การเตรียมนาโนคอมพอสิตพอลิพรอพิลีน/ไฮโดรโฟบิกซิลิกา

Preparation of polypropylene/hydrophobic silica nanocomposite

Presented in The 2nd Progress in Advanced Materials: Micro/Nano Meterials and Applications

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บทคัดย่อ

ในงานวิจัยนี้ได้เตรียมมาสเตอร์แบ๊ทช์คอมพอสิตพอลิพรอพิลีนและซิลิกา (ร้อยละ 18) ด้วยวิธีการหลอมเหลวโดยอาศัยเครื่องอัดรีดเกลียวคู่ และศึกษาผลของพอลิพรอพิลีนแว๊กเป็นสารช่วยผสมและช่วยกระจายตัว มาสเตอร์แบ๊ทช์ที่เตรียมได้ ถูกนำไปเตรียมเป็นนาโนคอมพอสิตพอลิพรอพิลีนและซิลิกาในเครื่องอัดรีดเกลียวคู่อีกครั้ง เพื่อให้ได้นาโนคอมพอสิตที่มีองค์ประกอบของซิลิกาที่ ร้อยละ 1, 2.5, 5 และ 7.5 ตามลำดับ หลังจากนั้นนำนาโนคอมพอสิตไปขึ้นรูปเป็นฟิล์มด้วยเครื่องอัดแบบ ฟิล์มนาโนคอมสิตที่ได้ถูกนำไปวิเคราะห์สมบัติทางความร้อนด้วยเครื่องดิฟเฟอเรนเชียลสแกนนิงแคลอริมิเตอร์ (DSC) และ เครื่องเทอร์โมกราวิเมทริกแอนาไลเซอร์ (TGA) วิเคราะห์สัณฐานวิทยาด้วยเครื่องกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด(SEM)และทดสอบสมบัติความแข็งแรงของฟิล์ม

Abstract

In this work, iPP composite masterbatch containing 18 wt% hydrophobic silica was initially prepared by melt mixing in a twin screw co-rotating extruder. The effect of PP wax addition on silica particle's dispersibility was also studied. The masterbatch then compounded with virgin PP again at various ratios to obtain the nanocomposites containing 1, 2.5, 5, and 7.5 wt% silica, respectively. After that, iPP/hydrophobic silica nanocomposite films were produced by compression moulding. The nanocomposites were characterized using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The mechanical properties were observed with tensile test.

คำสำคัญ: นาโนคอมพอสิต,ไฮโดรโฟบิกซิลิกา,พอลิพรอพิลีนแว๊กซ์
Keywords: nanocomposite, hydrophobic silica, PP wax

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1. Introduction

Polypropylene(PP) is a versatile polymer widely used in textiles and packaging. In practice, commercial PP products available in composite forms usually contain micron-sized fillers which function as property enhancer (Garcia M. et al., 2004). Recently, polymer nanocomposites have received great interest due to their superior properties when compared with conventional composite materials. Improvements in mechanical properties, such as stiffness and toughness, dimensional and thermal properties could be achieved with nanofillers. The dispersion degree of the filler greatly influences the enhancement efficiency(Jana S. C. and Jain S, 2001). Therefore, in order to meet those excellent properties, it is very important that the average size of fillers must be present in the nanometer-sized ranges with fine particle distribution in the polymer matrix. Carbon nanotube (CNT) and montmorillonite (MMNT) have taken a lead as the nano-filler for plastics as well as fibers(Bikiar D. N. et al., 2005). Another interesting choice is nano silica which has been explored as the filler for polymeric materials and held a great potential for developing high performance polymer. In this study, hydrophobic silica as nanofiller for PP fibers were studied. PP/ hydrophobic nanocomposite films were prepared. Then, properties of nanocomposite film were evaluated and discussed.

2. Experimenatal

2.1. Materials

-Isotactic polypropylene (iPP) is the isotactic polypropylene homopolymer resins from HMC Polymers Company Limited: Moplen HP 561R (MFI = 25 g/10 min at 190 °C)

-Hydrophobic silica (SiO_2) nanoparticles supplied from Degussa AG (Thailand): AROSIL R 974 (12 nm, surface treated with dimethyl dichlorosilane)

- Metallocene wax(TP Liconcene PP 6102) Polypropylene wax .

2.2. Nanocomposite preparation

5 kg of Masterbatch containing 18 wt% of SiO_2 nanoparticles in PP was initially prepared by melt mixing in twin screw extruder operating at 180-210 °C and 120 rpm in corrotating mode. The masterbatch was then add to PP and PP wax in appropriate amounts the composition of nanocomposites was given in Table 1 and 2 .These were compounded in twin screw extruder connected to the Thermo PRISM TSE-16-TC and operating at 180-210 °C and 120 rpm. Then were immersed immediately in a cold-water bath (18 °C) and palletized with an adjustable rotating knife located after the water bath, then nanocomposite pellet was compressed into film using condition in Table 3. Film with thickness of 0.7-1.2 mm was produced.

Table 1 The composition of nanocomposites

Recipe	1	2	3	4	5	6	7	8
Silica(wt%)	1.0	2.5	5.0	7.5	1.0	2.5	5.0	7.5
PP wax(wt%)	0	0	0	0	1	1	1	1
Recipe	9	10	11	12	13	14	15	16
Silica(wt%)	1.0	2.5	5.0	7.5	1.0	2.5	5.0	7.5
PP wax(wt%)	2.5	2.5	2.5	2.5	5.0	5.0	5.0	5.0

Table 2 Calculated amounts of silica in the final compounds

Recipe	Silica content	Masterbatch (g)		Virgin PP(g)	PP wax(g)
		Silica (g)	PP(g)		
1	1.0	0.2500	24.7500	425.0000	0
2	2.5	1.5625	60.9375	387.5000	0
3	5.0	6.2500	118.7500	325.0000	0
4	7.5	14.0625	173.4375	262.5000	0
5	1.0	0.2500	24.7500	420.5000	4.5000
6	2.5	1.5625	60.9375	383.0000	4.5000
7	5.0	6.2500	118.7500	320.5000	4.5000
8	7.5	14.0625	173.4375	258.0000	4.5000
9	1.0	0.2500	24.7500	413.7500	11.2500
10	2.5	1.5625	60.9375	376.2500	11.2500
11	5.0	6.2500	118.7500	313.7500	11.2500
12	7.5	14.0625	173.4375	251.2500	11.2500
13	1.0	0.2500	24.7500	402.5000	22.5000
14	2.5	1.5625	60.9375	365.0000	22.5000
15	5.0	6.2500	118.7500	302.5000	22.5000
16	7.5	14.0625	173.4375	240.0000	22.5000

Table 3 Processing conditionsfor the nanocomposites preparation.

Temp.(°C)	Cooling time(sec.)	Pressure (bar)	Pressing before Venting time(sec.)	Final pressing time(sec.)	Pre-heating time(sec.)
180	60	80	420	300	180
185	60	80	420	300	180
190	60	80	420	300	180
195	60	80	420	300	180
180	30	80	420	300	180
185	30	80	420	300	180
190	30	80	420	300	180
195	30	80	420	300	180

2.3. Tensile testing

Measurements of the mechanical properties, such as tensile strength and elongation at break were performed on Universal Testing Machine in accordance with ASTM D638 using a crosshead speed of 50 mm/min. Measurement was conducted for each sample, and the raw data was averaged to obtain a mean value.

2.4. Differential scanning calorimetry (DSC)

PerkinElmer Diamond differential scanning calorimetry (DSC), was used for the crystallization study. A sample of 4-7 mg was used in each test. They were sealed in aluminium pans and held at the temperature for 1 min at 50 °C. The sample was heated from 50 °C to 200 °C at a rate of 10 °C/min and held at the temperature of 200 °C for 5 min. Then cooling down from 200 °C to 50 °C was followed at a rate of 10 °C/min .

2.5. Scanning electron microscopy (SEM)

For this purpose fractured surfaces as well as thin films were used. All of the studied surfaces were coated with copper to avoid charging under the electron beam.

2.6. Thermo gravimetric analysis (TGA)

TGA/SDTA851^e Mettler Toledo thermal analyzer was used to study the composition of nanocomposite under nitrogen atmosphere. The range of scanning was 50-600 °C at the heating rate was 20 °C/min.

3. Results and discussion

The dispersion of silica particles in PP matrix was observed by SEM. Figure 1 shows that PP with 2.5 wt% silica loading exhibits uniform particle distribution. An increase in percent silica loading results in agglomeration problem and poorer particle distribution as shown in Figure 2. The addition of PP wax failed to improve the dispersibility of particles. Tensile strength values of composite film increase from 27 Mpa to 32 MPa and 32 Mpa with an increased silica loadings from 1 wt% to 2.5 wt%, respectively. At the silica content of 5 wt%, tensile strength is decreased due to the phase separation problem arising from particles' agglomeration. An effect of the addition of silica particles on composite film's elongation is profound. An increase in silica

content leads to an increase in the percent elongation. This is due to the fact that in the step of compression the filler particles interfered polymer chain orientation. During tensile testing, polymer chain was forced to elongate further. For example, the percent elongation increases from 14.5 % to 15 % when increasing the silica loading from 1 wt% to 2.5 wt%.

4. Conclusion

From SEM, composite films containing hydrophobic silica below 2.5 wt% show invisible silica particle when compared to films with silica contents of higher than 2.5 wt% which is indicative of the agglomeration problem. Good distribution of silica particles in case of low silica content (1wt%) results in improved tensile strength (Figure 3). Focused on elongation value, it is found that in all case, composites exhibit higher elongation when compared with virgin PP due to the interference effect of silica particles on pp polymer chain orientation during compression. Therefore, composite film is relatively more flexible.

Acknowledgement

This work was supported by Department of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand.

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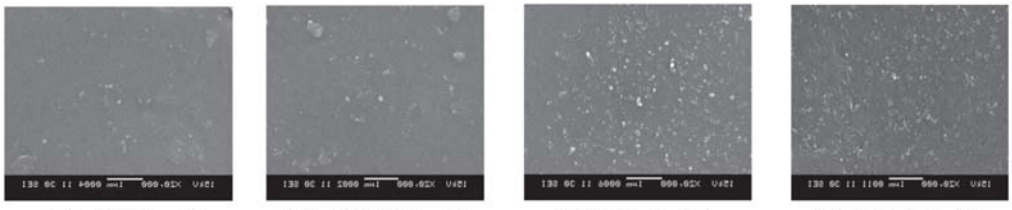


Figure 1. SEM micrographs of PP/SiO_2 nanocomposites.

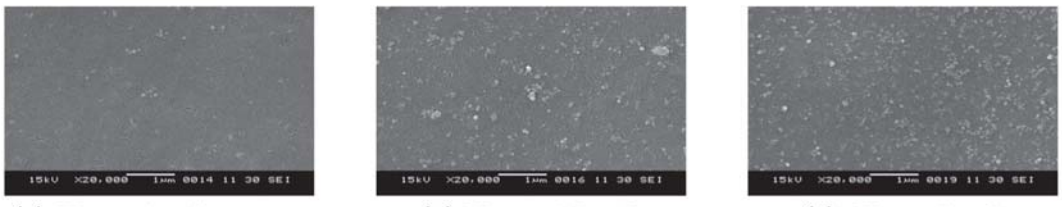


Figure 2. SEM micrographs of PP/SiO_2 nanocomposites 2.5 wt% of SiO_2 and different amounts of PP wax

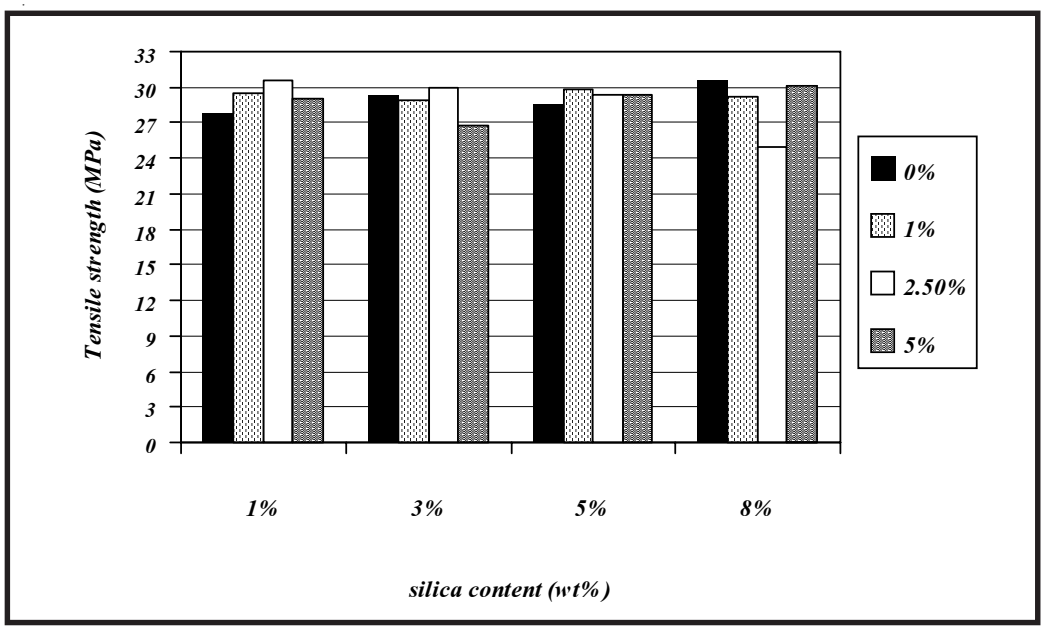


Figure 3. Tensile strength of PP/SiO_2 nanocomposites containing different amounts of PP wax as additive

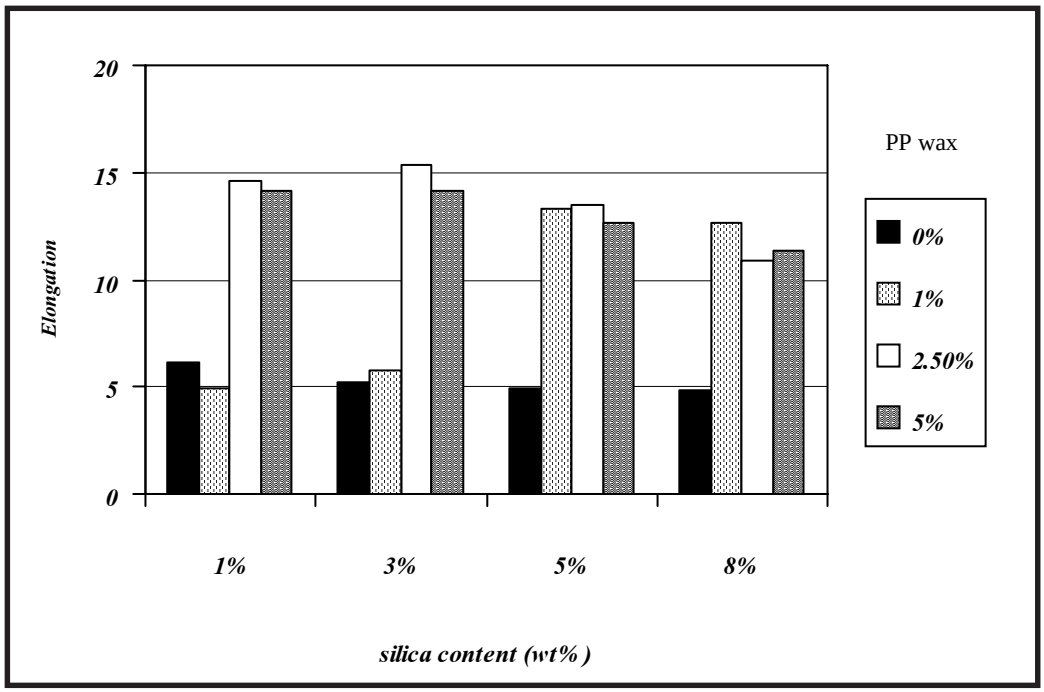


Figure 4. Elongation of PP/SiO_2 nanocomposite films containing different amounts of sio_2