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고상 압출된 폴리프로필렌/탈크 복합재료의 기계적 물성

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Mechanical Properties of Polypropylene/ Talc Composites Prepared via Solid-State Extrusion

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요 약: 본 연구에서는 고상압출을 통하여 제조된 폴리프로필렌/탈크 복합재료의 배향 전후의 비중과 기계적 물성을 조사하였다. 탈크 충진제의 함량이 증가할수록 복합재료의 비중이 증가하였는데, 배향에 따라 발생된 미세공극으로 인해 배향된 복합재료의 비중은 배향되지 않은 복합 재료에 비해 작은 것으로 나타났다. 미배향 시료일 경우 탈크의 함량이 10중량%일 때 인장물성이 증가하였으나 탈크의 함량이 더 증가하면 인장물성은 감소하였다. 배향 시료 경우, 중량% 증가에 따라 인장 물성은 단조 감소를 보였다. Halpin-Tsai 식에 의해 이론적으로 분석한 결과 10중량% 첨가 때는 이론식에 잘 맞았으나 20중량% 이상일 때는 탈크 함량의 증가에 따라 이론식에서 벗어나는 정도가 더 커졌다. 굴곡강도 경우, 미배향 시료 와 배향 시료 모두 탈크의 함량이 10중량%일 때 최대 굴곡 강도 및 굴곡 탄성률을 보였다.

Abstract: We investigated the specific gravity and mechanical property changes of solid-state extruded polypropylene (PP)/talc composites before and after orientation. The specific gravity of the composites increases with increasing the filler contents. The specific gravity of the oriented specimen containing filler in PP matrix is found to be much smaller than that of pre-specimen due to the formation of more micro-voids. It was found that the tensile properties of the composites are increased up to the talc content of 10 wt%, but after the contents exceeding 10 wt%, the tensile properties are decreased. For oriented specimens, the tensile strength of the composites showed monotonously decrease with increasing talc contents. When the contents of talc is 10 wt%, the theoretical values according to Halpin-Tsai equation are close to the experimental values but over 20 wt% of talc contents, the deviation of the experimental values from the theoretical prediction becomes higher. The maximum flexural strength and modulus were observed for PP/talc composites when the talc contents was 10 wt% for both pre-specimen and oriented specimen.

Keywords: *polypropylene, talc, composite, orientation, solid-state extrusion*

1. Introduction

General purpose polymers such as polypropylene (PP) and polyethylene have been used in many applications due to their good processibility and light weight. However, their poor mechanical properties sometimes limit their applications. There may be a few ways to improve the mechanical properties of polymers. One of the most widely used ways for that purpose is by adding inorganic fillers such as calcium carbonate, talc, mica, wollastonite, carbon fiber, glass fiber, nanoclay, etc. as well as blending a kind of engineering plastics that have better mechanical properties than the general purpose polymers. Sometimes, the mechanical properties of polymers can be enhanced by applying a particular processing technique including drawing or stretching for orientating the polymers.

Although the addition of inorganic fillers in the polymer matrix is one of the easiest ways to improve the mechanical properties, the specific gravity of inorganic fillers is usually two or three times higher than that of

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the matrix polymer. This increasing specific gravity of composites thus prepared frequently results in the decrease of other properties such as impact strength because the fillers act mainly as impurity[1-3].

On the other hand, it has been well known that highly ordered linear polymer materials by orientation provide enhanced mechanical properties mainly due to the strain-induced crystallization. In this way, solid state extrusion (SSE) has been known as a method to produce a highly oriented state of polymers, resulting in polymer deformation at temperatures just below the polymer melting points, or slightly above the glass transition temperature, for amorphous polymers[4,5].

In our previous works, therefore, we investigated the specific gravity, thermal, and mechanical properties of PP/calcium carbonate[6] and PP/mica composites[7] before and after solid-state extrusion. We found that on increasing the filler content, the specific gravity of the composites increased for both PP/mica and PP/calcium carbonate composites regardless of the orientation, though the specific gravity of the oriented specimen containing such fillers in PP matrix was found to be noticeably smaller than that of pre-specimen due to the formation of more microvoids. For oriented specimens, on increasing the filler contents, the specific gravity of PP/mica composites was decreased but that of PP/calcium carbonate composites was increased. For both composites, however, the presence of microvoids in the case of oriented composite specimen significantly affected the tensile and flexural properties of the composites.

As the third of a series of this work, we prepared the PP/talc composites prepared through SSE and investigated the effects of talc on their specific gravity and mechanical properties such as tensile and flexural properties.

Talc is a mineral composed of hydrated magnesium silicate with the chemical formula $H_2Mg_3(SiO_3)_4$ or $Mg_3Si_4O_{10}(OH)_2$[8]. In loose form, it is the widely used substance known as talcum powder. Talc is used in many industries such as paper making, plastic, paint and coatings, rubber, food, electric cable, pharmaceuticals, cosmetics, ceramics, etc.[8,9].

2. Experimental

2.1. Materials

The PP used in this work was TOPILENE J-700 (Hyosung Petroleum Co. Ltd.) with the following basic characteristics; MFI of 11 g/10 min (2.16 kg/190°C), tensile strength (yield) of 370 kg/cm^2, flexural modulus of 17,000 kg/cm^2, IZOD impact strength of 3.5. For talc, KSCA-400, manufactured by Koch, was used. The size of the talc powders was about 10 μm.

2.2. Preparation of PP/talc composites

For compounding process, 500 ml Kneader manufactured by Moriyama was used. The kneading temperature was 180~220°C, the screw speed was 50 rpm, and the kneading time was 5 min. The talc content ranged from 10 wt% to 50 wt%. Details of preparing pre-specimen and final specimen were already described in our previous works[6,7]. For final specimen, the pre-specimen was placed in the thermo-hygrostat with 155°C of temperature and 50% of relative humidity for 1 h. The temperature of 155°C was 10°C below of melting temperature of PP. After the whole pre-specimen went through the mold exit, the cross sectional size of pre-specimen changed from 2 mm × 200 mm to 1 mm × 100 mm and the length became 8 times longer than before. For measuring the properties, this final specimen was cut as proper size for each sample. Throughout the text, oriented PP based composites was noted as O-PP.

2.3. Measurements

The specific gravity was measured with an electronic densimeter (MD-300) according to the ASTM D 792 method. Three measurements were averaged. The tensile strength and modulus were measured with a universal testing machine (UTM, Instron 4465) by the ASTM D 638 method under the crosshead speed of 20 mm/min at room temperature. Three measurements were averaged. To measure flexural strength and modulus, the sample dimension was 10 mm × 127 mm rectangular type. Flexural strength and modulus was tested with UTM by the ASTM D 790 method at room temperature with the crosshead speed of 20 mm/min. Three measurements were averaged.

3. Results and Discussion

The specific gravity is one of the most important properties in practical applications, since it affects on the cost, easy handling, and properties of final products.

Figure 1 shows the specific gravity of the PP/talc composites according to different contents of KSCA-400

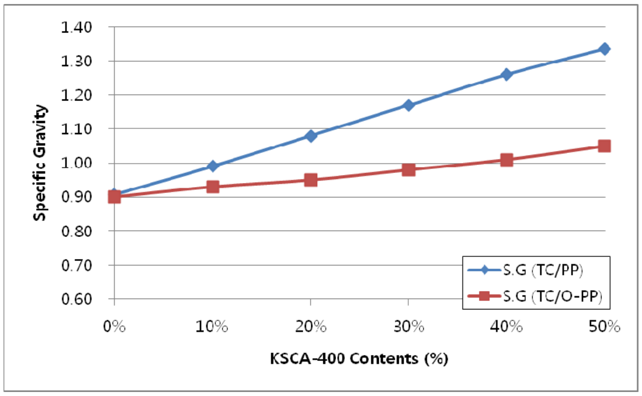

Figure 1. Specific gravity according to KSCA-400 (Talc) contents, where S.G. TC and O-PP stand for specific gravity, talc, and oriented PP, respectively.

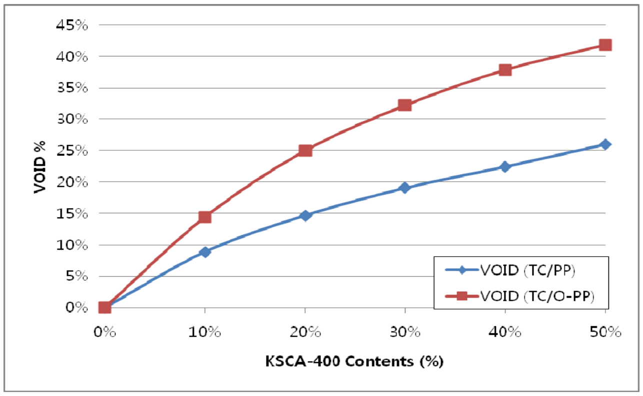

Figure 2. The void content according to KSCA-400 (talc) contents, where TC and O-PP stand for talc and oriented PP, respectively.

(talc). When loading from 30 wt% to 50 wt% of KSCA-400, the specific gravity of normal pre-specimens ranged from 1.17 to 1.34, while the specific gravity of oriented final specimen was from 0.98 to 1.05.

It was already shown in our previous works, re-arrangement of micro structure of the polymer matrix occurs during SSE and poor interface interactions between polymers and fillers make fine micro-voids and the micro-voids decrease specific gravity. This specific gravity reduction can lead to the cost savings of materials. The void contents after orientation is estimated from the equation 1[6,10].

$$(\text{SG of PP} \times \text{\% of PP}) + (\text{SG of filler} \times \text{\% of filler}) = \text{Theoretical SG} \qquad (1)$$

where SG is specific gravity and % is weight content.

Then

$$\text{Void content (\%)} = \text{Measured SG} \,/\, \text{Theoretical SG} \qquad (2)$$

As shown in Figure 2, the void content also increases for both pre-specimen and oriented specimen, but more voids are formed for oriented specimen than for pre-specimen. For instance, the calculated void content for the composites of 30~50 wt% of talc loading was 19% to 26% for normal pre-specimen and 32% to 42% for oriented final specimen, respectively. This data shows that the microvoids are increased with orientation, as expected[6,7].

Figure 3 illustrates the effects of talc contents on the tensile strength of the PP/talc composites. The tensile strength of the composites was increased up to the content of the filler of 10 wt%, but after the contents exceeding 10 wt%, the tensile strength was decreased. When filler is added to a polymer matrix, the mechanical properties are usually a little bit increased up to a certain contents, but too much amounts of filler decrease the mechanical properties rapidly[11-13].

For oriented specimens, however, the tensile strength of the composites showed monotonously decreases with increasing talc contents. Such decreases in the tensile strength for oriented specimen are due to the increasing microvoids[6,7]. When comparing the oriented final specimen to the normal pre-specimen with the same talc contents of 10 wt%, the tensile strength of the oriented one is three times higher than that of normal pre-specimen. The result is surely due to the effects of orientation. It should be noted that even though the composites of loading 50 wt% of talc, the tensile strength of the composites is still higher than that of the normal pre-specimen. When the pre-specimen is stretched in machinery direction, the polymer chain is also orientated in the same direction, leading to the increasing tensile strength through machinery direction[14].

The theoretical predictions for the modulus were determined using the Halpin-Tsai theory, a widely used model for prediction the modulus of undirectionally or randomly distributed filler-reinforced composite[15]. The composite moduli for the oriented composite are given by the following equations:

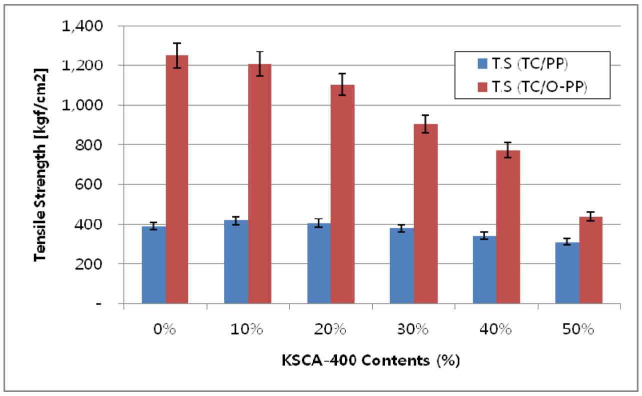

Figure 3. The tensile strength according to KSCA-400 (talc) contents, where TC and O-PP stand for talc and oriented PP, respectively.

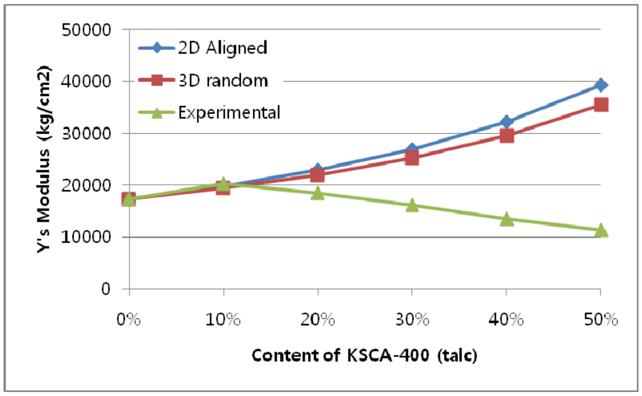

Figure 4. Young's modulus of normal pre-specimen according to talc contents.

$$E_c = E_m \times \left[\frac{3}{8} \times \frac{1 + \frac{(E_g/E_m) - 1}{(E_g/E_m) + (2l_g/3t_g)} \times \frac{2l_g}{3t_g} \times V_c}{1 - \frac{(E_g/E_m) - 1}{(E_g/E_m) + (2l_g/3t_g)} \times V_c} + \frac{5}{8} \times \frac{1 + 2 \times \frac{(E_g/E_m) - 1}{(E_g/E_m) + 2} \times V_c}{1 - \frac{(E_g/E_m) - 1}{(E_g/E_m) + 2} \times V_c} \right] \tag{3}$$

$$E_n = E_m \times \left[\frac{1 + \frac{(E_g/E_m) - 1}{(E_g/E_m) + (2l_g/3t_g)} \times \frac{2l_g}{3t_g} \times V_c}{1 - \frac{(E_g/E_m) - 1}{(E_g/E_m) + (2l_g/3t_g)} \times V_c} \right] \tag{4}$$

In these equations, E_c and E_{ll} represent the Young's modulus of the randomly distributed filler and the aligned filler parallel to the surface of the composite films, respectively, E_g and E_m are the Young's modulus of the filler and the polymer, respectively. The symbols l_g and t_g refer to the length and thickness of the filler respectively, whereas V_c refers to the volume fraction of the filler. We put proper values in the equations (3) and (4) that were taken from experimental values and plotted in the Figure 4 with comparing the experimental values.

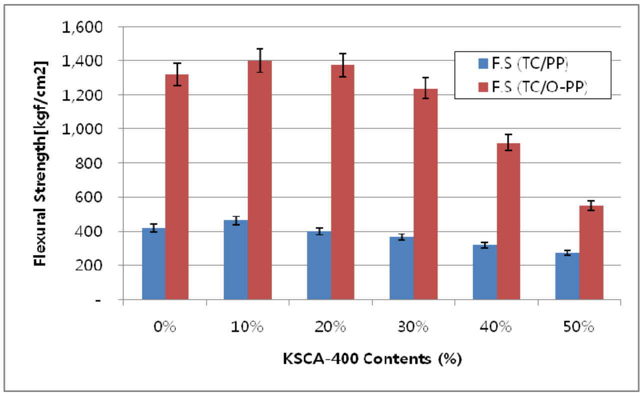

Figure 5. The flexural strength according to KSCA-400 (talc) contents, where F. S., TC, and O-PP stand for flexural strength, talc, and oriented PP, respectively.

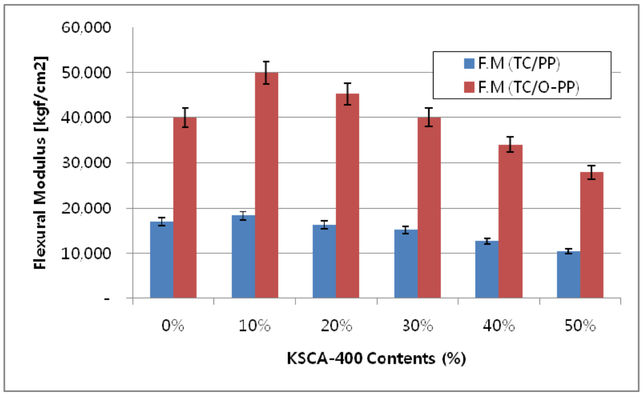

Figure 6. The flexural modulus according to KSCA-400 (talc) contents, where F. M., TC, and O-PP stand for flexural modulus, talc, and oriented PP, respectively.

Figure 4 shows the comparison of experimentally measured Young's moduli of the normal PP/talc pre-specimen composites and the theoretical prediction according to the Halpin-Tsai equations. When the contents of talc is lower than 10 wt%, the theoretical values are close to the experimental values but over 20 wt% of talc contents, the deviation of the experimental values from the theoretical prediction becomes higher. On increasing the talc contents, the theoretical prediction shows higher Young modulus than the experimental values regardless of the 2-dimensional (2-D) alignment model or 3-D random distribution model. This result may be due to the presence of microvoids, which plays as a defect in the composites[9].

Figures 5 and 6 show respectively the flexural strength and the flexural modulus of the KSCA-400 (talc) containing different contents of talc. Similar trend was observed in comparison to those of tensile properties. However, the maximum flexural strength and modulus were observed for PP/talc composites when the talc contents was 10 wt% for both pre-specimen and oriented specimen. The flexural strength was maximized as 463 kg/cm^2 when the talc loading was 10 wt%, and was 367 kg/cm^2 at 30% of loading, while the flexural modulus was 18,300 kg/cm^2 at 10 wt% of loading , and 15,200 kg/cm^2 at 30 wt% of loading. In case of oriented final specimen, there was no increasing effect on the increase of KSCA-400 content for the tensile strength. However, it should be noted that in case of flexural properties, there was improvement when loading KSCA-400 less than 30 wt%. Maximum flexural strength was 1,400 kg/cm^2 and flexural modulus was 49,900 kg/cm^2 when the loading level was 10 wt%, while the talc content becomes 30 wt%, the strength was 1,200 kg/cm^2 and modulus was 40,000 kg/cm^2.

4. Conclusions

We have demonstrated that the specific gravity of the oriented final specimen containing talc in PP matrix is much smaller than normal pre-specimen. We found the more the talc contents is, the bigger the differences is at the oriented one compared to normal one. We also have demonstrated the mechanical properties of oriented final specimen is much more improved than normal one. But normally the more the filler content is, the less the amount of improvement is.

It was found that the mechanical properties of the composites are increased up to the content of the filler of 10 wt%, but after the contents exceeding 10 wt%, the mechanical properties are decreased. For oriented specimens, the tensile strength of the composites show monotonously decreases with increasing talc contents. It should be noted that even though the composites of loading 50 wt% of talc, the tensile strength of the composites is still higher than that of the normal pre-specimen. When the contents of talc is 10 wt%, the theoretical values are close to the experimental values but over 20 wt% of talc contents, the deviation of the experimental values from the theoretical prediction becomes higher. It was also found that the experimental values was slightly closer to the 3-D prediction values than the 2-D prediction values. The maximum flexural strength and modulus were observed for PP/talc composites when the talc contents was 10 wt% for both pre-specimen and oriented specimen.

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