₂O₃ reinforced polyamide-6 composites^[3], polyamide-6/attapulgite nanocomposite^[4], titanate-modified boehmite-polyamide-6 nanocomposites^[5], polyamide-6-boehmite nanocomposites^[6], expandable graphite/polyamide-6 nanocomposites^[7], polyamide-6/clay nanocomposites^[8], nylon 6-montmorillonite nanocomposite membranes^[9], polyamide-6/maleated styrene-butylene-co-ethylene-styrene nanocomposites^[10] and so on have been prepared.

Recently we also prepare a new polyamide-6/graphite composite, and the composite is also by way of a middle substance and has a very especial physical property. When it is heated at 300°C, it can be expanded. Therefore, the composite is called as expandable polyamide-6/graphite composite (expandable P-6/GC). An expandable reagent plays an important role in expandable process. The composite expanded is called as well as polyamide-6/graphite composite exfoliated (P-6/GC exfoliated). P-6/GC exfoliated possesses a specific morphology like graphite worm^[11] and be covered evenly by polyamide-6. Meanwhile, P-6/GC exfoliated is provided with stronger electron transfers property. If P-6/GC exfoliated was applied to produce some materials, we would believe it should be a very potential polyamide-6 composite.

EXPERIMENTAL

Materials

Nature graphite(NG) which carbon content was 99% and an average of flake size was 320 μm . Potassium dichromate with purity of 99.8wt.%. Glacial acetic acid, perchloric acid, caprolactam and 6-amino-caproic acid with percentages were 97.0wt. %, 72.0wt.%, 99.5wt.% and 99.5wt.% respectively.

Fabrication of expandable reagent

According to the previous work^[12] 5.0g(0.417mol) of flake graphite, 7.0g(0.070mol) of perchloric acid, 4.0g(0.067mol) of glacial acetic acid and 2.0g(0.007mol) of potassium dichromate were placed into a dry three-neck flask equipped with a thermometer, a stirrer and a condenser. Continually stir the mixture for 60min at 45 $^{\circ}\text{C}$, and then wash to neutrality in water, dehydrate and dry at the temperature of 50~60 $^{\circ}\text{C}$. Finally obtain the expandable reagent.

Preparation of expandable polyamide-6/ graphite composites

Under a dry nitrogen gas stream, expandable reagent, caprolactam and 6-amino-caproic acid were mixed, continually stir at 70~80 $^{\circ}\text{C}$, then distilled water and catalyzer were put into the mixture, raise the temperature to 260 $^{\circ}\text{C}$ and react for 12h, filtrate and dry in vacuum at the temperature of 50~60 $^{\circ}\text{C}$, finally expandable P-6/GC was obtained. Putting 1g of expandable P-6/GC into a tubular furnace at 300 $^{\circ}\text{C}$ for 1 min, and get P-6/GC exfoliated.

RESULTS AND DISCUSSION

SEM and FTIR analysis of expandable P-6/GC and P-6/GC exfoliated

SEM(S-570, Japan.) images of expandable P-6/GC and P-6/GC exfoliated are shown in figure 1. Figure 1a is an image of expandable P-6/GC, and figure 1b-d is images of P-6/GC exfoliated. Figure 1a displays the expandable P-6/GC is a heap of flakes, but the flakes are different from graphite flakes, because the flakes have been covered by white materials. Figure 1b is an image which expandable P-6/GC is heated to produce P-6/GC exfoliated, and comes from a piece

of expandable P-6/GC flake. Comparing the image to one of exfoliated graphite^[13], it is not difficult to discover that their morphology is very similar. Thereby the morphology is called as graphite worm. In addition, we also see there are some clusters of petals on the graphite worm, and it is very apparent that the petals are also covered by white materials.

In order to determine the structure of white materials, we applied Fourier transform infrared(FTIR-8900 Shimadzu Corporation, Japan) set up spectra of expandable P-6/GC and P-6/GC exfoliated, the result showed that both of the FTIR spectra had the same absorptive peaks formation, and all of them had the same place of absorption wavenumbers. They were at 1570 cm^{-1} (N-H wag), 1630 cm^{-1} (C=O stretch), 2880 cm^{-1} (-CH-stretch), 2940 cm^{-1} (-CH₂-stretch) and 3420 cm^{-1} (N-H stretch), respectively. Whereas, the characteristic absorption peaks of polyamide-6 existed in the spectra, we could confer the white materials might be polyamide-6, and the covering was also quite even.

XRD analysis of graphite, expandable reagent and expandable P-6/GC

Figure 2 is XRD patterns of graphite (a), expandable reagent (b) and expandable P-6/GC (c). We can see there are two characteristic diffraction angles, they are at $2\theta=26.82^{\circ}\text{C}$ and $2\theta=55.21^{\circ}\text{C}$, respectively. If it is taken for characteristic diffraction peaks that the characteristic diffraction angles correspond to peaks, well then flake graphite has two characteristic diffraction peaks. Analyzing the pattern of expandable reagent, the characteristic diffraction peak which $2\theta=55.21^{\circ}\text{C}$ is

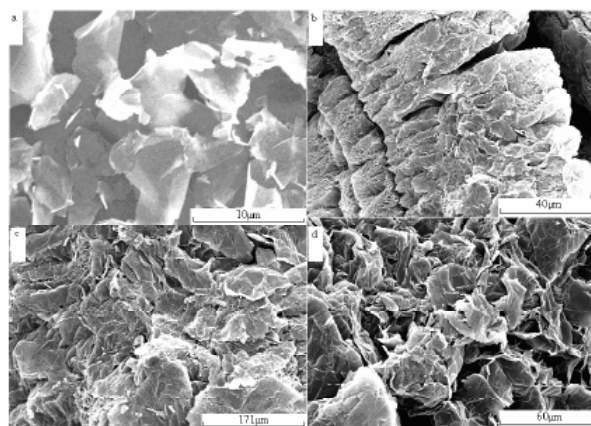


Figure 1 : SEM images of expandable P-6/GC and P-6/GC exfoliated

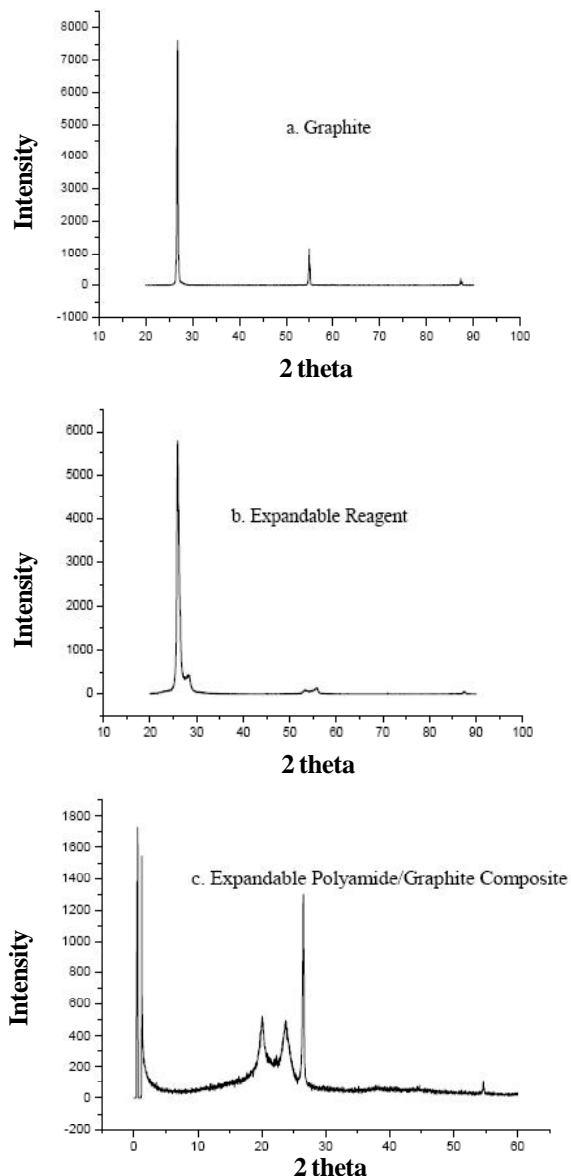


Figure 2 : XRD patterns of graphite, expandable reagent and P-6/GC

TABLE 1 : The volume resistivity values of expandable P-6/GC and P-6/GC exfoliated

Composite	ρ (Ω -cm)	Composite	ρ (Ω -cm)
	10^{14}		2.3×10^6
Expandable P-6/GC	3.6×10^8	P-6/GC exfoliated	9.8×10^3
	1.4×10^6		1.6×10^3
	9.5×10^3		385
	380		55

homologous in graphite is divided into two. This explains expandable reagent is very like a kind of graphite intercalation compounds (GIC)^[12]. $2\theta=26.82^\circ$ of the characteristic diffraction peak is reserved illuminates

graphite layers structure still exist in expandable reagent. Both of difference is merely on layers distance. The characteristic diffraction peaks at $2\theta=26.82^\circ$ in expandable P-6/GC is also retained. It shows that expandable P-6/GC is a flak graphite structure. But the structure is different from flake graphite or GIC, the surface and endothercium of flake graphite have been covered and filled by polyamide-6. This condition has been proved that characteristic diffraction peaks are at about $2\theta=1.16^\circ$, 20.13° and 23.91° in expandable P-6/GC. Because three characteristic diffraction peaks represent coexistence crystal of α and γ polyamide-6 structure.

Analysis of electron transfer property on expandable P-6/GC and P-6/GC exfoliated

Here is volume resistivity values delegated as electron transfer ability, the bigger volume resistivity values are, the smaller the electron transfer ability is. The values are calculated according to the following equation:

$\rho=RA/l$. Where ρ is a value (Ω /cm) of volume resistivity; R is a value (Ω) of sample resistivity, and l the length of sample (cm), and A the area of sample (cm^2).

For reviewing the electron transfer ability of expandable P-6/GC and P-6/GC exfoliated, five kinds of expandable P-6/GC and P-6/GC exfoliated were prepared apart, and the expandable reagent of mass ratios (wt. %) were 1, 2, 4, 6 and 8%, respectively. Their volume resistivity values were calculated and shown in TABLE 1.

When the mass ratio is 1%, the volume resistivity value of expandable P-6/GC is almost equal to pure polyamide-6 ($\rho=10^{14}$ Ω -cm). The values of expandable P-6/GC decreases fast from 3.6×10^8 to 380Ω -cm, while expandable reagent mass is added from 2% to 8%. It implies that the electron transfer ability of expandable P-6/GC is reinforced surely in the process. Comparing P-6/GC exfoliated to expandable P-6/GC, the value of P-6/GC exfoliated is $2.3 \times 10^6 \Omega$ -cm, moreover, the value of expandable P-6/GC is $10^{14} \Omega$ -cm while the mass ratio is 1%. It is apparent that the value of the front is out and away smaller than the latter. It also suggests that the electron transfer ability of P-6/GC exfoliated is much stronger than expandable P-6/GC.

CONCLUSION

Expandable P-6/GC is not only a new composite; it is but also a very important middle composite. When heated to produce P-6/GC, the electron transfer ability is strengthened, and P-6/GC exfoliated has an especial morphology of graphite worm. In addition, expandable P-6/GC is prepared very industrially. We can expect P-6/GC exfoliated will have more physical and chemical properties to be discovered in the future, due to having the morphology of graphite worm. Of course, this article reports merely a way to modify the physical or chemical properties of polyamide-6 composites. But we think that the way possesses a directive sense for preparing other expandable composites, therefore, we recommend the way is applied to modify polymers and reinforce electron transfer ability of polymers.

REFERENCES

- [1] M.V.Pandya, M.Subramaniam, M.R.Desal; *Eur. Polym.J.*, **33**, 789 (1997).
- [2] Ying Liang, Xiaohong Xia, Yongsong Luo, Zhijie Jia; *Mater.Lett.*, **61**, 3269 (2007).
- [3] Li-xin Zhao, Li-yun Zheng, Shu-guo Zhao; *Mater. Lett.*, **60**, 2590 (2006).
- [4] Liang Shen, Yijian Lin, Qiangguo Du, Wei Zhong; *Compos.Sci.Technol.*, **66**, 2242 (2006).
- [5] Ceren Ozdilek, Krzysztof Kazimierczak, Stephen J.Picken; *Polym.*, **46**, 6025 (2005).
- [6] Ceren Ozdilek, Krzysztof Kazimierczak, David van der Beek, Stephen J.Picken; *Polym.*, **45**, 5207 (2004).
- [7] Fawn M.Uhl, Qiang Yao, Hiroyoshi Nakajima, E. Manias, Charles A.Wilkie; *Polym.Degrad.Stab.*, **89**, 70 (2005).
- [8] I.Gonzalez, J.I.Eguiazabal, J.Nazabal; *Compos.Sci. Technol.*, **66**, 1833 (2006).
- [9] Picard, A.Vermogen, J.F.Gerard, E.Espuche; *J. Membr.Sci.*, **292**, 133 (2007).
- [10] I.Gonzalez, J.I.Eguiazabal, J.Nazabal; *Eur.Polym. J.*, **42**, 2905 (2006).
- [11] Ji-hui Li, Li-li Feng, Zhi-xin Jia; *Mater.Lett.*, **60**, 746 (2006).
- [12] Ji-hui Li, Hui-fang Da, Qian Liu, Shu-fen Liu; *Mater. Lett.*, **60**, 3927 (2006).
- [13] Ji-hui Li, Qian Liu, Hui-fang Da; *Mater.Lett.*, **61**, 1832 (2007).