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Characteristics of titanium oxide filled polymer film with crazes

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Craze, which consists of voids and fibrils, is the unique incipient failure of polymers. We have developed an unique crazing processing method accompanied with sharp-edged bending in which the crazes were regularly and continuously generated. A remarkable feature of crazed film was an anisotropic optical property (view-field selectivity). We discussed the properties of a novel crazed Poly(ethylene terephthalate) film containing particles of titanium oxide (TiO_2). For the films with TiO_2, the periodical craze layers were generated by crazing-processing. Effect of photochemical oxidization on the disappearance of methylene blue was examined. Comparing with the non-crazed film included TiO_2, the photocatalystic effect of the crazed film was excellent. The concentration of acetaldehyde gas after ultraviolet (UV) irradiation was remarkably decreased. The particles of TiO2 were effectively exposed through the voids in the craze region, because a crazing generation was initiated at the polymer matrix-TiO_2 particle interface.

Key words: Craze, Photocatalyst, Ultraviolet light, Gas permeability, Void, Fibril

1. INTRODUCTION

Many investigations have been put emphasis on the discovery of the new functional materials and the development of the technology. We must also take environmental characteristics into consideration in the design of the polymeric materials. From this standpoint polymeric composites are excellent in light-weight, mechanical properties and moldability. But, many improvements for individual material in adhesive strength made separation of materials difficult, and caused problems for recycling.

We have developed a method to generate crazes uniformly and regularly with ordered structures and fabricate mono-component polymer composites that mixed regions of different high-order structures[1)]. The polymer films with crazing-processing have characteristics such as an anisotropic optical property and gas permeability.

Many photocatalysts, which react by absorbing light energy and have excellent antifungal properties, have been developed to improve the environmental deleterious effects[2~4)].

In this report, we tried to improve the efficiency of the photocatalyst. A photocatalyst was mixed at the various fraction in the polymer film, and the film was crazing- processed.

2. EXPERIMENTAL

2.1 Specimen preparation

The TiO_2 used in this experiment is the muskmelon type[5)] that the main body of TiO_2 covered with the porous membrane as shown in Fig.1. Although the conventional TiO_2 have conventionally deteriorated the organic materials, the muskmelon type of TiO_2 has hardly deteriorated them.

First, the regenerated Poly(ethylene terephthalate, PET) pellets were added to HFIP(1.1.1.3.3.3-Hexafluoro -2-propanol), in which the content of pellets was 5wt%, and then stirred at room temperature.

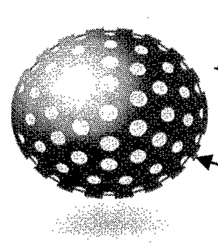

Fig.1 Schematic diagram of Muskmelon type of photocatalyst.

Second, titanium oxide (TiO_2) was also added during stirring. Third, the dissolving solution was poured on the glass plate mold, and was dried for one day in the atmosphere. Then, the sample was set in the oven and heated from room temperature to 55℃ in 17 h and continued drying for 30 min in vacuum. Then, it was heated to 90℃ in 5 h and continued drying for 1 h. PET films mixed TiO_2 (1, 3, 5wt%) were prepared in this manner.

Following two experiments (liquid phase and gas bag methods) were conducted in accordance with the test procedure[6)] by the Hikari Shokubai Seihin Gijyutsu kyogi-kai in Japan. All test specimens were in advance subjected to the ultraviolet (UV) irradiation of 1.0 W/cm^2 for 3h.

2.2 Crazing-processing

The crazing-processing used in this study is shown in Fig.2, and is essentially the same as that used in a previous paper[2)]. The film was bend sharply at the crazing-edge under a constant tension. The pulling tension was controlled by the friction resistance of a revolving roller (the tension roller in Fig.2). In the crazing-processing, the film was bent sharply and the stress was concentrated at the crazing edge as schematically shown Fig.2(a). The crazing in the film at the crazing edge is caused by stress without leading to fracture Fig.2(b), because the concentrated stress was released at the same time as the generation of he crazes which had the lower Young's modulus and elastic properties as reported in a previous paper.[2] The crazing edge had been shifted to a non-crazing region of the film according to the moving of the sample film Fig.2(c). The stress would have been concentrated and the next craze would have grown in much the same manner as the previous craze, and crazes were caused periodically and continuously.

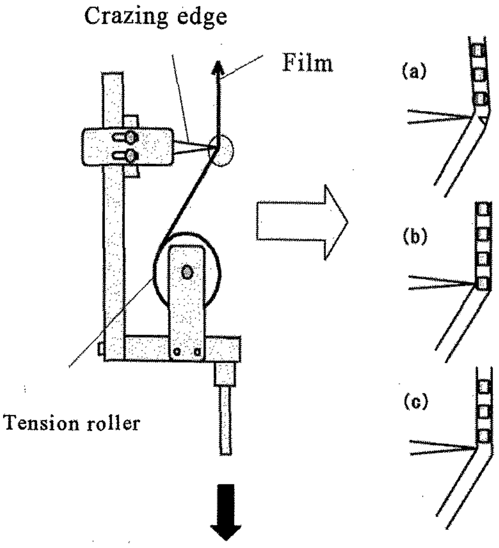

Fig.2 Schematic diagram of crazing device.

2.3 Liquid phase method

Methylene blue liquid was used as the test agent. Methylene blue liquid was directly placed in contact with test specimens. We then applied the UV light of 1.0 W/cm^2 to test specimens, and measured the color of methylene blue every the given time.

2.4 Gas bag method

Acetaldehyde gas was used in this experiment. Acetaldehyde gas was packed into tetra-bag, in which a test specimen was placed beforehand, and then the ultraviolet lights of 1.0 W/cm^2 were applied. An effect of optical catalyst was evaluated by the change in concentration of the acetaldehyde after the given time.

2.5 Gas permeation method

We examined the change in concentration of acetaldehyde gas in the direction of the film thickness.

First, the specimen was vertically set in the vicinity of middle of tube made of quartz glass. Second, the ultraviolet lights of 1.0W/cm^2 were irradiated to the specimen in the tube.

Next, acetaldehyde gas was then permeated in the tube. We examined the change in concentration of the acetaldehyde gas passed through the thickness of specimen.

3. RESULTS AND DISCUSSION

3.1 Craze morphology

Fig.3 shows the optical transmittance micrographs of crazes. The crazing-processing direction is the horizontal direction in the pictures in Fig.3(a). Crazes are seen as the black stripes perpendicular to the processing direction while the non-craze regions are seen as the white regions. This is because the incident light was scattered by voids in the crazes. Crazes were generated uniformly and regularly by the crazing-processing. Fig.3 (b) is a optical picture of the film cross-section parallel to the crazing-processing direction. It is seen that crazes were completely traversing the film.

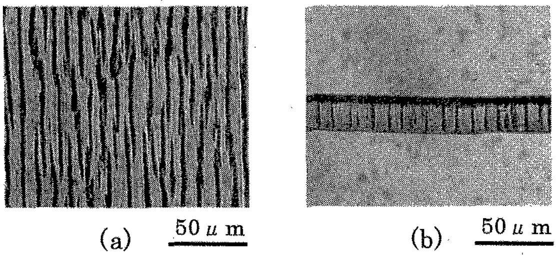

Fig.3 Optical micrographs of crazed film. (a) Surface, (b) cross-section.

Fig.4 shows the width and interval of the crazes. The width and interval of crazed film with 1wt% TiO_2 content are the widest, and decrease as the content of TiO_2 increases. We considered that in the case of the content of TiO_2 is high (3 and 5wt%), a number of narrower crazes were generated, while at 1wt% TiO_2 a small number of wider crazes were generated. We examined the craze fraction of the crazed film with TiO_2.

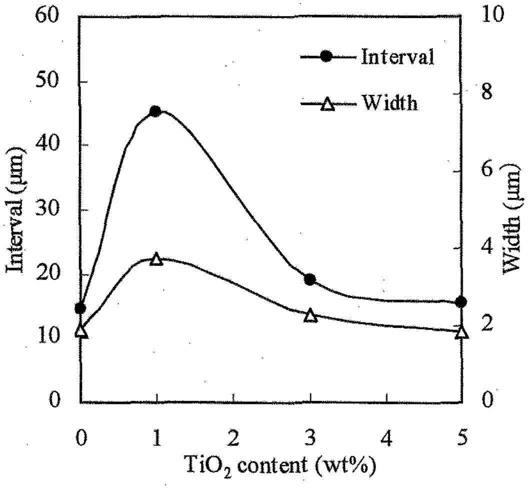

Fig.4 Width and interval of crazed film with TiO_2 content.

Fig.5 shows the craze fraction of the crazed film with TiO_2. The craze fraction is the value of width divided by the sum of width and interval. The craze fraction is almost unchanged regardless of the content of TiO_2 expect for 1wt% TiO_2. From Figs.4 and 5, we found that the crazes for the film with 1wt% TiO_2 is low in number.

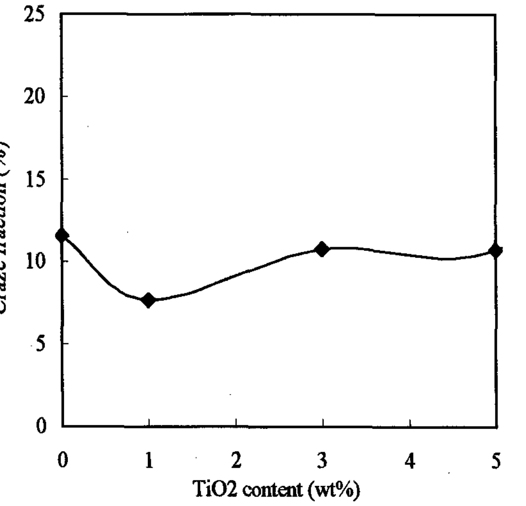

Fig.5 Craze fraction of crazed film with TiO_2 content.

3.2 Liquid phase method

We first examined the change in the color of methylene blue contacted with the surface of film with 5wt% TiO_2 in the dark room. It wasn't found that any change in the color by both the adsorption of methylene blue on the film and the absorption in the film.

Fig.6 shows the color change of methylene blue with irradiation time of UV lights. Values in the ordinates axis are expressed in values relative to a reference value of blue color. The back color shows the color of methylene blue disappeared completely. The color of methylene blue decreases gradually with irradiation time. In the case of irradiation of UV lights for 60 min, any color of methylene blue couldn't be found for the film with 5wt% TiO, while some color could be found for the film without TiO_2.

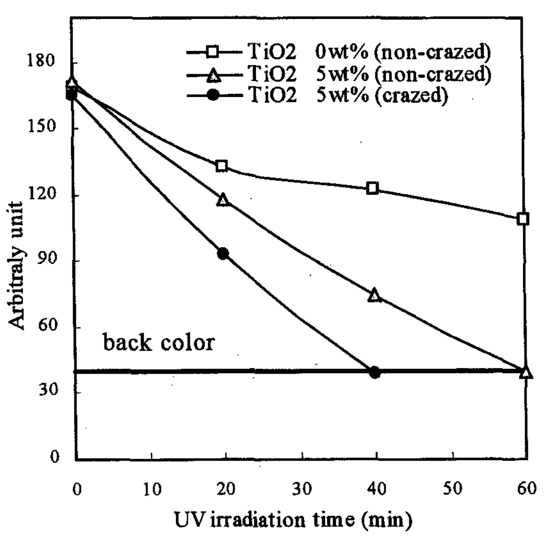

Fig.6 Color change of methylene blue by UV irradiation.

Furthermore, for the crazing-processed film with TiO_2, the disappearance of the color of methylene blue is more remarkable than that for the non-crazing-processed film with TiO_2. It is considered that this effect is due to an increase in the active surface area of TiO_2 existing in the vicinity of the surface of crazes.

Next, we examined an effect of TiO_2 content on the color disappearance of methylene blue. As was expected, the efficiency of the film mixed 5wt% TiO_2 is the highest, followed the film mixed 3wt% TiO_2, the lowest the film mixed 1wt% TiO_2.

3.3 Gas bag method

Fig.7 shows the concentration of acetaldehyde measured by the gas bag method for the film mixed 5wt% TiO_2.

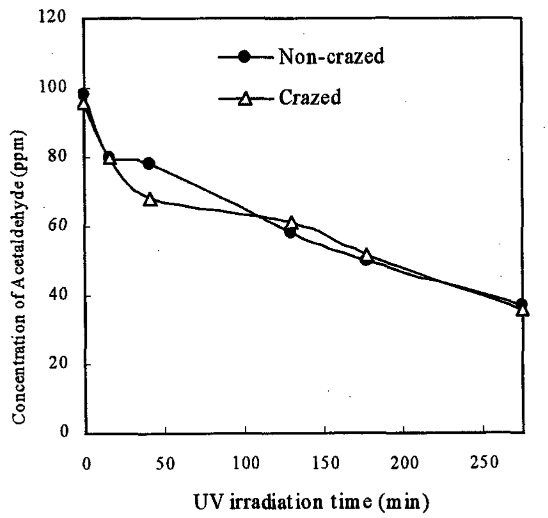

Fig.7 Relation between concentration of acetaldehyde and UV irradiation time for film with 5wt% TiO_2.

The concentration of acetaldehyde decreases with UV irradiation time for both the crazing-processed and non-crazing-processed film. Also, the concentration of acetaldehyde for the crazed film is almost the same as that for the non-crazed film. For the gas bag method used in this experiment, an acetaldehyde gas was only poured into the tetra-bag, and the gas wasn't passed through the thickness of the film. Accordingly, the activity by TiO_2 existing in the vicinity of crazes surface may be not expected. It is therefore considered that the concentration of acetaldehyde gas for the crazed film is almost the same as that for non-crazed film. Within a short time (~60min), the concentration of acetaldehyde gas for the crazed film is lower than that for the non-crazed film.

3.4 Gas permeation method

Concentration change of acetaldehyde gas after 60 min for the film mixed the TiO_2 is shown in Fig.8. By the gas permeation method through the thickness of the crazed film, the concentration of acetaldehyde decreases with the TiO_2 content. At 1wt% TiO_2 content, the concentration of acetaldehyde gas decreases remarkably. This implies that many TiO_2 included in the film become active by the UV irradiation.

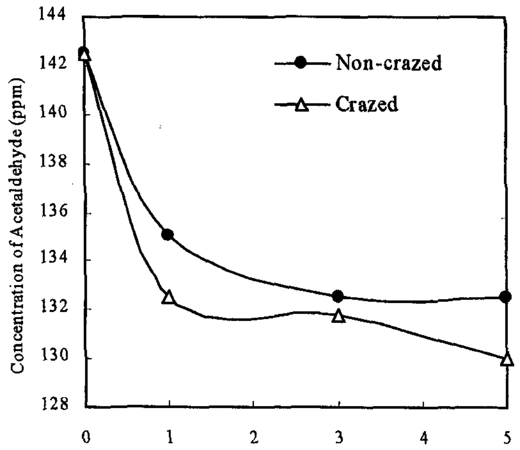

Fig.8 Relation between concentration of acetaldehyde after 60 min and content of TiO_2

Also, the decrease in concentration of acetaldehyde gas for the crazed film is higher than that for the non-crazed film. It is considered that many TiO_2 existing in the vicinity of the craze surface activate vigorously.

We examined gas permeability by using the instrument of measurement of gas permeability[7]. N_2 gas was used in this experiment.

Figs.9 and 10 show the permeability of N_2 gas and the difference in concentration, which is the value subtracted the concentration of acetaldehyde for the crazed film from that for the non-crazed film. Gas permeability increases with TiO_2 content. For the crazed and non-crazed films, the increasing tendency of the difference in concentration is almost the same as that of gas permeability.

The increase in gas permeability for the non-crazed and crazed films with 1wt% TiO_2 is remarkable. This means that the crazes penetrate in the direction of film thickness.

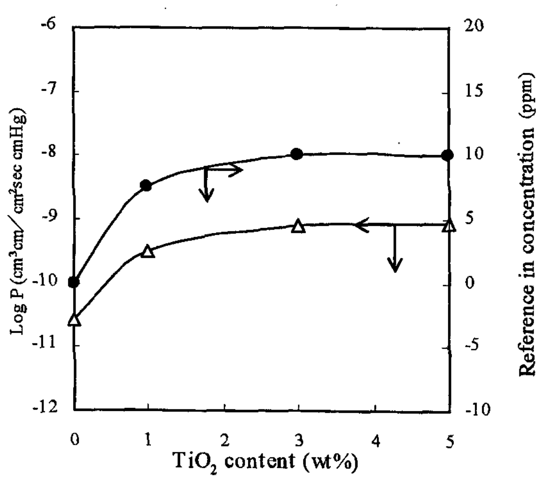

Fig.9 Relation between permeability (N_2 gas) and difference in concentration of acetaldehyde for non-crazed film with TiO_2 of 5wt%.

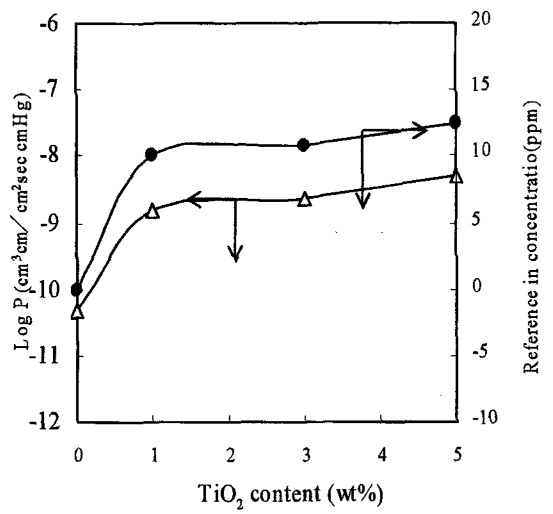

Fig.10 Relation between permeability (N_2 gas) and difference in concentration of acetaldehyde for crazed film with TiO_2 of 5wt%.

4 CONCLUSIONS

Regenerated PET films with TiO_2 were prepared by the cast method and crazing-processed by our unique method. Using three methods (liquid phase method, gas bag method and gas permeation method), we discussed the effect of crazing-processing on photocatalyst TiO_2. For the liquid phase method, the color of methylene blue decreased with the UV irradiation time. The decreasing tendency became remarkable for the crazed-films because the TiO_2 existing in the vicinity of surface of the craze region demonstrated the activity. On the other hand, for the gas bag method which the gas didn't pass through the thickness of film, the effect of the crazing-processing wasn't found. For the gas permeation method which the gas passed through the thickness of film, the concentration of acetaldehyde decreased with the TiO_2 content, and the decreasing tendency was more remarkable for the crazed film. It was found the performance of the photocatalyst contained film was higher by the crazing-processed.

5. REFERENCES

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