

MODIFIED RECYCLED GLASS FIBER REINFORCED FLAME RETARDANT PBT WITH IMPROVED MECHANICAL PROPERTIES BY NANO-PARTICLES

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Abstract: To improve the mechanical properties of recycled glass fiber reinforced flame retardant PBT(RGFFRPBT), three kinds of nano-particles including silicon dioxide (SiO₂), montmorillonite(MMT) and mica were blended with RGFFRPBT by twin-screw extruder, respectively. The effect of nano-particle contents on physical properties of nanocomposite was investigated, including the mechanical properties, electrical and flame retardant properties. The results illuminated that when the content of nano-SiO₂ and nano-mica was 1%, the notched impact strength, tensile strength and flexural strength of nanocomposites were markedly improved, once the content of nano-particles ranged from 2% to 5%, the mechanical properties decreased, while heat distortion temperature increased. The content of MMT had not significantly enhanced on the mechanical properties of nanocomposite. The addition of nano-particle did not significantly affect the electrical and flame retardant properties.

1. Introduction

It is known that polybutylene terephthalate (PBT) have excellent comprehensive properties, such as good dimensional stability, thermal and arc tracking resistance and so on[1-3]. Today, glass fiber reinforced flame retardant PBT is used in various insulating parts for electrical engineering and electronics, such as electronic relay, communication and automobile applications[4-7], and the ratio of RGFFRPBT was higher than 35 wt%. The improvement of recycled glass fiber reinforced flame retardant PBT (RGFFRPBT) is becoming increasingly important [8]. Nano-particle-filled polymers have been a subject of active topic in the past decades due to their unique physical and chemical properties [9-11]. When filled in polymer, nano-particles can insert into the defects of the polymers in the nano-size. The phenomenon of stress concentration in the polymer can be conquered via the cross-linking interaction of polymer molecule chains and nano-particles, as well as the effect of interfacial energy transmission. Many attempts have been made to improve these properties of PBT by blending it with various fillers [12-14]. It was found that nano-particles have

obvious strengthening and toughening effects thus can improve largely the physical properties of the composite polymers. With the addition of only a few percent of nanocomposites, polymer nanocomposites exhibit thermal, mechanical, and barrier properties that are greatly improved over those of the pristine polymers. Numerous methods for the preparation of polymer nanocomposites have recently been developed by several groups[15-18]. Nano-silica was used to modify thermoplastics polybutylene terephthalate (PBT) to improve the thermal stability, tensile strength, and notched impact strength of PBT. Clays such as MMT, mica, and so on were applied to increase the mechanical properties of nanocomposites [19] [20]. Li et al[12] [21] prepared PBT-clay nanocomposites by the method of melt intercalation with MMT, and investigated the influence factors on the mechanical properties of nanocomposites[18]. mica is a different kind of clay that has been widely used as a reinforcing filler in polymeric matrices because of its excellent mechanical, electrical and thermal properties[22]. When the glass fiber reinforced flame retardant PBT (GFFRPBT) was mold-injected, the mold-injection process decreased the characteristic viscosity of PBT and the length of glass fiber, caused the decreases of mechanical properties. Few lectures focused on the modified the RGFFRPBT with an improved mechanical properties. In this paper, to improve the mechanical properties of RGFFRPBT, nano-particles including silicon dioxide (SiO₂), montmorillonite(MMT) and mica were chosen to blended with RGFFRPBT by twin-screw extruder, respectively. The effect of nano-particle contents on properties of nanocomposite was investigated, including the mechanical properties, electrical and flame retardant properties.

2. Experiment

2.1 Materials

Flame retardant PBT with 30 wt% glass fibers was prepared by the paper^[23], the recycled glass fiber reinforced flame retardant PBT collected by injection molding was processed with one times mold-injection(by ARBUR 420M, at 275 °C),The commercial organic montmorillonite (MMT), 10 A, modified with dimethyl, benzyl, hydrogenated tallow quaternary ammonium (2MBHT) was provided by Southern Clay Co., USA. Nano-silica was provided by Hai-Tai, Nanjing, China, with the specific area of 380 m²/g (N₂, BET), an average diameter of 22 nm. Mica is a platy potassium aluminium silicate, and is supplied with no surface treatment with particle size of 100-150 nm was offered by Zhong Lan Chen Guang Research Institute of Chemical Industry, Chengdu, China.

2.2 Preparation of nano-particles-filled with GFFRPBT

Nanocomposites were prepared by direct melt compounding SiO₂, MMT, mica with RGFFRPBT was mixed by high-speed stir and then compounded in a twin-screw extruder (L/D=25/1) at 250 °C and 25 rpm, and the nano-particle loading was 0 % (presented by EGFFRPBT), 1 wt% (presented by RGFFRPBT/SiO₂-1, RGFFRPBT/MMT-1, RGFFRPBT/

mica-1, respectively) %, 2 wt% (presented by RGFFRPBT/SiO₂-2, RGFFRPBT/MMT-2, RGFFRPBT/mica-2, respectively), 5 wt% (presented by RGFFRPBT/SiO₂-5, RGFFRPBT/MMT-5, RGFFRPBT/mica-5, respectively), respectively. The extruded strands were passed through a water bath and pelletized. The nanocomposites were further dried at 120 °C, for 4 h before injection molding the test specimens for properties determination.

2.3 Characterization

The mechanical properties of such as Tensile (ASTM D638-03) and flexural (ASTM D790-07) properties evaluation were done on a Universal test machine (Reger, RGT-20A). The notched impact strength (ASTM D 256) was performed using a impact tester (Sans Tested, ZBC1400-2) at room temperature. Glow-wire ignitability test on materials was processed by IEC 60695-2-1/3(1994-03) and the test temperature was 750 °C. To measure the tracking, 50 drops of 0.1% ammonium chloride solution are dropped on the material, and the voltage measured for a 3mm thickness is considered representative of the material performance. Heat distortion temperature (HDT) of nanocomposite was characterized by the procedure given in ASTM D-648. All the standard test bar were prepared by mold-injection. The morphologies of the fractured surfaces of the standard test bar were investigated using a Hitachi S-3700 scanning electron microscope (SEM).

3. Results and Discussion

3.1 Effect of content of nano-particles on the mechanical properties of modified RGFFRPBT

Tab.1 shows the notched impact strength, tensile strength and flexural strength of nano-particles-filled RGFFRPBT as a function of filling content, with the tensile strength of the original EGFFRPBT as control. For the original version EGFFRPBT modified by SiO₂ and mica, the mechanical properties initially increases until the filling content reaches 1%. The reason was that nSiO₂ and mica have high modulus and tensile strength. After being filled with RGFFRPBT, the particles present good compatibility with the resin matrix through the polymer. At the interface of the grafting polymer and the resin matrix, a thick gradient layer can be formed for the rigid particles to pass their mechanical strength to the PBT resin matrix. This makes the adhesion even stronger and provides an effective bridge for the organic resin to pass the stress to the inorganic particles. Thus, the notched impact strength, tensile strength and flexural strength can be improved. All of the notched impact strength, tensile strength and flexural strength decreases with the content instead, and their values are even lower than that of EGFFRPBT when the content is higher than 5 wt%. This decrease in ultimate strength is mainly due to the agglomeration of nano-particles above nano-particles loading [24, 25] and the incompatibility of nanocomposite. However, for MMT-filled RGFFRPBT, mechanical properties sharp decreases and reaches its minimum when the content is 5 wt%, even lower than those of original version RGFFRPBT. This indicates that the toughness was poor after being filled with MMT. Different to SiO₂ and mica, the figure of MMT is layered structure,

which restricted it to disperse in the matrix of RGFFRPBT, decreased the adhesion of molecule chains and a network structure forms [26]. As a result, the mechanical properties of MMT-filled RGFFRPBT could not be improved due to the debonding around the polymer-clay interfaces and void formation.

Tab. 1 Effect of content of nano-particles on the mechanical properties of modified RGFFRPBT

Samples	Notched impact strength (J/m)	Tensile strength (MPa)	Flexural strength (MPa)
EGFFRPBT	40.2	62.6	115.2
RGFFRPBT/SiO ₂ -1	52.1	73.1	138.1
RGFFRPBT/SiO ₂ -2	45.3	69	126.2
RGFFRPBT/SiO ₂ -5	39.3	66.3	117.1
RGFFRPBT/MMT-1	33.3	55.1	110.3
RGFFRPBT/MMT-2	29.7	45.3	101.3
RGFFRPBT/MMT-5	28.8	36.3	96.2
RGFFRPBT/mica-1	49.9	72.4	129.5
RGFFRPBT/mica-2	42.5	68.8	118.4
RGFFRPBT/mica-5	36.8	60.4	110.1

3.2 Effect of nano-particles content on the flammability, comparative tracking index and Heat distortion temperature of modified RGFFRPBT

Tab. 2 Effect of nano-particles content on the Glow-wire ignitability time, CTI and HDT of modified RGFFRPBT

Samples	Glow-wire ignitability time (s)	CTI (V)	HDT (°C)
EGFFRPBT	18.7	225	191
RGFFRPBT/SiO ₂ -1	19.6	225	192.5
RGFFRPBT/SiO ₂ -2	20.5	225	194.3
RGFFRPBT/SiO ₂ -5	21.3	200	196.6
RGFFRPBT/MMT-1	17.6	225	188.6
RGFFRPBT/MMT-2	16.3	200	190
RGFFRPBT/MMT-5	15.2	200	186.9
RGFFRPBT/mica-1	20.1	225	194.1
RGFFRPBT/mica-2	21.3	225	194.2
RGFFRPBT/mica-5	22.5	200	194.4

Tab. 2 exhibited the nano-particles content influenced on the flammability properties, CTI and HDT. The data demonstrated that with the increased of mica and SiO₂ content from 1 wt% to 5 wt%, respectively, the electrical and flame retardant properties of modified

RGFFRPBT show a few degraded, while the HDT of SiO₂ modified RGFFRPBT was improved from 192.5 °C to 196.6 °C, HDT of maci modified RGFFRPBT was insignificant changed and kept as 194 °C. The results illuminated that when the recycled glass fiber reinforced flame retardant PBT were extruded with nano-SiO₂, the nano-particle play as the reinforced material of RGFFRPBT. The reason was that even a small amount of nano-particle was significant affected on the free volume of PBT, confinement of the intercalated polymer chains, and would prevent the segmental motion of the polymer chains[27]. With increased of MMT content from 1 wt% to 5 wt%, the glow-wire ignitability time decreased from 17.3 second to 15.2 second. The reason was that when MMT was filled in polymer, it show higher thermal stability [28]. Due to MMT-filled RGFFRPBT could not be improved due to debonding around the polymer-clay interfaces and void formation[26], the HDT of modified RGFFRPBT had not significantly improved, even with the MMTcontent increased to 5 wt%, its HDT was lower than that of EGFFRPBT and was only 186.9 °C.

3.3 Characterization of SEM

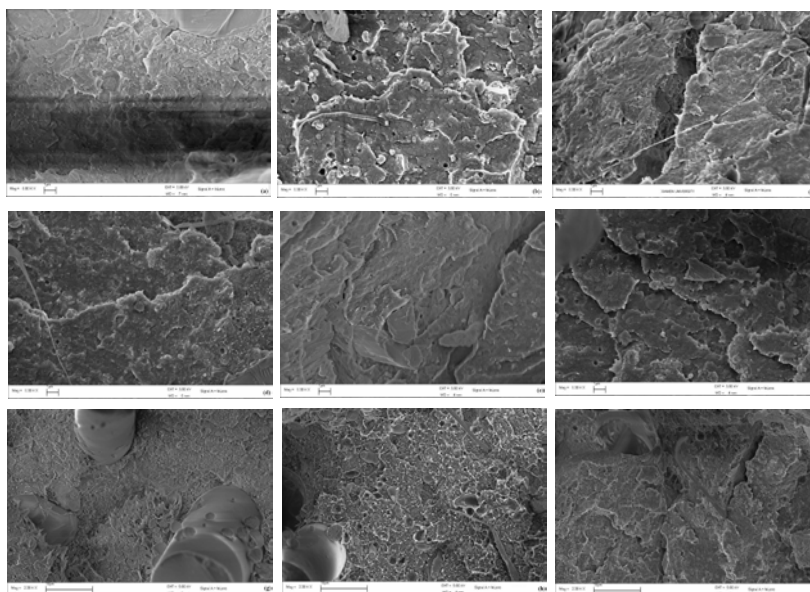


Fig. 1 SEM micrographs of nano-particles modified RGFFRPBT with various contents:
 (a)RGFFRPBT/SiO₂-1, (b)RGFFRPBT/SiO₂-2, (c) RGFFRPBT/SiO₂-5
 (d) RGFFRPBT/MMT-1, (e)RGFFRPBT/MMT-2, (f)RGFFRPBT/MMT-5
 (g)RGFFRPBT/mica-1, (h)RGFFRPBT/mica-2, (i)RGFFRPBT/mica-5

The morphologies of the extruded RGFFRPBT obtained from nano-particls with up to 1 wt%to 5 wt% in the PBT matrix were examined by observing their fracture surfaces with an SEM, and the results are shown in Fig. 1 . These micrographs show that there is an increase in the roughness and crack of the fracture surfaces due to the addition of particles. Indeed, the apparent roughness and crack of the fracture surfaces varies significantly from one composite to another: picture (a), (d) and (g)where the micrographs are of composites which all contain

1 wt% of nano-particles, RGFFRPBT/SiO₂-1 and RGFFRPBT/mica-1 show smoother surface than that of RGFFRPBT/MMT-1, indicated that the roughness varies significantly depending upon the type of particle employed. Picture (a), (b) and (c) show the fracture surfaces of the samples change in appearance as the nano-SiO₂ content increased. At low nano-SiO₂ contents, the surface was relatively smooth and featureless, with the rougher areas being associated with the nano-SiO₂ particles. As the loading increased, the smoother areas become smaller in size and roughness and crack of the fracture surfaces dominated^[22]. Picture (e) and (i) for example, the surface becomes uniformly rough and larger crack between the figure. The SEM micrographs of nano-particles modified RGFFRPBT could be explained when the nano-particles content was less than 1%, the mechanical properties of nano-particles modified RGFFRPBT improved, while when the nano-particles content was higher than 2%, it decreased the mechanical properties. Picture (d), (e) and (f) show that most of MMT are agglomerated at greater size, these agglomerated layers could not form polymer-clay interfaces[26], as a result, the MMT modified RGFFRPBT show little improved mechanical properties.

4. Conclusion

When silicon SiO₂, MMT and mica were extruded with RGFFRPBT to modify its mechanical properties, it was found that

when the content of nano-SiO₂ and nano-mica was 1%, the notched impact strength, tensile strength and flexural strength of nanocomposites were markedly improved, once the content of nano-particles ranged from 2% to 5%, due to the agglomeration of nano-particles above nano-particles loading and the incompatibility of nanocomposite, the mechanical properties decreased, however. The content of MMT had not significantly enhanced on the mechanical properties of nanocomposite. The addition of nano-particle did not significantly affect the electrical and flame retardant properties. The results illuminated that when RGFFRPBT was modified by nano-SiO₂ and nano-mica in 1 wt% content, it could improve the mechanical properties and HDT of RGFFRPBT.

Reference

- [1] N. G. Sahoo, C. K. Das, H. Jeong, C. S. Ha *J Elastomers Pla*, **2004**, 36, 77.
- [2] M. C. Jeng, C. P. Fung, T. C. Li, *Wear*, **2002**, 252, 934.
- [3] K. C. Chiou, F. C. Chang *J Polym Sci B Polym Phys*, **2000**, 38, 43.
- [4] S. Hashemi *Polymer*, **2002**, 43, 4033.
- [5] C. P. Fung *Wear*, **2003**, 254, 298.
- [6] G. Blinne, K. Kunstst *Plast Eur*, **1999**, 89, 33.
- [7] K. Song, J. L. White *Polym Eng Sci.*, **2000**, 40, 902.
- [8] T. Yoshioka, M. Tsuji, Y. Kawahara, S. Kohjiya, N. Manabe, Y. Yokota *Polymer*, **2005**, 46, 4987.

- [9] J. Zhu, P. Start, *Polym Sci A Polym Chem.*, **2001**, *40*, 1498.
- [10] S. P. Gubin *Colloids Surf A Physicochem Eng Asp*, **2002**, *202*, 155.
- [11] K. E. Gonsalves, X. Chen, M. I. Baraton *Nanostruct Mater*, **1997**, *9*,181.
- [12] X. Li, T. Kang, W. J. Cho, J. K. Lee, C. S. Ha *Macromol Rapid Commun*, **2001**, *22*, 1306.
- [13] J. H.Chang, R. J. Farris *Polym J*, **1995**, *27*, 780.
- [14] J. H.Chang, B.W. Jo *J Appl Polym Sci.*, **1996**, *60*, 939.
- [15] A. Okada, A. Usuki *Mater Sci Eng.*, **1995**, *C3*, 109.
- [16] J. W. Gilman *Appl Clay Sci.*, **1999**, *15*, 31.
- [17] E. P. Gianneli *Adv Mater*, **1996**, *8*, 29.
- [18] Z. Wang, T. Lan, T. Pinnavaia *J Chem Mater*. **1996**, *8*, 2200.
- [19] K.Yano, A. Usuki, A. Okada *J Polym Sci Part A: Polym Chem.*, **1997**, *35*, 2289.
- [20] J. M. Garcia-Martinez, O. Laguna, S. Areso, E. P. Collar *J Polym Sci Part B: Polym Phys.*, **2000**, *38*, 1564.
- [21] X. C. Li *Polym Eng Sci.*, **2002**, *42(11)*, 2156.
- [22] J. H. Chang, M. K. Mun, J. C. Kim. *J Appl Polym Sci.*, **2007**, *106*, 1248.
- [23] S. D. Zhang, Q. Ban, H. X. Huang, Y. Z. Li *ISFR2009(Accepted)*.
- [24] J. H. Chang, D. K. Park, K. J. Ihn *J Polym Sci Part B: Polym Phys*. **2001**, *39*, 471.
- [25] J. H. Chang, D. K. Park, D. Cho, H. S. Yang, K. J. Ihn *J Polym Eng Sci.*, **2001**, *41*, 1514.
- [26] T. J. Che, B. Luan, X. J. Yang, L. D. Lu, X. Wang *Mater Let.,t* **2005**, *59*, 1603.
- [27] J. H. Chang, B. S. Seo, D. H. Hwang *Polymer*, **2002**, *43*, 2969.
- [28] D.Y Wang, Y. Z. Wang, J. S. Wang, D. Q. Chen, Q. Zhou, B. Yang, W. Y Li, *Polym Degrada Stab*. **2005**, *87*,171.