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MECHANICAL PROPERTIES OF STARCH FILLED POLYPROPYLENE UNDER EXPOSURE OF HYGROTHERMAL CONDITIONS

(Sifat-sifat Mekanikal Bagi Komposit Polipropilena Terisi Kanji di Bawah Pendedahan Higroterma)

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Abstract

The hygrothermal properties of starch filled polypropylene (PP) composites with different types of starches; sago, tapioca, and corn content at 20 wt% were studied. The PP composites were compounded using Brabender Plasticoder machine and the composites samples were prepared through by compression molding technique. The hygrothermal absorption test was conducted out to investigate the moisture absorption at different temperatures (i.e. room temperature, 40°C and 70°C). Thus, the flexural test was carried out to study the effect of hygrothermal conditions on mechanical properties and scanning electron microscopy (SEM) used to verify the obtained results through morphological study. The results revealed that the mechanical properties of PP composites deteriorate after a period of immersion time and the hygrothermal aging of composites was accelerated as the temperature increased.

Keywords: polypropylene composites, starch filled polypropylene, hygrothermal absorption, mechanical properties

Abstrak

Sifat-sifat higroterma bagi komposit polipropilena (PP) terisi kanji; sagu, ubi kayu, dan jagung yang terkandung 20% berat telah dikaji. Komposit-komposit PP telah disebatikan menggunakan mesin Brabender Plasticoder dan sampel-sampel komposit disediakan menggunakan teknik pengacuanan mampatan. Ujian penyerapan higroterma telah dijalankan untuk menyiasat kadar serapan lembapan pada beberapa suhu yang berbeza (suhu bilik, 40°C, dan 70°C). Seterusnya, ujian lenturan telah dijalankan untuk menkaji kesan keadaan higroterma ke atas sifat-sifat mekanikal dan mikroskopi pengimbasan electron (SEM) digunakan untuk mengesahkan keputusan yang diperolehi melalui kajian morfologi. Keputusan menunjukkan bahawa sifat-sifat mekanikal bagi komposit-komposit PP merosot selepas direndam untuk suatu tempoh masa dan kadar penuaan higroterma bagi komposit-komposit telah dipercepatkan apabila suhu meningkat.

Kata kunci: komposit polipropilena, polipropilena terisi kanji, serapan higroterma, sifat-sifat mekanikal

Introduction

Polyolefin is not degraded by microorganisms in the environment, which contribute to large volume of plastic waste [1]. For this reason, there is a growing interest in the development of composite materials since the starch is cheap, biodegradable, renewable, and majorly form of stored carbohydrate which can be found in plants such as corn, wheat, rice, sago, tapioca, and potatoes [2]. The compounding of the biodegradable materials, such as starch with inert polymers, such polyethylene (PE), polypropylene (PP), low density poly ethylene (LDPE), have been receives considerable attention among the researcher.

Thus, natural fillers have been receiving considerable attention as substitutes for synthetic fiber reinforcements such as glass in plastics due to their low density, acceptable specific strength, good thermal insulation properties, reduced tool wear, reduced thermal and respiratory irritation as well as renewable resources and the end product would be biodegradable and cheap [3, 4]. Generally, starch is a semicrystalline polymer composed of two polymers with

repeating α-D-glucopyranosyl units. These substances are amylose and amylopectin, a linear and a highly branched polysaccharide, respectively. The repeating units in amylose are linked by α (1–4) linkage. The amylopectin has an α(1–4) linked backbond and about 5% α(1–6) linked branches [5, 6].

In previous research, a lot of studies have been carried out, for examples Liu et al. [7], Zullo and Iannace [8] and Guimarães et al. [9] in optimizing the processing conditions of the starch. Besides that, many have dedicated in modifying or induce cross-linking of the starch. Garg and Jana [10], Kim and Lee [11], Kuniak and Marchessault [12], and Delval et al. [13] were among those who had studied the interfacial properties using the cross-linked or modified starch. In engineering practice, moisture absorption test was done for quality control purposes and to measure the degradation of the quality for the composite materials [14]. The study on the moisture absorption and hygrothermal aging properties also has captured an interest of a scientist in the polymer field [15-19].

The chemical and physical changes can be determined through the aging process. Natural aging tests are very representative to reproduce identical conditions of exposure that is biodegradation, but they require longer time which will take several years [20]. To accelerate the aging process, the hygrothermal testing condition is applied. However, study on the aging behaviors of the starch filled polypropylene exposed in hygrothermal environment is rarely reported. In this paper, we focuses on study of hygrothermal effect on the mechanical properties of starch filled polypropylene composites that exposed under hygrothermal conditions at different temperatures.

Materials and Methods

Materials

The grade of PP used is Titanpro SM340, produced by Titan Petchem (M) Sdn. Bhd. This type PP resin provided their density at 0.9 g/cm^3 and a melt flow index value (MFI) at 4.0 g/10 min (2.16 kg at 230 °C). The starch (i.e. corn (C), sago (S), and tapioca (T) starch) was supplied by Zarm Scientific Sdn. Bhd., Malaysia.

Preparation of samples

Compounding process of PP composites was carried out using the Brabender Plasticoder machine at the temperature of 170 °C and a rotary speed of 50 rpm. The PP/starch composites were compounded according to Table 1. First, PP was added in the mixing chamber for 4 minutes until completely melted. Then, starch was added and mixing was continued for another 4 minutes. Compounded samples were prepared by using compression molding machine (GoTech GT7014-A30C, Taiwan). Samples were pressed into flexural shaped mould at 180 °C using pressure of 15 MPa for 6 minutes and cooled under pressure for 2 minutes.

Table 1. Formulation of PP/starch composite

Designation	Part (wt%)
PP	100
PP/20C	80/20
PP/20S	80/20
PP/20T	80/20

Melt flow index (MFI)

MFI measurements of PP/starch composites were conducted by using Melt Flow Indexer at temperature of 180 °C and load 2.16 kg. Extruded samples were cut every one minute and five samples of each composition were taken to be analyzed.

Mechanical properties

The flexural tests were conducted using Instron 5569 universal testing machine according ASTM D790. The crosshead speed 5 mm min^{-1} was used with a support span of 50 mm. Five samples of each composition were selected for this testing method and the mechanical test was carried out under ambient temperature.

Moisture absorption

The composite samples were dried inside the oven at 70 °C for 24 h and then, the moisture absorption test was carried out by the immersion of the samples in distilled water that was placed in the water bath (Memmert, Germany) at room temperature (RT), 40 °C, and 70 °C. The moisture uptake was determined through periodically recorded the composite sample weight using Sartorius M-pact Analytical Balance AX224. The percentage of moisture absorbed, M_t, at any time t was calculated using equation (1):

$$M_t\ (\%) = (W_w - W_d) / W_d \times 100 \quad (1)$$

where W_d denote, weight of the initial specimens and W_w is the weight of the specimens after exposure to the moisture respectively.

In the previous report, several models had been introduced to analyze the diffusion molecules in the polymeric materials [18, 19, 21, 22]. Fick's law is the popular method that usually used to describe one dimensional moisture absorption process with dependence of time [23]. The weight gained from the moisture absorption can be measured through equation (2):

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\, exp\left[-\left(\frac{Dt}{h^2}\right)\pi^2\right] \quad (2)$$

where M_∞ representing the percentage of equilibrium content of sample, h is the thickness of the test sample, while D is diffusion coefficient or diffusivity which is related to rate of diffusion into the sample and it can be calculated from the slope of the absorption curve.

Results and Discussion

Melt flow index (MFI)

Table 2 shows the MFI value of PP and PP/starch composites. The results reveal that the MFI values of PP/starch composites were decreased with the presence of 20 wt% of starch content (i.e. corn, sago, and tapioca starch) compared to neat PP. Since the MFI could be indirectly method to measure the viscosity, the starch must act as rigid filler since the main effect of rigid fillers is to increase the elastic modulus of a composite or the viscosity of a fluid suspension [24].

Table 2. MFI values of neat PP and PP/starch composites

Designation	MFI value (g/10 min)
PP	1.3952
PP/20C	1.3302
PP/20S	1.3596
PP/20T	1.1656

Moisture absorption

The relations of percentages of moisture uptake, M_t under exposure of different hygrothermal conditions with respect to exposure square root of time, $t^{½}$ are shown in Fig. 1, 2, 3 and 4. It can be seen that the moisture absorption

rate for all samples were significantly change after being exposed to hygrothermal conditions at RT, 40 °C, and 70 °C for several days. In all exposure conditions, the M_t values increase linearly with $t^{½}$ until it reached its equilibrium state.

Refer to the absorption curves of PP and PP/starch composites in figures below, it can be seen that the rate of M_t has a small effect on tested samples after exposed at RT and 40 °C. However, at higher temperature of 70 °C, the rate of M_t rapidly increased in PP/starch composites with respect to neat PP. These proved that the degradability of the PP/starch composites were accelerated at high temperature of 70 °C compared to RT and 40 °C. Besides that, the M_t values in the composites can attributed to the hydrophilic nature of the starch (corn, sago, and tapioca) by presence of a hydroxyl groups which are available for interaction with of water molecules. Preechawong et al. [25] stated that starch was absorbed the water due to its hygroscopic nature. It was acted as a natural plasticizer in starch which provided the flexibility in starch as compared to hard and rigid filler in it while in dry state.

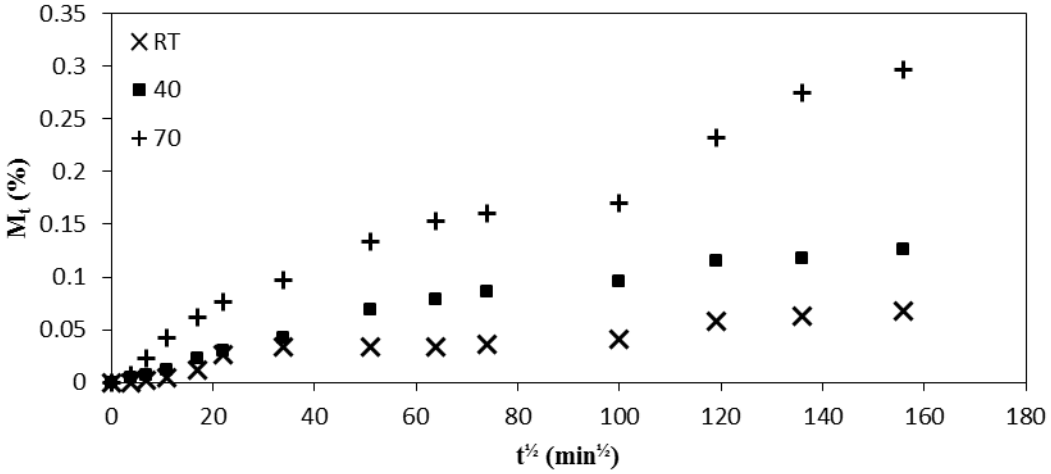

Figure 1. The effect of hygrothermal condition on PP sample at different temperatures

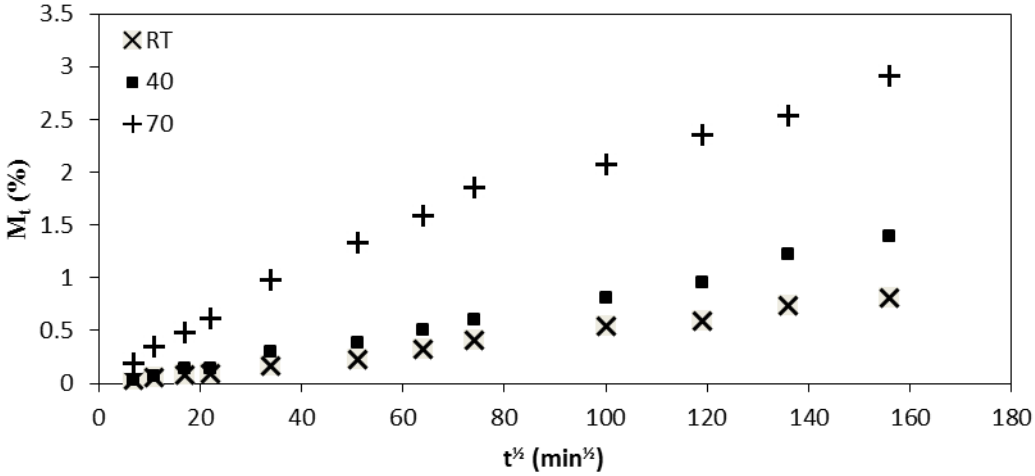

Figure 2. The effect of hygrothermal condition on PP/20C composite at different temperatures

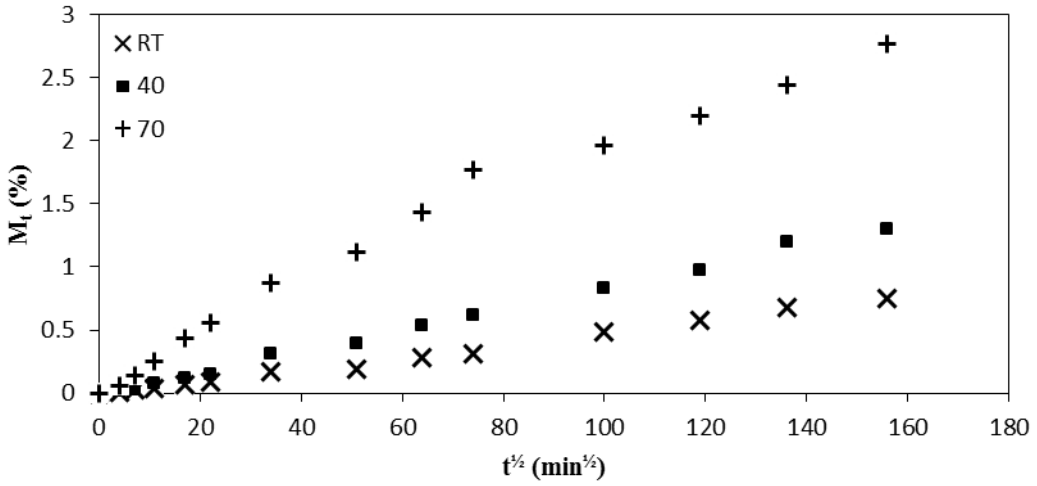

Figure 3. The effect of hygrothermal condition on PP/20S composite at different temperatures

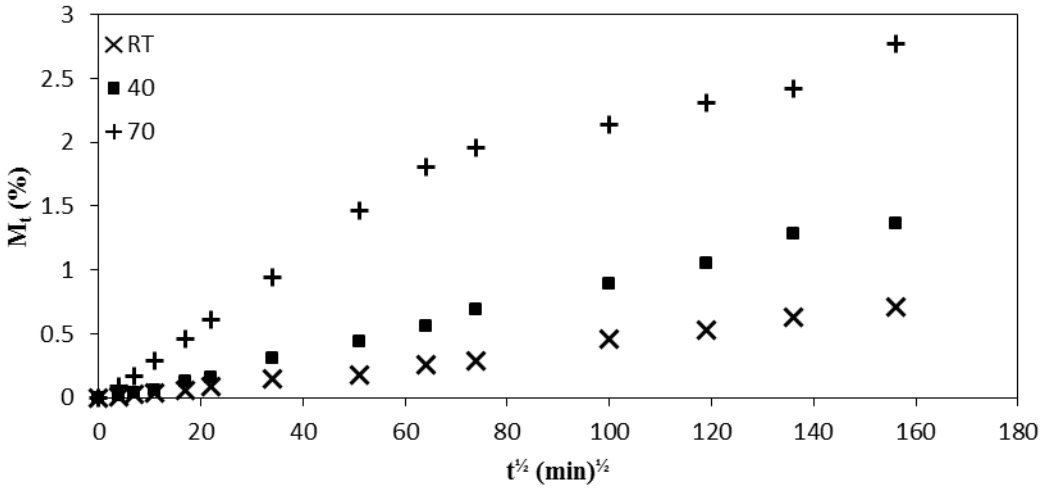

Figure 4. The effect of hygrothermal condition on PP/20T composite at different temperatures

Mechanical properties

Table 3 shows the mechanical properties of the PP/starch composites. The mechanical properties decreased slowly when water aging approach with time and temperatures. Before being exposed in a hygrothermal conditions, most of the samples have lower flexural strength compared to the neat PP. As expected the flexural strength of the composites were reduced after exposed at difference hygrothermal conditions for two weeks. In this particular test, at higher testing temperature (i.e. 70 °C) the samples tend to deteriorate which significantly reduce their mechanical properties. Meanwhile, the flexural strength of the neat PP showed a slower reduction rate even at temperature of 40 °C or 70 °C.

Table 3. The flexural properties of neat PP and PP/starch composites before and after exposed under hygrothermal conditions.

Compound	Mechanical Properties	Controlled	Test Temperature (°C)		
			RT	40	70
PP	FS (MPa)	31.25	31.02	30.9	30.65
	FM (MPa)	691.55	690.66	687.61	665.15
PP/20C	FS (MPa)	26.81	24.55	24.36	23.41
	FM (MPa)	825.28	798.61	774.34	683.92
PP/20S	FS (MPa)	26.30	26.02	24.96	23.20
	FM (MPa)	817.56	811.50	746.27	649.82
PP/20T	FS (MPa)	27.19	26.89	26.48	26.25
	FM (MPa)	830.24	798.61	781.35	727.98

Note: FS = Flexural Strength, FM = Flexural Modulus

Thakore et al. [26] have demonstrated that the mechanical properties of composites reduced as increasing of the biodegradable component or starch were incorporated. Whereas, Wang et al. [27] founded, the moisture content has absolute effect on the interfacial bonding between starch and plastic. The starch granules that embedded in the plastic were observed to be swollen, thus resulting poor mechanical strength. They had also reported that the mechanical properties will drop as the moisture content increased. It is attributed to the hydrophilic characteristic of the components. Since this composite involved starch which is hydrophilic in nature hence, the homogeneity and adhesion between starch (C, S, and T) and the hydrophobic PP has substantially reduce.

As can be seen in Table 3, the modulus of all the PP/starch composites were slightly higher than neat PP. 690.66 MPa of flexural modulus value was recorded for controlled or unexposed sample of PP, while there are no significant changes of PP samples although they were exposed in hygrothermal condition at RT and 40 °C. In comparison with controlled PP, a different result was recorded for PP sample which was exposed at 70 °C. The decrement of modulus property almost dropped until 3.8 %. It may be due to the moisture content inside the composites is not in an equilibrium state within the test time. Although, the modulus between those three types of the starch used has not significantly affected but there is an obvious reduction after the immersion at 70 °C compared to the controlled samples. Ke et al. [28] suggested that the increasing modulus in the starch blends can be explained by the crystallinity, hydrogen bonding and stiffening effect of the starch granules.

However, the reduction of the mechanical properties also indicates the presence of a weak adhesion between the starch and matrix. Some of the researchers have discussed about the microcavities phenomena inside the composites which effected by the moisture inside the material and cause the disruption of the filler-matrix bonds. Athijayamani et al. [29], Mohd Ishak et al. [30], & Vlasveld et al. [31] conclude, these microcavities will act as crack concentrators which initiate the internal cracking and subsequently reduce the stiffness and strength of the composites. Duanmu et al. [22] studied the hygro-mechanical properties of the thermoplastic starch reported that the moisture uptake significantly reduces the strength and stiffness of the samples. The presences of moisture also cause the plasticization effect on the composites. The water that filled inside the microcavities will act as a plasticizer and to reduce the stiffness [32].

Morphological studies

SEM micrographs taken from the fractured surface of controlled PP highlight the hygrothermal effects on the morphology of the sample at 70 °C states are shown in Figs. 5(a) and (b). There are some evidences of plastic deformation in the form of matrix drawing or yielding. A contrasting view is observed for neat PP after it was exposed to hygrothermal condition of 70 °C, where the fracture surfaces of exposed sample are flatter and less yielding compare to controlled sample.

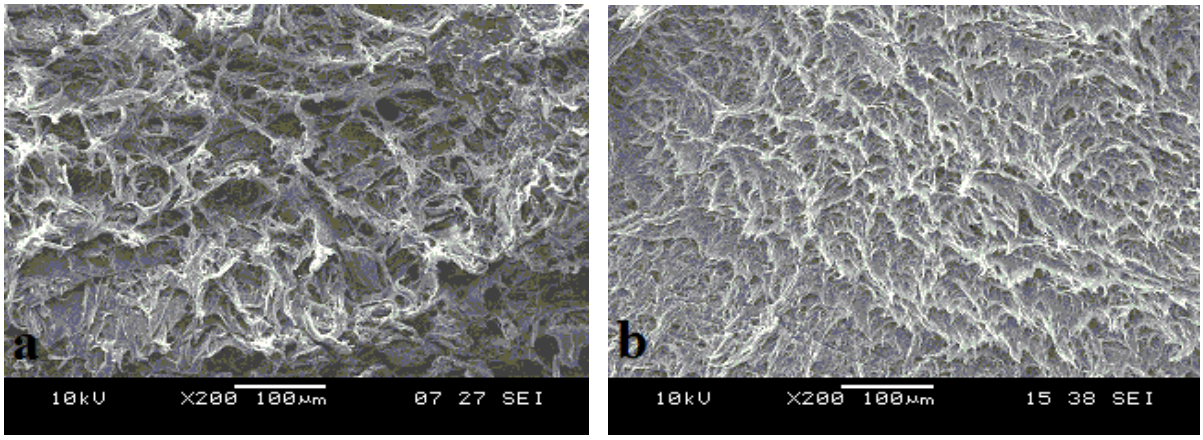

Figure 5. SEM micrographs taken from the fracture surface of (a) controlled PP and (b) neat PP after exposed in hygrothermal condition of 70 °C.

The surface appearence of starch filled PP composites shown by the SEM micrographs in Fig. 6(a-b) and 7(a-b) clearly provide good evidences to prove the effect of the hygrothermal environment on the composites properties. As it can be seen from the figure, the fracture surfaces of the hygrothermally exposed PP/20S and PP/20T shows flatter than unexposed samples. Normally, the fracture surfaces are flat with no evidence of plastic deformation. This explains the hygrothermal conditions are totally effect which cause the brittle behavior of composite samples during the flexural test.

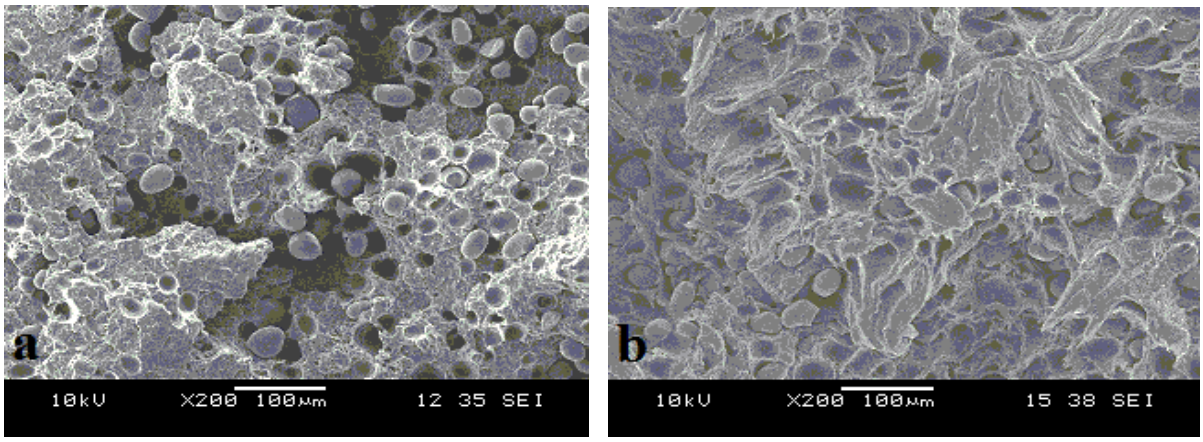

Figure 6. SEM micrographs taken from the fracture surface of (a) PP/20S and (b) PP/20S after exposed in hygrothermal condition of 70 °C.

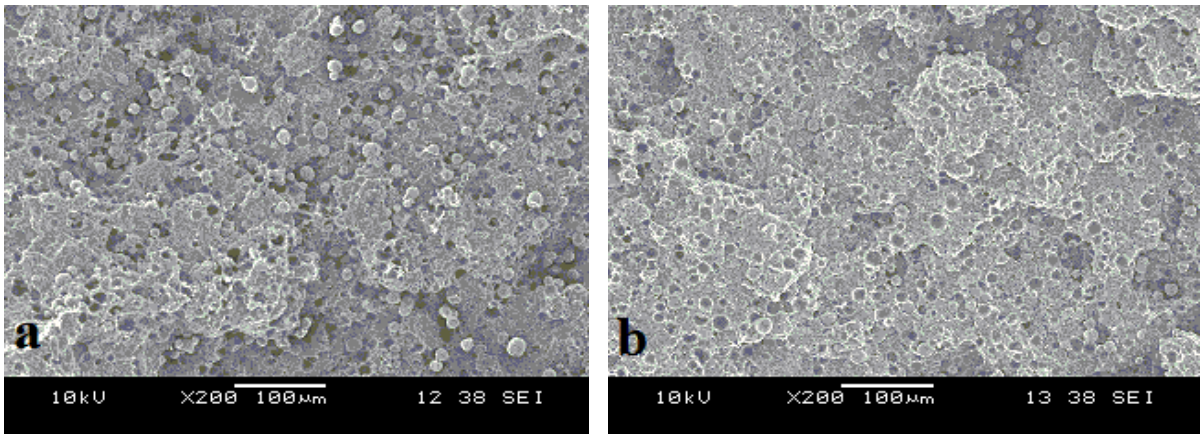

Figure 7 . SEM micrographs taken from the fracture surface of (a) PP/20T and (b) PP/20T after exposed in hygrothermal condition of 70 °C.

In addition, these micrographs strongly evidence to relate the dropped of mechanical properties of PP/20S than PP/20T samples. The bigger size of granule can cause the voids or cavities formation after it was exposed to hygrothermal environments. These formations will act as stress concentration point and further decrease the mechanical properties of the PP/starch composites. The fine particle size of T granule causing the filler well dispersed throughout the composites and well coated by PP matrix thus, reducing the voids and cavities formation. This is agreed with the observed embritllement of the composites and explains the dramatic drop of mechanical properties of the composites after they were exposed in hygrothermal environments.

Conclusion

In the present study, the mechanical properties of the PP/starch blends were reduced after being exposed under hygrothermal conditions. The mechanical properties of PP/starch composites decreased drastically upon exposure at 70 °C of hygrothermal condition. The results also show that PP/20T composite was found to be more stable in hygrothermal conditions due to better flexural properties compared to PP/20C and PP/20S composites that proven by morphology analysis.

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