

SHORT COMMUNICATIONS

Anti-deterioration Effect of Lignin as an Ultraviolet Absorbent in Polypropylene and Polyethylene

Kazuko TOH,^{1,†} Satoshi NAKANO,² Hidekatsu YOKOYAMA,¹ Kenichi EBE,²
Kiichi GOTOH,² and Hiroyuki NODA³

¹National Institute of Advanced Industrial Science and Technology, AIST,
2266-98, Anagahora, Shimoshidami, Moriyama-ku, Nogyo 463-8560, Japan

²Yamagata Research Institute of Technology, 2-2-1 Matsuei, Yamagata 990-2473, Japan

³Institute for Life Support Technology, Yamagata Promotional Organization for Industrial Technology,
2-2-1 Matsuei, Yamagata 990-2473, Japan

(Received April 15, 2005; Accepted May 11, 2005; Published August 15, 2005)

KEY WORDS Lignin / Ultraviolet Absorbent / Plant Wastes /
[DOI 10.1295/polymj.37.633]

A large quantity of plant wastes (such as wood scrap, rice bran, used tea leaves, and the dregs from squeezed fruit) is generated by the woodworking and food industries and agriculture. The recycling of these wastes is limited to their use in feed, fertilizer, fuel, and cosmetics. In this study, by using lignin that is one of the main components in plants, a new recycling method for plant wastes was designed. Lignin is a phenolic high-molecular-mass biopolymer based on phenylpropanoid units that are unique to vascular land plants.^{1,2} It accounts for approximately one-third of the organic matrix of wood and makes up a large component of grasses, leaves, and coniferous tree needles.^{2–5} It is known that lignin absorbs ultraviolet rays well in the wood components.⁶ Hirabayashi and Shimizu developed the lignocellulose film which was made from lignin and cellulose and showed high absorption of ultraviolet rays.⁷ The lignocellulose is an ultraviolet rays absorption filter. However, it is not clear whether lignin defends matrix in the film from deterioration caused by the ultraviolet rays. In this study, the effect of lignin in synthetic polymer was examined. The influence of lignin as an ultraviolet absorbent to the synthetic polymer as a matrix is now under way. Polypropylene (PP) and polyethylene (PE), popular polyolefin resin plastics in many fields, are commonly used together with an ultraviolet absorbent because tolerance of these plastics to ultraviolet rays is relatively low.⁸ Usually, the synthetic ultraviolet absorbent, benzotriazole or benzophenone series was used for this purpose. It is feared that the use of synthetic ultraviolet rays absorbent such as benzotriazole affects the environmental status. Use of lignin may decrease the load to the environment

because lignin is one of natural materials. Furthermore, it can contribute effective use of botanical wastes. In this study, PP and PE test pieces containing lignin were fabricated, and the anti-deterioration effect of lignin as an ultraviolet absorbent was investigated through an outdoor exposure test. In our knowledge, this is the first report to use lignin as an ultraviolet rays absorbent in the polyolefin resins.

EXPERIMENTAL

Lignin (Kanto Chem. Co.) was mixed with PP (melt flow rate = 0.5 g/10 min) and high density PE (melt flow rate = 12 g/10 min) in various concentrations. The mixtures were kneaded in a kneading machine (LABO PLASTOMILL MODEL 30C150, Toyoseiki Ltd.) at 50 rpm for 10 min at a temperature of 190 °C (PP) or 140 °C (PE). The kneaded samples were degassed in a vacuum oven at a temperature of 200 °C (PP) or 150 °C (PE), then pressed to a thickness of 1 mm. From this seat, dumbbell-shaped test pieces were obtained (Figure 1; parallel part of the dumbbell-like form, 10 mm wide by 50 mm long).

These test pieces were exposed outdoors for 3 to 6 months (starting in June) by using an exposure stand (JIS Z 2381, Yamagata city); then yield strength (tensile stress at yield) was measured by a tensile test. The strain occurs when stress is applied to the material. The yield point is the point at which the slope of the stress–strain curve reaches zero. Stress beyond the yield point causes permanent strain in the material. The tensile stress at yield (σ_0) is obtained from $\sigma_0 = P_0/A$ (P_0 , load at yield point; A , sectional area of the test piece). The tensile test was conducted

[†]To whom correspondence should be addressed (Tel: +81-52-736-7323, Fax: +81-52-736-7149, E-mail: k-tou@aist.go.jp).

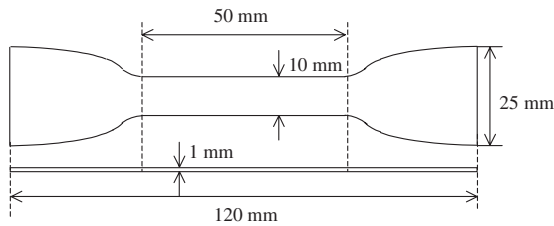


Figure 1. Outer view of test piece.

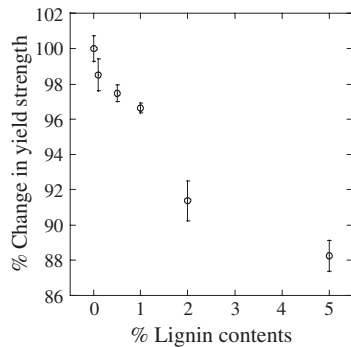


Figure 2. Change in yield strength according to concentration of lignin in the test piece without exposure. Values are mean \pm standard error obtained from five independent measurements.

at 1000 N and 0.8 mm/s by using a tensile machine (AUTO GRAPH AG-100kNE, Shimadzu Co.). The density of the test piece was measured by a pycnometer (Yuasaionics Ltd.). Observation of the test pieces by a microscopy was also made.

RESULTS AND DISCUSSION

Relationship between the lignin content in the PP test piece and yield strength is shown in Figure 2. Because the yield strength of the lignin-containing test pieces markedly decreased at a concentration of 2% and reduced by 5% compared with that of the test pieces without lignin, test pieces with lignin content of 1% or less were used in the exposure experiment. The yield strength retention rate of each test pieces, which is calculated by dividing the yield strength after exposure by that before exposure, is shown in Figure 3. For the PP test pieces, the yield strength retention rate with 0% and 0.1% lignin was less than 60% after a 3-month exposure. After a 6-month exposure, the yield strength retention rate with 1% lignin remained around 75%, while with 0.5% lignin it was reduced to less than 60% (Figure 3a). This rate for the test pieces with 1% lignin was significantly larger than that of the test pieces without lignin (Student's *t*-test, $P < 0.01$).

For the PE test pieces, the yield strength retention rate for 0 and 0.1% lignin decreased to about 80%

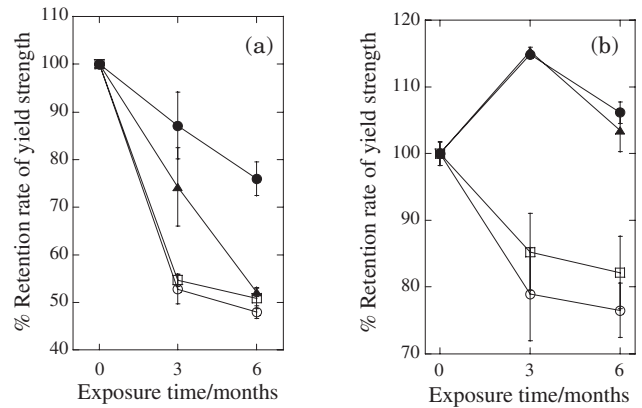


Figure 3. Yield strength retention rate of PP (a) and PE (b) test pieces after outdoor exposure. ○, 0% lignin; □, 0.1% lignin; ▲, 0.5% lignin; ●, 1% lignin. Values are mean \pm standard error obtained from five independent measurements.

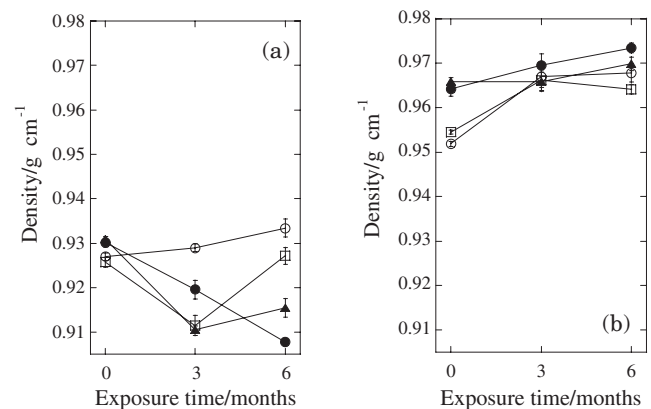


Figure 4. Density of PP (a) and PE (b) test pieces after outdoor exposure. ○, 0% lignin; □, 0.1% lignin; ▲, 0.5% lignin; ●, 1% lignin. Values are mean \pm standard error obtained from five independent measurements.

after a 6-month exposure. The yield strength retention rate for 0.5 and 1% lignin increased after a 3-month exposure, and decreased 6 months later. Both values, 3 and 6 months later, exceeded 100% and were significantly larger than those for the test pieces without lignin ($P < 0.05$; Figure 3b). It is thought that augmentation of the density caused by development of crystallization of PE enhanced the yield strength.

The density of the test pieces is shown in Figure 4. The density of the PP test piece without lignin increased with exposure time, indicating the development of crystallization in the PP. However, the density of the PP test piece with lignin decreased after a 3-month exposure. It is thought that lignin was removed from the PP and the opening in the matrix caused a decrease in density. In the PP test pieces at lower concentrations of lignin, the density increased after a 6-month exposure (Figure 4a). It is thought that the development of crystallization near the opening hole

shrank the hole. On the other hand, in the PE test piece, the density of all lignin contents increased with exposure time, indicating that the development of crystallization caused the increase of the density (Figure 4b).

It is thought that the difference in yield strength and density between PP and PE is caused by the difference in the degree of crystallization between the two plastics: *i.e.*, in the PP used in this study, the non-crystal parts may be relatively rich, which permits lignin to be removed from the matrix; while in the PE used here, non-crystal parts may be relatively small, which keeps lignin in the crystalline sections. The yield strength retention rate after outdoor exposure did not exceed 100% in the PP test piece in spite of developing the crystallization. In the PP test pieces, the influence of deterioration due to the outdoor exposure might be greater than that of crystallization.

These findings suggest that lignin, as an ultraviolet absorbent in PP and PE, suppresses the deterioration from outdoor exposure. Because the yield strength of the test pieces without exposure decreases as the concentration of lignin increases, the lowest concentration where the test pieces have a high yield strength retention rate after exposure was defined as an optimum lignin concentration to be 1 and 0.5% in the PP and PE test pieces, respectively.

The microscopic findings showed that the color of the lignin particles in the test pieces changed from black to red or yellow after exposure. It is thought that this color variation occurred because quinone was generated in the lignin structure. It is well known that lignin in wood generates a phenoxy radical by absorb-

ing ultraviolet rays, which causes the lignin to be degraded into lower molecules through a radical chain reaction.^{6,9-12} Furthermore, a phenoxy radical forms quinone *via* a reaction with oxygen.⁴ Therefore, these findings suggest that lignin protects the plastics from ultraviolet rays by absorbing these ultraviolet rays and rendering itself into smaller molecules.

REFERENCES

1. K. V. Sarkanen and C. H. Ludwig, in "Lignins; Occurrence, formations, structure and reactions," John Wiley & Sons Inc., New York, N.Y., 1971.
2. J. M. Lobbes, H. P. Fitznar, and G. Kattner, *Anal. Chem.*, **71**, 3008 (1999).
3. M. A. Goni and J. I. Hedges, *Geochim. Cosmochim. Acta.*, **54**, 3073 (1990).
4. J. I. Hedges and K. Weliky, *Geochim. Cosmochim. Acta.*, **53**, 2659 (1989).
5. S. Opsahl and R. Benner, *Geochim. Cosmochim. Acta.*, **59**, 4889 (1995).
6. D. N.-S. Hon, in "Wood and Cellulosic Chemistry," D. N.-S. Hon and N. Shiraiishi, Ed., Marcel Dekker, New York, N.Y., 1991, p 525.
7. Y. Hirabayashi and K. Shimizu, Japan Kokai Tokkyo Koho, JP2560221 (1992).
8. S. Yamaguchi and S. Amano, *Plastics*, **23**, 31 (1972).
9. K. Kringstad and S. Y. Lin, *Tappi J.*, **53**, 2296 (1970).
10. G. Gellerstedt and E.-L. Pettersson, *Svensk Papperstidning*, **80**, 18 (1977).
11. H. Takagi, I. Fosskåhl, H. Perakyla, S. Omori, and C. W. Dence, *Holzforshung*, **44**, 217 (1990).
12. A. Schmidt and C. Heitner, *J. Wood Chem. Technol.*, **13**, 309 (1993).