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Influence of Nut Shell Powder Content on the Tribological Properties of Recycled Polyolefin Composites

Kazuma Mikawa[1], Akinori Hoshikawa[2], Yosuke Nishitani[2, a)], Tsubasa Shimizu[3], Eiichi Takahashi[3] and Takeshi Kitano[4]

[1]Department of Mechanical Engineering, Graduate School of Engineering, Kogakuin University, 2665-1 Nakano, Hachioji, Tokyo 192-0015, Japan
[2]Department of Mechanical Engineering, Faculty of Engineering, Kogakuin University, 2665-1 Nakano, Hachioji, Tokyo 192-0015, Japan
[3]Miraijushi Co., Ltd., 7-6 Nissaihanamizuki, Sakado, Saitama 350-0269, Japan
[4]Polymer Centre, Faculty of Technology, Tomas Bata University in Zlin, T.G.M. 275, Zlin 767 72, Czech Republic

[a)] Corresponding author: at13152@ns.kogakuin.ac.jp

Abstract. The purpose of this study is to investigate the influence of nut shell powder (NSP) content on the tribological properties of recycled polyolefin (R-PO) composites. NSP was previously grinded the dried nut shell by crusher machine cryogenically in liquid nitrogen. NSP/R-PO composites with NSP content of 5, 10 and 20 vol.% were prepared in this study. These composites were extruded by a twin screw extruder and injection-molded. Their tribological properties were measured by a reciprocating type sliding wear tester at constant normal load and sliding speed under dry condition. It was found that NSP is effective for reducing the wear resistance of R-PO, and the influence of NSP content on the tribological properties of NSP/R-PO composites does not remarkably appear, but they are improved with the addition of low content such as 5 vol.%. This may be attributed to the change of wear mechanism according to the filling of NSP.

INTRODUCTION

Recycling of plastics has come to be a necessary part of the development of sustainable society in recent years. The disposal of waste plastic is a serious environmental problem in recent years. This problem has become an important issue for economic and environmental reasons[1), 2)]. The Containers and Packaging Recycling Law was established in Japan in 1995 to reduce the volume of solid waste and to make full use of recyclable resources [3)]. In particular, the reuse of recycled polyolefin (R-PO) which is collected and sorted by this law is a strong demand, because polyolefin such as polyethylene (PE) and polypropylene (PP) accounts of almost half of the annual production of thermoplastics[4)]. In our previous studies, we investigated the effect of addition of fillers on the tribological properties of recycled polyolefin (R-PO) and the polymer blends of virgin PE and PP (virgin PE/PP blends) as a model of R-PO. It was found that the tribological properties of R-PO and virgin PE/PP blend are improved with the filling of PTFE powder and the organic fillers such as nut shell powder (NSP) [5)-8)]. Especially, NSP as a reinforcing filler has significant competitive advantages for thermoplastic composites because of low cost, low density and environmental resistant performance. However, in our knowledge, there are no experimental data on the influence of NSP content on the tribological properties of these R-PO composites. The purpose of this study is to investigate the influence of NSP content on the tribological properties of recycled polyolefin (R-PO) composites experimentally.

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EXPERIMENTAL

The materials used in this study were nut shell powder (NSP) filled recycled polyolefin (R-PO) composites. Recycled polyolefin (R-PO), which is collected and sorted by the Containers and Packaging Law in Japan was used as a matrix polymer. Polyolefin rate in R-PO was about 95% and the ratio of polyethylene (PE) to polypropylene (PP) in R-PO was almost 50/50 by wt.%. The remaining parts of 5% are the impurities such as polystyrene and the other polymers. Nut shell powder (NSP) was previously grinded the dried nut shell (Rustic Co.) by crusher machine (Wonder blender, Osaka chemical Co. Ltd., Japan) cryogenically in liquid nitrogen. Successively, NSP was classified into the over-size NSPs and the undersize ones with #200 screen (300μm mesh) (see Fig.1). In this study, these undersize ones was used as a filler for composites. The volume fraction of NSP in the NSP/R-PO composites was varied from 5, 10 and 20 vol.%, and the codes of these composites are NSP5, NSP10 and NSP20 in order from front. R-PO and NSP were dried in an oven at 80^{o}C for 3h. All the components were dry blended in the small bottle, subsequently melt mixed at 85rpm and 200^{o}C on a twin screw extruder (TEX-30, Japan Steel Works, Ltd., Japan). After mixing, extruded strands of NSP/R-PO composites were cut in about 5mm by a pelletizer, and were dried again at 80^{o}C for 3h in an oven. Various shaped samples for mechanical and tribological properties testing were injection molded (NS20-A, Nissei Plastic Industrial, Japan). The molding conditions were as follows: cylinder temperatures of 200^{o}C, mold (cavity) temperature of 30^{o}C and injection rate of 6cm^3/s. To keep the drying condition of specimens for all measurements, they were kept in accordance with JIS K 6922-2 for at least 24h at 23^{o}C in desiccators after injection molding. Mechanical (tensile, bending, impact and hardness) and tribological properties were evaluated. Tensile testing (Number of sample n=5) was carried out with dog-bone samples on Toyo Seiki testing machine V-10, in accordance to the JIS K 7161, at the cross-head speed of 10 mm/min. Three point bend testing (Number of sample n=3) was carried out with coupon specimens on the V-10, in accordance to the JIS K 7171, and at the cross-head speed of 2mm/min. Impact characteristics were determined by Izod impact test (Number of sample n=10). Izod impact tests were conducted using coupon specimen with a notch depth of 2.5mm on Toyo Seiki impact machine DG-IB at room temperature, in accordance to JIS K 7110. Hardness characteristics were determined by type D of durometer hardness. Durometer hardness testing (Number of sample n=10) was carried out using coupon specimen on Toyo Seiki digital hardness testing machine (ASTM D). Tribological properties such as frictional coefficient μ and wear loss V were measured by a ball on type reciprocating type sliding wear tester (HEIDON Type38, Shinto Scientific Co., Ltd., Japan) at constant normal load (P=10N), sliding speed (v=0.02m/s) and sliding distance (L=80m) under dry condition (Number of sample n=3). The carbon-chromium bearing steel (SUJ2) ball (ϕ=3mm) was used as counterpart. The wear loss is calculated by the height of sample measured by laser displacement sensor. The worn surface of the polymer composites, the transfer film on the counterface and wear debris were observed by digital microscope (VHX-1000, Keyence Co., Japan) and scanning electron microscope (SEM, VE-8800S, Keyence Co., Japan) for understanding the wear mode. To understand the internal structure of these composites, the surface of samples fractured cryogenically in liquid nitrogen was observed using SEM (EDX-WET SEM, JSM-6360LA, JEOL Ltd., Japan, voltage: 15kV). These surfaces were stained in ruthenium tetroxide (RuO_4) for 6h to obtain the contrast of dispersed PE particles, polystyrene (PS) ones and so on[4), 9)].

(a) Nut shell (b) Nut shell powder (NSP) (c) SEM photograph of NSP

FIGURE 1. Image of nut shell and nut shell powder

RESULTS AND DISCUSSION

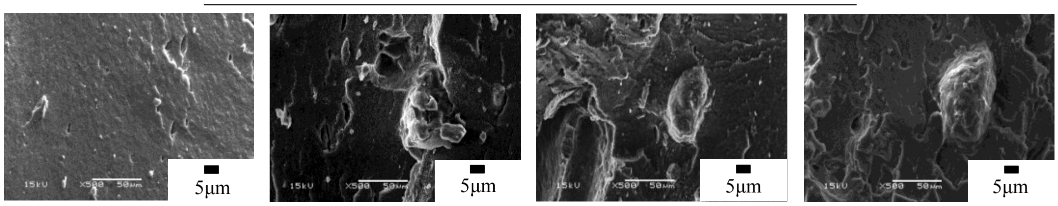
First, the influence of nut shell powder (NSP) content on the mechanical properties such as tensile, bending, Izod impact and durometer hardness properties of NSP filled composites (NSP/R-PO) is discussed. Table 1 shows the results (average value and standard deviation SD) of various mechanical properties of NSP/R-PO composites. The influence of NSP content V_f on the mechanical properties of NSP/R-PO composites differs for each property. The tensile modulus E_t, bending modulus E_b, Izod impact strength α_{iN} and durometer hardness HDD of NSP/R-PO composites increase with increasing V_f, although the tensile strength σ_t, bending strength σ_b and elongation at break ε_t decrease with increasing V_f. Thus, it was found that the apparent modulus such as E_t, E_b and *HDD* equivalent to hardness increases with filling NSP and increasing V_f.

Second, for the better understanding of the structure formation of NSP/R-PO composite with various NSP content, we observed the cryogenically fractured surfaces of these composites. Fig.2 presents SEM photographs of cryogenically fractured surfaces of NSP/R-PO composites with various NSP content. These SEM photographs show a homogenous distribution of NSP, which is a good dispersibility of NSP. Fig.3 shows SEM photographs of cryogenically fractured surfaces, which were stained in ruthenium tetroxide (RuO_4) to obtain the contrast of the dispersed PE particles, PS ones and so on. R-PO (100%) (Fig.3 (a)) indicates the typical separate spherical phases, which are dispersed small and large white particles, in continuous PP (black) matrix domains. The small white dispersed particles are PE, and the big ones are combination between PE and the impurities, which is the remaining parts of 5% such as polystyrene and other polymers (polyolefin rate in R-PO was about 95%). On the other hand, the morphologies of NSP/R-PO composites with various NSP content (Fig.3 (b)-(d)) are the similar one as that of R-PO (100%). However the morphologies of NSP/R-PO composites differ for each NSP contents. The morphology of NSP5 composites (Fig.3 (b)) has the two sizes of stained white particles in continuous PP (black) matrix domains. One is many small white particles, and the other is big white particles. In particular, the size of big white particles becomes smaller than that of R-PO (100%). To the contrary, the morphologies of NSP10 and NSP20 filled R-PO composites are that size of big white particles becomes bigger according to increasing NSP although the size of small ones is the same as NSP5/R-PO systems. Therefore, the internal structure formation of NSP/R-PO composites changes with NSP contents.

TABLE 1 The mechanical properties of NSP/R-PO composites.

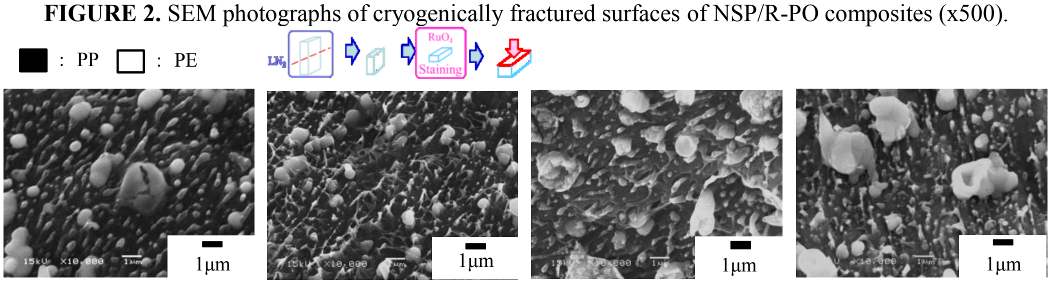
Code	NSP content V_f (vol.%)	Tensile strength σ_t (MPa) Ave.	Tensile strength σ_t (MPa) *SD*	Tensile modulus E_t (GPa) Ave.	Tensile modulus E_t (GPa) *SD*	Elogation at break ε_t (%) Ave.	Elogation at break ε_t (%) *SD*
R-PO	0	30	0.87	0.7	0.10	404	18.4
NSP5	5	25	0.75	0.8	0.04	204	40.9
NSP10	10	20	0.48	0.8	0.02	149	23.0
NSP20	20	17	0.49	0.5	0.22	57	12.8

Code	NSP content V_f (vol.%)	Bending strength σ_b (MPa) Ave.	Bending strength σ_b (MPa) *SD*	Bending modulus E_b (GPa) Ave.	Bending modulus E_b (GPa) *SD*	Izod impact strength α_{iN} (kJ/m^2) Ave.	Izod impact strength α_{iN} (kJ/m^2) *SD*	Durometer hardness *HDD* Ave.	Durometer hardness *HDD* *SD*
R-PO	0	21	0.32	0.7	0.05	5.8	0.69	60	0.77
NSP5	5	22	0.18	0.7	0.04	6.7	0.27	61	0.79
NSP10	10	19	0.43	0.8	0.05	7.2	0.93	61	0.70
NSP20	20	18	0.43	0.8	0.06	7.3	0.54	63	0.72



(a) R-PO (b) NSP5 (c) NSP10 (d) NSP20

FIGURE 2. SEM photographs of cryogenically fractured surfaces of NSP/R-PO composites (x500).



(a) R-PO (b) NSP5 (c) NSP10 (d) NSP20

FIGURE 3. SEM photographs of cryogenically fractured surfaces, which were stained in ruthenium tetroxide of NSP/R-PO composites (x10,000)

Next, the tribological properties of NSP/R-PO composites by constant normal load and sliding speed testing using a ball on plate type reciprocating sliding wear tester are discussed. Fig.4 shows the influence of NSP content V_f on the frictional coefficient μ and wear loss V of NSP/R-PO composites. μ of NSP/R-PO is almost constant values of 0.24 independent on NSP content. On the other hands, the influence of NSP content on V show a different tendency with μ. V of R-PO is improved with filling NSP, and increases slightly with increasing NSP content. In particular, V of NSP5/R-PO composite has a minimum peak. These results may be attributed to the change in the mode of wear mechanism by filling NSP content. Because the tribological behavior of polymer composites are highly influenced by their ability to form a transfer film on the counterface, wear debris and worn surface, it is essential to observe these phenomena for understanding the mechanisms of tribological behavior [10)]. Fig.5 shows SEM photographs of the wear debris after ball on plate type reciprocating sliding wear testing of R-PO and NSP/R-PO composites. The shape of wear debris of all materials used in this study have a flaky particles, and their sizes are different according to the filling NSP and its content. The size of wear debris of NSP/R-PO composites increases with increasing NSP content, and the smaller the sizes of wear debris are, the better the wear resistance becomes. Fig.6 presents SEM photographs of worn surface after ball on plate type reciprocating sliding wear testing of R-PO and NSP/R-PO composites. Fig.7 shows the profile of cross section of wear track. The wear scar width W (average), which is shown by two vertical direction arrows in the figure, and the wear scar depth D (maximum) were measured by 3D laser scanning confocal microscope W and D (average value and standard deviation SD) of R-PO and NSP/R-PO composites are listed in Table2 (Number of sample n=3). W and D of R-PO are 832μm and 62μm, respectively, and those of NSP5 filled ones are 683μm and 23μm, respectively, which means the wear track of NSP5 is smoother, narrower and shallower than unfilled one (R-PO). W and D of NSP/R-PO composites increase with increasing NSP content. These results indicate that the sizes of wear scar and wear debris are closely related with the tribological properties in the constant wear mode.

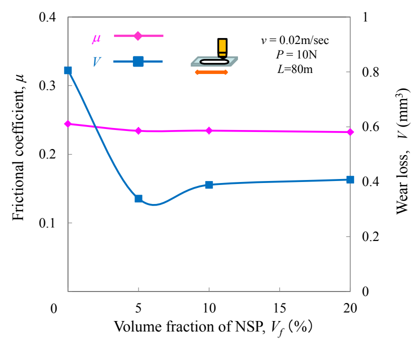
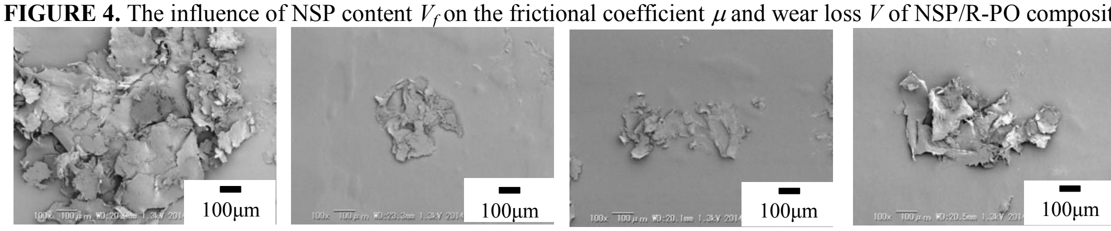
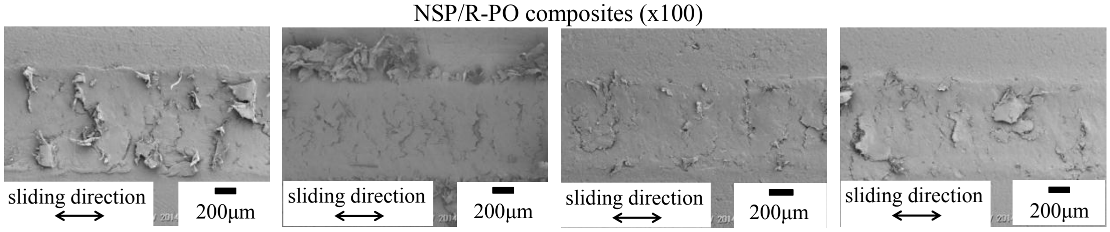


FIGURE 4. The influence of NSP content V_f on the frictional coefficient μ and wear loss V of NSP/R-PO composites



(a) R-PO (b) NSP5 (c) NSP10 (d) NSP20

FIGURE 5. SEM photographs of the wear debris after ball on plate type reciprocating sliding wear testing of R-PO and NSP/R-PO composites (x100)



(a) R-PO (b) NSP5 (c) NSP10 (d) NSP20

FIGURE 6. SEM photographs of worn surface after ball on plate type reciprocating sliding wear testing of R-PO and NSP/R-PO composites (x50)

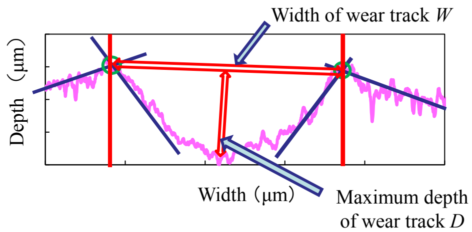


FIGURE 7. The profile of cross section of wear track

TABLE 2 The wear scar depth *D* (maximum) were measured by 3D laser scanning confocal microscope *W* and *D* of R-PO and NSP/R-PO composites

CONCLUSION

The purpose of this study was to investigate the influence of NSP content on the tribological properties of recycled polyolefin (R-PO) composites experimentally. It was found that NSP is effective for reducing the wear loss of R-PO, and the influence of NSP content on the tribological properties of NSP/R-PO composites do not remarkably appear, however they are improved with the addition of low content such as 5 vol.%. This may be attributed to the change of wear mechanism according to the filling of NSP.

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