APCOM'07 in conjunction with EPMESC XI, *December 3-6, 2007, Kyoto, JAPAN*

Mechanism of the striped deterioration caused on automotive bumper by using the coupled analysis of heat transfer and stress: PP/rubber binary blend as a model.

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Abstract A unique deterioration with striped pattern caused by UV (ultra-violet) irradiation has been reported for PP (polypropylene)/rubber blend, by authors. This stripe is formed by repeating a pair of low and high density of the aggregation of micro voids inside the injection molding. Then, the micro voids do not generate at the PP matrix nor the interface but just inside the dispersed rubber domains. However, the reason why the micro voids generate is unclear. The purpose of this study is to estimate the mechanism of the micro voids generated in this striped deterioration by using FEM (Finite Element Method). Equivalent stress calculated for the rubber domain strongly depended on the morphology of the dispersed domain, especially in its orientation. In addition, some defects existing in the rubber phase; e.g. a fine crystalline composed of polyethylene chain, become a trigger to induce the micro voids.

Key words: polypropylene, rubber, automotive bumper, tiger stripe, FEM

INTRODUCTION

In recent two decades, PP/rubber/talc blend has grown as a main material for automotive bumper which requires not only mechanical properties but also industrial design controlling image of a car.[1,2] However, after a bumper is assembled in a real car, the deterioration with striped pattern occurred on the bumper with lapsed time of several years or more. This striped deterioration becomes a factor which spoils design of the car. Figure 1 shows a typical striped pattern deterioration of an injection-molded bumper without light stabilizers (UV absorber free) after exposure for a year in Okinawa Island, a southern part of Japan. The striped pattern formed by alternation of strongly and weakly whitened parts can be easily seen by naked eyes. The deterioration with striped pattern should be distinguished from flow mark (tiger stripe) generally known as a surface defect on the injection molding composed of PP/rubber blend. The flow mark (tiger stripe) is a phenomenon which occurs on the surface of the resin just after the molding (as the initial state).[3,4] On the other hand, the striped deterioration pattern discussed in this study is not severe like this photograph just after molding (as the initial state), both the sun shine and weather induce such the severe deterioration on the stripe pattern. Although this striped deterioration can be effectively improved with adding light stabilizers for current bumpers. However, the mechanism of the striped deterioration is unclear; therefore we studied for a simple model of PP/rubber binary blend in order to estimate mechanism of the striped deterioration caused by UV irradiation.

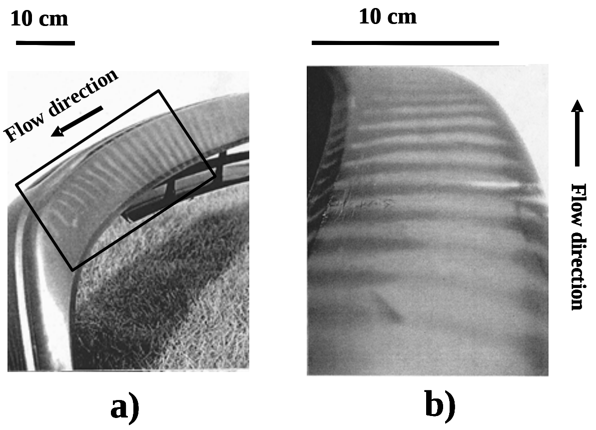

Fig. 1 Model sample without light stabilizers (UV absorber free) exposed for 1 year at Okinawa: (a) left half of the bumper and (b) macrograph bumper.

The results of UV irradiation experiment[4] were shown in Figure 2. The model sample (PP/rubber binary blend) indicates severe pattern which can be recognized easily by naked eye observation. The severity of this striped pattern increased with increasing the UV irradiation time. Even though the conspicuous stripe was developed on the irradiated area, no striped traces were observed on the surface. Thus, the striped deterioration of PP/rubber binary blend caused by UV irradiation did not exist on the surface. Interestingly, internal observation by using ultrasonic echo imaging indicates that aggregation of micro voids[4] was observed inside the specimen. The micro voids increased and grew with time lapse of UV irradiation, and it was large in the strongly whitened part (S) in comparison with the weakly whitened part (W). That is, it became clear that the deterioration with striped pattern by UV irradiation generates not on the surface of the sample but inside the specimen.

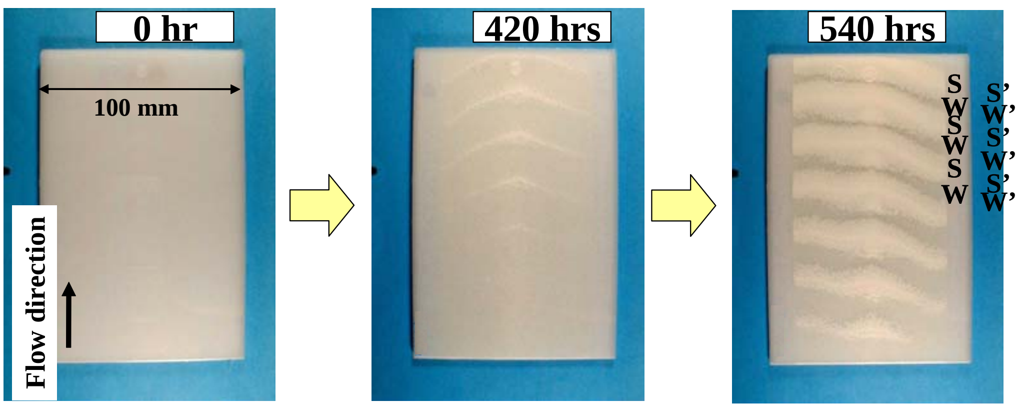

Fig. 2 Striped deterioration of a PP/rubber binary blend

The transmission electron micrographs (TEM) of the cross sections of the specimen were shown in Figure 3 [4]. In these photographs, the dark colored domains are assigned to the dispersed rubber domains. At the region near the surface (0-20μm), the domain size is relatively small and highly orientated along the flow direction. At the shallower region (30-50μm) and the deeper region (90-110μm), the domain size is relatively large and moderately orientated. The micro voids can be seen in only the shallower region (b: 30-50μm); especially left and underside of the photograph. The other two regions do not have any micro voids, except for the cracks caused by the glass knife operation, and the micro voids do not generate at the PP matrix nor the interface but just inside the dispersed rubber domains.

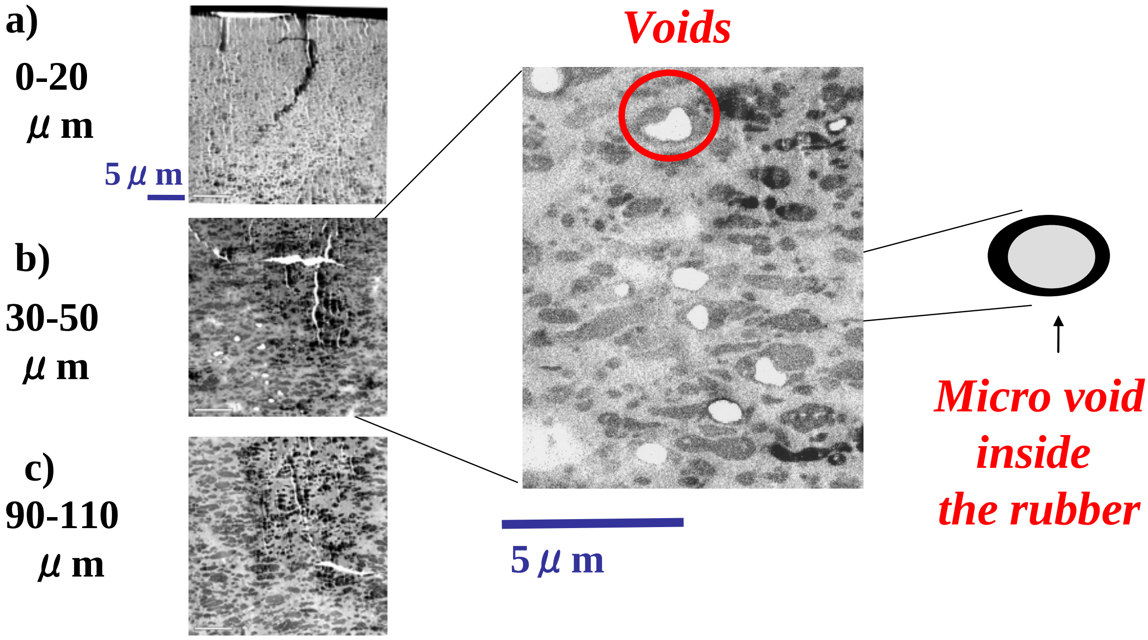

Fig. 3 TEM photographs of the deteriorated stripe

A morphological schematic view of the specimen was shown in (Figure 4). Highly oriented rubber domains exist in shallow region from the surface. Moreover, under this zone having the highly oriented rubber domains, weakly oriented rubber domains exist. UV irradiation causes the micro voids inside these weakly oriented rubber domains. While the highly orientated rubber domains near the surface do not have the micro voids inside it. In strongly whitened part (S), the thickness where the highly oriented rubber domains exist is thin. And in weakly whitened part (W), the thickness where the weakly oriented rubber domains exist is thick. Then, the difference of the depths where the micro voids occur provides the stripe having alternation of the strongly whitened (S) and weakly whitened (W) parts approximately perpendicular to the flow direction. The depth generating the micro voids is shallow for the strongly whitened part and deep for the weakly whitened part, respectively. As a result, the stripe is formed by repeating low and high density of the aggregation of micro voids inside of the specimen.

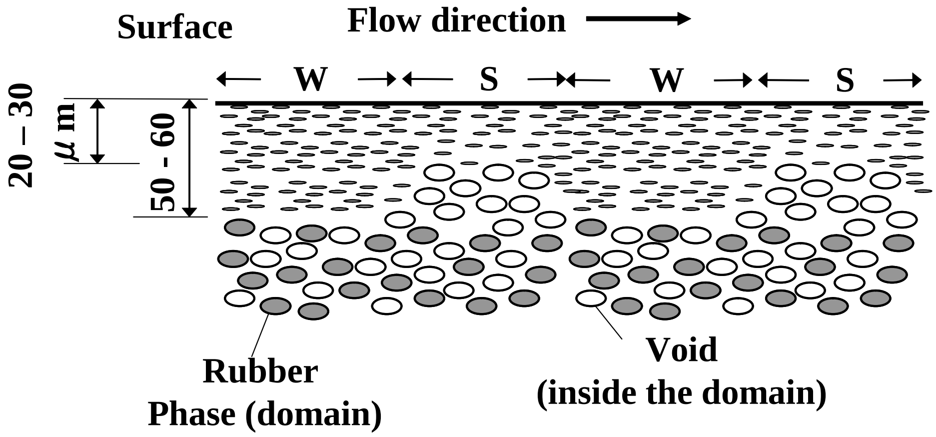

Fig. 4 Morphological schematic view of the deteriorated stripe

Finally, the feature of micro voids is summarized in Table 1. In general, PP is apt to deteriorate in comparison with the rubber. However, UV irradiation causes the micro voids inside the rubber domains in this case. In addition, it is well known that the interface of PP matrix and rubber domain tends to exfoliate easily due to its weakness of adhesive strength. Otherwise the micro voids generate just inside the dispersed rubber domains. And then, it seems that the highly orientated rubber domains have higher stress and strain in comparison with the weakly oriented domain. Therefore, the highly oriented rubber domain may tend to deteriorate. Otherwise UV irradiation causes the micro voids inside the weakly oriented rubber domains selectively. Furthermore, chemical oxidation cause by UV (trace of photo-degradation) does not describe the phenomenon because the surface is mostly chemical-oxidized by UV irradiation. Already mentioned, the micro voids exist in the deeper region from the surface. Thus, general knowledge for degradation of polymeric material cannot explain the micro voids generation. For these reason, to estimate the mechanism is interesting in terms of not only durability of automotive parts but also basic polymer science for blend system.

Table 1. Relationship between general knowledge and the experimental results for the micro voids.

Phenomenon	General knowledge	The results obtained
Existence of micro voids in a specimen	PP is apt to deteriorate in comparison with the rubber.	The micro voids generate just inside the rubber domains.
	The interface of PP matrix and rubber domain tends to exfoliate easily.	The micro voids generate just inside the rubber domains.
	The highly orientated rubber domain has high stress and tends to deteriorate.	The micro voids cause inside the weakly oriented rubber domains.
	The surface of the specimen is mostly oxidized. (having the highest C=O content).	The micro voids are caused in the deeper region from the surface of the specimen.

Stress and strain acted on the polymeric material accelerate the degradation under UV irradiation.[5] Then, stress and strain should be notified to estimate also the mechanism of the micro voids generation. However, it is hard to experimentally measure stress and strain for small dimensional sizes of the dispersed rubber domain. Here, we describe estimation of the reason why the micro voids occur in the striped deterioration by using FEM with the coupled analysis of heat and transfer and stress.

EXPERIMENTAL

The viscoelastic analysis for estimating the mechanism of the micro void generation was carried out by FEM using a non-linear computer program, MARC2001 and Fortran Subroutine. In order to simplify, a four node quadrilateral axial symmetry elements model was adopted. Moreover, the equation of alignment viscoelasticity as equation (1) is used.

$$\sigma(t,T) = \int_0^t Er(t' - \tau, T_0)\frac{d\varepsilon(\tau)}{d\tau}d\tau \qquad (1)$$

A two-dimensional-model constructed for FEM analysis is shown in Figure 5. One particle of a rubber was embedded in a PP matrix. The volume ratio of PP/rubber was set at 59/41 which was calculated for 60/40 PP/rubber weight ratio taking into account the density of each component polymer (density of the PP is 910 kg/m^3 and that of the rubber is 860 kg/m^3). The master curves of the relaxation modulus for the PP and rubber were obtained on the basis of Time-Temperature conversion rule, and they were approximated by Prony series as equation (2).

$$E_r(t,T_o) = E_e + \sum_{i=0}^{n} E_i e^{-t/\tau_i} \qquad (2)$$

Other properties used here are shown as follows: the specific heat J/(kg K) of 1900 for PP and 2200 for the rubber, the heat conductivity W/(m K) of 0.15 for PP and 0.28 for the rubber, the poisson's ratio (-) of 0.45 for PP and 0.49 for the rubber, respectively. Moreover, adhesive strength at the interface between the PP and rubber domain was assumed to be infinitely strong because the interface does not exfoliate after UV irradiation.

Furthermore, analytical model used here considers two cases. Figure 5 (a) is a weakly oriented rubber model in which the micro void generates inside it, and Figure 5 (b) is a highly oriented rubber model in which the micro void does not generate. These two models are corresponding to the deeper region inside the specimen and the shallower region near the surface of the specimen, respectively.
Temperatures were variable between 20 and 60 deg. C considering the UV irradiation experiment. Coefficient of heat transfer at the open air was set to 10 W/ (m^{2}K). One computation was performed by time increment every 0.02 s. And it was terminated when the time reached 10s because the temperatures become stable at 60 deg. C in every parts of the model during this 10 s. And all the results were judged by equivalent stress.

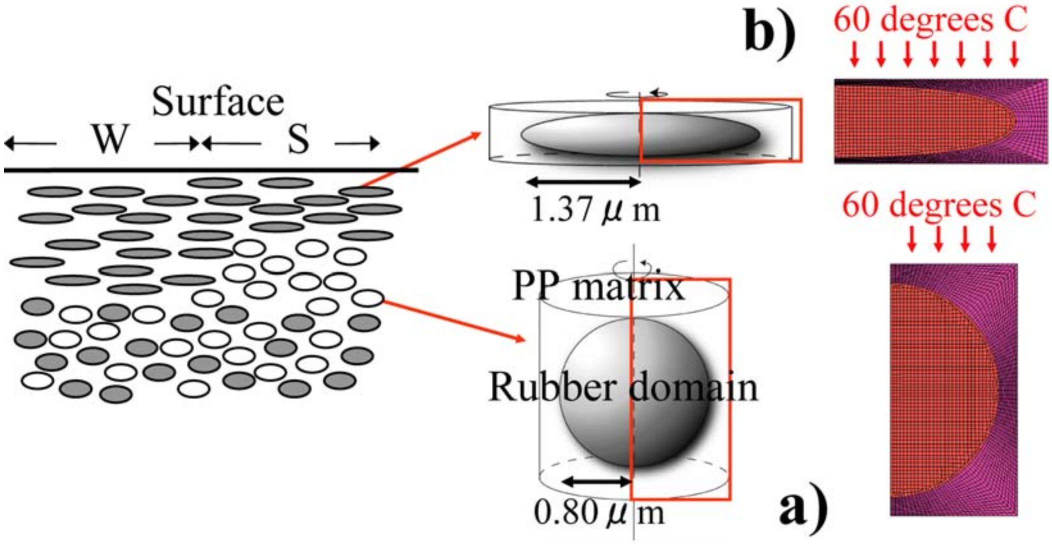

Fig. 5 Model used in this study for FEM
(a) weakly oriented rubber model and (b) highly oriented rubber model

RESULTS AND DISCUSSION

Effect of the rubber shape

At first, the influence of the domain shape in the dispersed rubber phase was discussed. Here, it was assumed that both cases of spherical shape for the weakly oriented rubber model (a) and of elliptical shape for the highly oriented rubber model (b) behave isotropic thermal expansion. That is, coefficients of linear thermal expansion (CLTE) of three directions (Machine Direction (MD), Transverse Direction (TD) and Normal direction (ND)) are equal. As a result, the average stress for the weakly oriented rubber model was smaller than that of the highly oriented rubber model. This result could not explain the mechanism because the stress obtained for the weakly oriented rubber domain (to cause micro void inside it) is smaller than that for the highly oriented rubber (not to cause the void).We note that higher stress becomes a trigger to generate the micro void inside the rubber domain.

Effect of CLTE along the spatial directions

Then, direction dependence of the CLTE was taken into consideration. Because the compression-molding (having spherical shape of the rubber domain) and injection-molding (having oriented shape of the domain) are different in the direction dependence of the CLTE. It is known that a compression molding of PP/rubber blend indicates approximately isotropic thermal expansion along each direction, while an injection molding of the blend indicates anisotropic thermal expansion. The injection molding has extremely higher CLTE along ND in comparison with two plane directions (MD, TD).[6]Therefore, these isotropic and anisotropic thermal expansions were applied to the models for the spherical and elliptical shapes, respectively. As a result, both the cases considering anisotropic expansion for the highly oriented rubber model and isotropic expansion for the weakly oriented rubber model provided approximately equal value in the stress. Then, the two models did not have remarkable difference of the stress. This result also could not explain the mechanism of the micro void generation. Therefore, other factor should be needed to estimate the mechanism.

Heterogeneous structure of the dispersed rubber domain

In order to aim novel factor, we carefully re-observed the dispersed rubber phase in terms of morphology. A TEM photograph of a cross section is shown in Figure 6; the section was sliced out from the deeper region (120-140 μ m) in the depth of the specimen before UV irradiation.

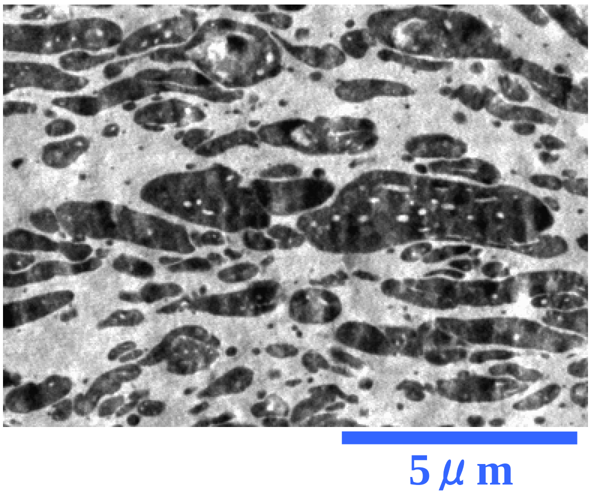

Fig. 6 Heterogeneous phase of the rubber domain

In this photograph, the white particles at the dark colored rubber domain are observed. These particles might be assigned to fine crystalline of polyethylene which is part of the backbone of the rubber polymer.

We notified that the heterogeneous phase (white particles in the rubber domain assumed as the fine crystalline) resembles a defect in the rubber domain. Since the melting point of the added rubber is about 50 deg. C, it was thought that the particle is melting and not adhesive to the rubber surrounding the particle at a temperature of 60 deg. C during UV irradiation. In order to discuss the effect of the heterogeneous rubber domain, a defective part was placed at the center of the analytical model as shown in Figure 7.

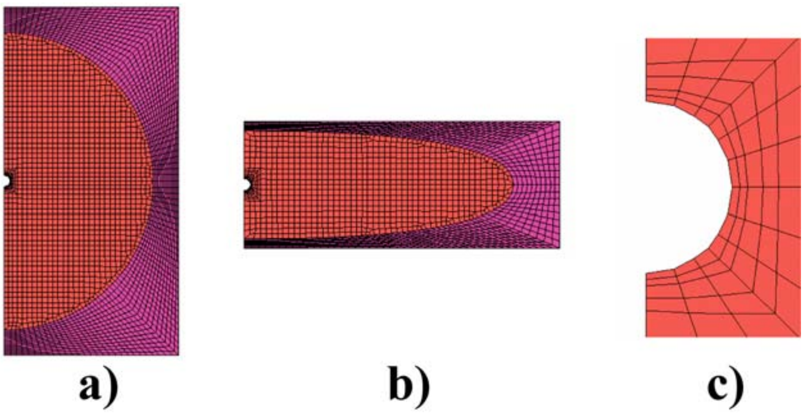

Fig. 7 FEM model for the rubber domain having a defect:
(a) The weakly oriented rubber model and (b) The highly oriented rubber model
and (c) Macro graph surrounding of the defect

The results for the model having the defective part are shown in Figure 8. These results (a) and (b) are corresponding to the weakly oriented rubber model (considering isotropic thermal expansion) and the highly oriented rubber model (considering anisotropic thermal expansion), respectively. They indicated that a high stress concentration occurs around the defective part at the weakly oriented rubber model in comparison with the highly oriented rubber model. Then, in case that the radius of the defective part is 0.03 μm, the maximum equivalent stress around the defect part at the weakly oriented rubber model is about 9 times of that at the highly oriented rubber model. These two models have a remarkable difference in the stress. This result could explain the mechanism that the micro void generates at only the weakly oriented rubber domain.

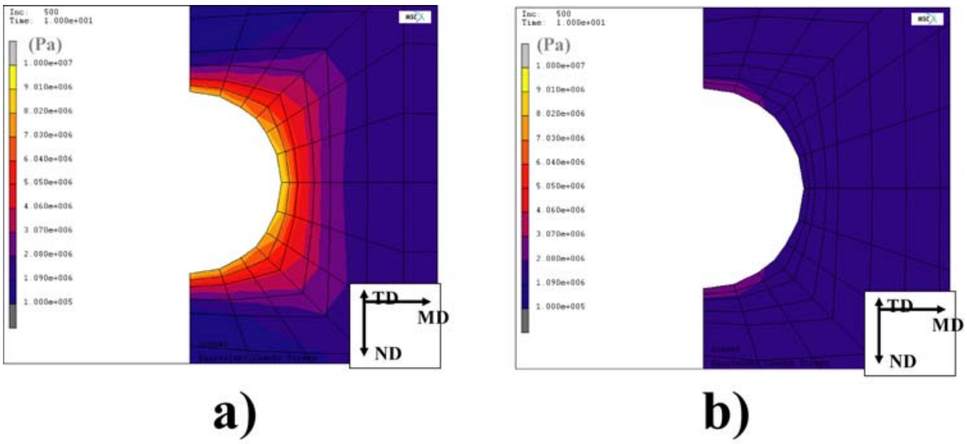

Fig. 8 Equivalent stress distribution of the rubber domain:
(a) The weakly oriented rubber model (Considering isotropic expansion)
and (b) The highly oriented rubber model (Considering anisotropic expansion)

Moreover, the maximum equivalent stress around the defective part by changing the radius from 0.01 to 0.05 μm is shown in Figure 9. The stress acting to the surround of the part only for the weakly oriented rubber model increase with increasing the radius of the defect. The gradient is large for the weakly oriented rubber model in comparison of the highly oriented rubber model. Concretely, magnification of the stress is e.g. 4.25 times (= 4.67/1.10) and 11.9 times (= 13.1/1.10) for the radius of 0.01 and 0.05 μm respectively. Thus, a heterogeneous phase is the important factor to estimate the mechanism because higher value of the stress acetates t internal strain for a material. Here, we notified PE fine crystalline as the heterogeneous phase, but more discussion will be needed to estimate the detailed mechanism.

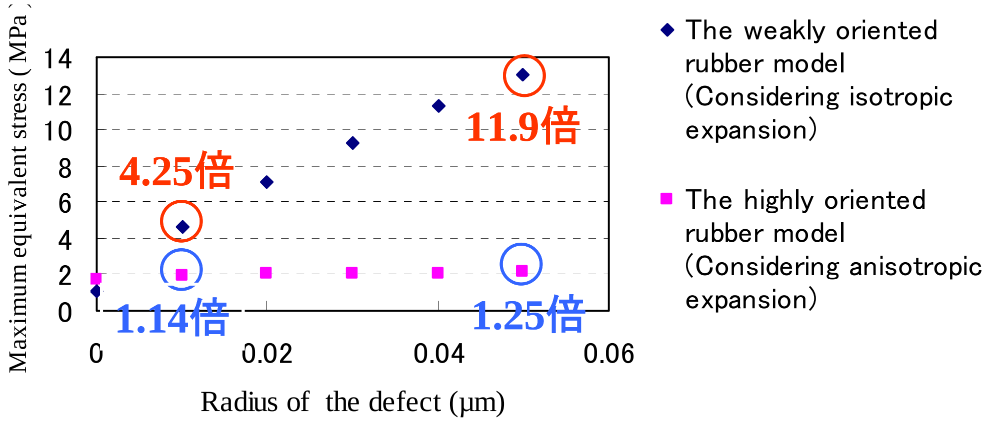

Fig. 9 Maximum equivalent stress dependant on the radius of the defect

CONCLUSIONS

In this study, we reported a unique deterioration having striped pattern for PP/rubber binary blends caused by UV irradiation. Some cases considering the shape of the dispersed rubber, direction dependence of linear thermal expansion were computed by using the coupled analysis of heat transfer and stress. The obtained results are summarized as follows:

1. When the anisotropy of CLTE along the spatial directions is applied to the highly oriented rubber model. The average stress of the highly oriented rubber domain decreases as a result. However, this case considering the anisotropic CLTE is inadequate to explain the mechanism of the micro void generation.
2. A novel model in which a defective part is placed at the center of the rubber domain provides a reasonable result. That is, a high stress concentration occurs around the defective part only for the weakly oriented rubber model.
3. Consequently, it should be noted that heterogeneous phase in the rubber domain, e.g. PE fine crystalline, become a trigger to induce the unique deterioration with striped pattern.

Influence of some heterogeneous phases of the rubber domain is currently studied by the authors in terms of crystalline, micro-phase separation of added rubbers.

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