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Stress-Whitening Phenomenon and Relaxation Behavior Therefore

Masayuki KASAJIMA*, Katsuhiko ITO*, and Makoto TSUTSUI*

Abstract

The amount of stress-whitening was measured by light transmission, permitting quantitative determination of the whitening ratio of high impact polystyrene. The relationship between stress relaxation and stress-whitening behavior, and the relaxation behavior of the stress-whitening were investigated. The influence of temperature on deformation as well as stress-whitening behavior was investigated. On loading the specimen, a change in the whitening ratio in the elastic range was observed which could not be observed with the naked eye. When the stress or strain were restored to zero, however, the whitening in the elastic range disappeared. The rate of increase of the whitening ratio increases with strain, irrespective of the test temperature, and becomes maximum in the vicinity of yielding. Whitening ratio-strain curves plotted for several different levels of temperature show the following features: the higher the temperature the lower the whitening ratio in the region of small strain below the yield point as well as large strain above the yield point, with the reversed tendency in the vicinity of yielding. The effect of temperature on the whitening ratio is greater at lower strain rate than at higher. When the starting point of the stress relaxation is at or above the yield point, stress-whitening inertia occurs. The stress-whitening inertia value is largest in the vicinity of the yield point, and decreases with increase in the rate of plastic deformation. Change in stress-whitening with the passing of time depends more on temperature in the restrained state than in the unrestrained state. If a stress-whitened specimen is heated to temperature below the glass-transition point, the whitening ratio of the specimen decreases. The decrease of stress-whitening for each tensile deformation-whitening removal cycle is smaller with a specimen gradually heated to the glass-transition temperature to remove whitening and then gradually cooled down to room temperature than with a specimen rapidly heated and rapidly cooled.

1. Introduction

Whitening of polymeric materials is known to be caused by e.g., water, chemicals and solvents, light, leaching, crystallization, stress, and abrasion1). Only a few reports, however, have described the whitening processes; little is known as to their mechanisms. It has been shown that stress-whitening is caused not by cracks, but by crazes; its mechanism thus differs from those of the other whitening processes2)-7). Crazing of amorphous polymeric materials as well as stress-whitening of rubber-reinforced micro-composite thermoplastics have been studied8)-13); materials studied include ABS resins14)-17) and high impact polystyrene (HIPS) resins5),14),18)-20). In these studies, the craze and whitening were examined microscopically; stress-whitening was also studied in relation to the mechanical properties of the resins. Still another study examined the relationship between crazing and mechanical properties of resins21). Other studies are concerned with the measurement of crazes in polystyrene (PS) resins by the change in light reflec-

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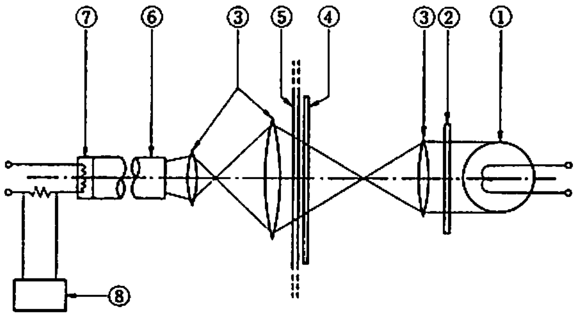
tance[22] or measurement of stress-whitening in transmission[23]. In none of these studies, however, was the relationship between deformation and stress-whitening behavior examined on a quantitative and continuous basis. In addition only a few reports have been concerned with quantitative analysis of whitening at different temperatures. Examination of the stress-whitening process will not only give informaiton on the deformation mechanism of micro-composite resins, but also provide basic physical data on materials for development of cold forming and other plastic working.

In the present work, the whitening of styrene-based two-component polymer HIPS was studied quantitatively by measuring changes in light transmission; the temperature effect on the deformation—stress-whitening relationship was also examined; the relationship between stress relaxation and stress-whitening as well as the relaxation behavior of stress-whitening was investigated.

2. Experimental

The specimen used was a 1 mm-thick Denkikagaku Kogyo HIPS sheet, Denka Styrol HI-R-5, of a dumbbell-like shape.

Tension load was applied to cause stress-whitening. Equipment was devised to measure continuously the light transmission of a specimen simultaneously with its mechanical deformation. Changes in light transmission were measured as changes in electric resistance generated as light was absorbed by a CdS photoconducting cell with a constant applied voltage and converted into changes in electric current; its main sections are schematically shown in **Fig. 1**. Light from light source ① passes through filter ②, is diverged by lens ③, passes through slit ④, and, after passing through the specimen ⑤, is converged by another lens ③. It is then detected by a CdS photoconducting cell ⑦, via light guide ⑥, and recorded on recorder ⑧. The filter is used to apply a uniform light onto the sample, while the slit is to send the light to the desired spot on the specimen surface. The light guide is to lead the light to the photoconducting cell located outside the constant-temperature bath.



① Lamp
② Filter
③ Lens
④ Slit
⑤ Specimen
⑥ Light guide(Glass fiber)
⑦ CdS photo conductive cell
⑧ Recorder

Fig. 1 Schematic illustration of measuring equipment of whitening ratio.

As stress-whitening occurs, light transmission decreases. The whitening ratio ϕ was defined as shown in Eq. (1):

$$\phi=\frac{I_0-I}{I_0} \tag{1}$$

where I_0 and I are the photoconducting cell current [mA] for a non-deformed, non-whitened sample and that for a deformed and whitened sample, respectively.

3. Results and Discussion

3.1 Influence of temperature on stress-whitening

The relationship between tensile stress (σ) and strain (ε) at various temperatures, obtained as tension loads were applied to cause stress-whitening, is shown in **Figs. 2** and **3**. They clearly show the presence of yield points. The $\sigma-\varepsilon$ curves move upward as temperature decreases. At each temperature, a linear relationship is observed between σ and ε within the elastic limit; the modulus of longitudinal elasticity is found to increase as temperautre decreases. Elongation, and thus ε at which rupture occurs, on the other hand, decreases with decreasing temperature.

Figs. 2 and 3 also show that yield stress, yield strain, and modulus of longitudinal elasticity all decrease with decreasing strain rate. The ratio of post-yield-stress relative to the yield stress is found to increase with decreasing strain rate and increasing temperature (T). When $\sigma-\varepsilon$ curves are examined as functions of T the change with T is smaller with a higher strain rate, indicating a larger temperature dependence with a lower strain rate, which seems to result from the competition between the rate of stress relaxation and the rate of forced deformation by external loading.

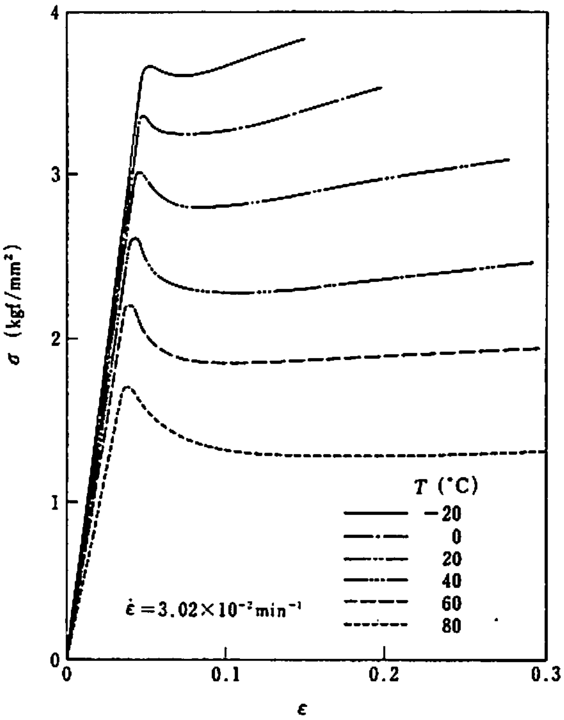


Fig. 2　Tensile stress (σ)–strain (ε) curves at various temperatures (T); strain rate ($\dot{\varepsilon}$) $=3.02\times10^{-2}\,\mathrm{min}^{-1}$.

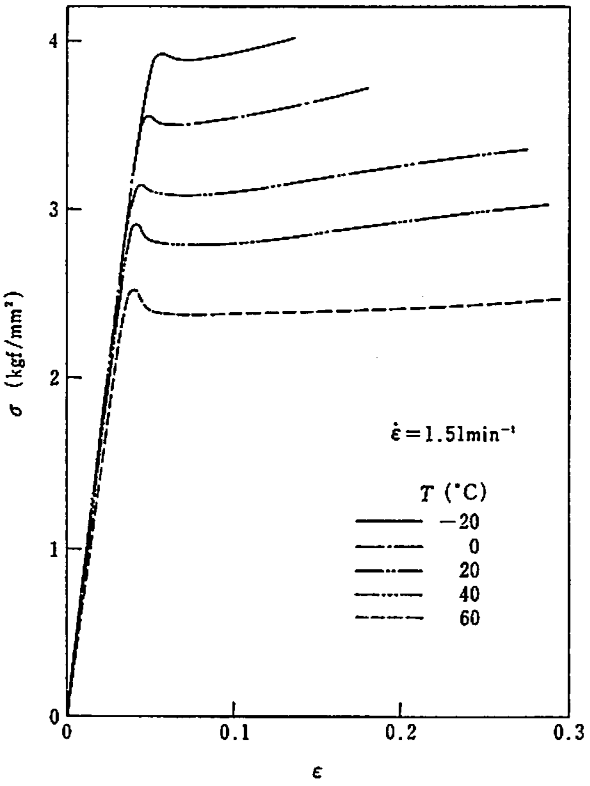


Fig. 3 Tensile stress (σ)–strain (ε) curves at various temperatures (T); strain rate ($\dot{\varepsilon}$) = 1.51 min^{-1}.

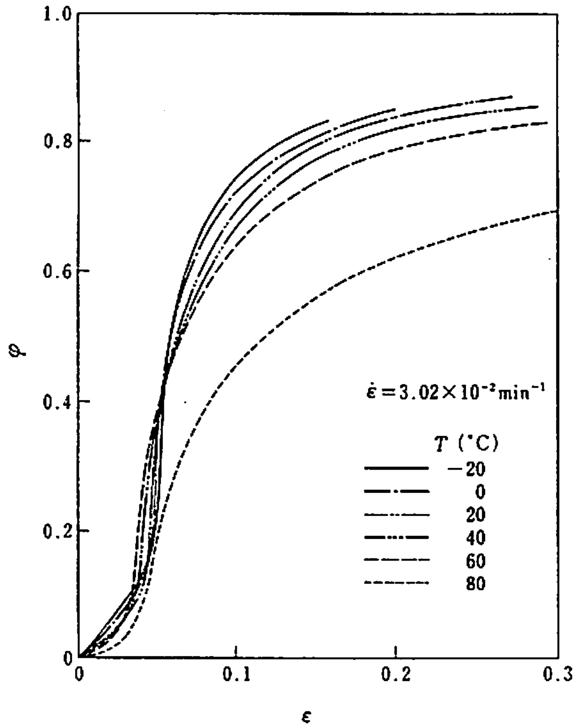


Fig. 4 Whitening ratio (ψ)–strain (ε) curves at various temperatures (T); strain rate ($\dot{\varepsilon}$) = 3.02 × 10^{-2} min^{-1}.

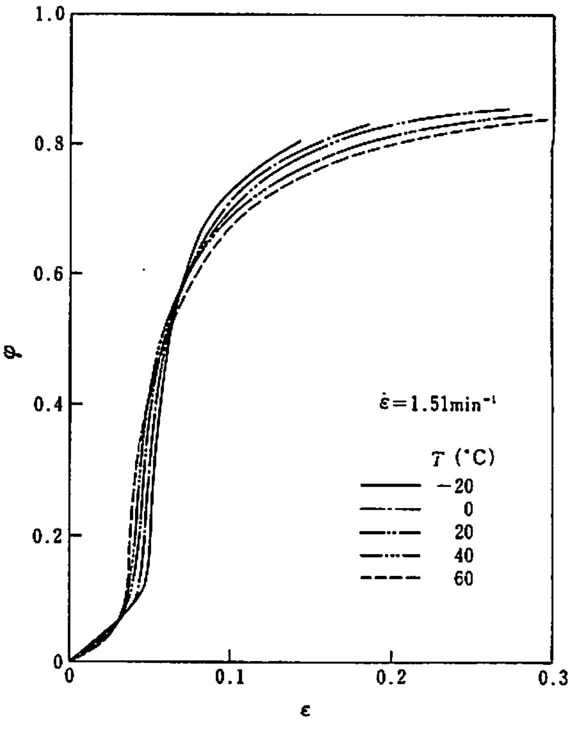


Fig. 5 Whitening ratio (ψ)–strain (ε) curves at various temperatures (T); strain rate ($\dot{\varepsilon}$) = 1.51 min^{-1}.

Figs. 4 and **5** show the relationship between whitening ratio (ϕ) and ε with T as a parameter. As clearly seen in these figures, ϕ changes even in the elastic region and increases with ε. Changes in ϕ observed in the elastic region are not detectable with the naked eye. At each temperature, ϕ increases abruptly around the yield strain, giving the largest rate of increase in ϕ with respect to ε; the rate of increase is larger as temperature is lower. Stress-whitening becomes clearly visible around the yield point, and it increases further with increasing strain. At each temperature, ϕ reaches a maximum at the rupture point.

The same temperature dependence as in Fig. 4 is observed in Fig. 5, where the data for higher strain rates are shown. The difference in strain rate causes the values of ε at which the inversion of $\phi-\varepsilon$ relationship takes place to be somewhat different in Figs. 4 and 5; the way the $\phi-\varepsilon$ curves cross each other at two points, the shapes of the curves, and other general features, however, are quite similar in Figs. 4 and 5. As seen above, ϕ decreases with increasing temperature in the strain region below the yield point, while in the yield strain region, which begins earlier at a higher temperature, the opposite temperature dependence is observed. As strain increases further, another inversion of the $\phi-\varepsilon$ relationship is observed: the higher the temperature, the lower the value of ϕ. The observed inversion are believed to be caused by the following: (1) at each temperature, the rate of increase of whitening becomes maximum in the vicinity of the yield strain, (2) the lower the temperature, the higher the rate of increase of whitening, and (3) the relative position of the yield point varies with temperature. Therefore, even when the $\phi-\varepsilon$ curve of a higher temperature reaches the region of th yield point, that of a lower temperature is still in the strain region below the yield point. Accordingly, the former curve starts to climb earlier, giving a higher ϕ value than that of the $\phi-\varepsilon$ relationship of a lower temperature. This is what one observes in the first inversion of $\phi-\varepsilon$ relationship. The rate of increase of whitening ratio in the post-yield-point region of strain, however, is larger for a lower temperature, and as strain increases further, ϕ of a lower temperature overtakes and becomes larger than that of a higher temperature, giving the second inversion of $\phi-\varepsilon$ relationship. The $\phi-\varepsilon$ curve at 80°C in Fig. 4 behaves differently from those of the other temperatures, and its rate of increase of whitening ratio after the yield point is much lower. This seems to be due to an increased mobility of the polymer chains (or molecules) as compared with that at lower temperatures, since 80°C is close to the glass-transition temperature of the of the base polymer PS.

The present study thus reveals the occurrence of stress-whitening even in the elasitc region, while it was previously reported that stress-whitening begins in the region between the elastic limit and yield point and increases as strain increases further[14),18)]. When we stopped deformation in the elastic region and brought the stress and strain back to zero, we found that the whitening totally disappeared. However, when stress and strain were removed after deformation close to or beyond yield point, some whitening was found to remain in the specimen. The above observation indicates that it is not practical to apply a load, cause stress-whitening, take out the specimen, and measure stress-whitening, as previously done is observing stress-whitening in the elastic region. Even with a specimen whitened in the plastic region, therefore, measurement of its whitening after removal of a load does not give a true value of whitening caused by stress deformation, as some of it is lost upon removal of the load.

The above results indicate that even in the region, where the $\sigma-\varepsilon$ relationship measured macroscopically behaves in an elastic manner, some sort of localized deformation still occurs microscopically. The observation that stress-whitening, caused by localized deformation in the elastic region, vanishes upon removal of a load, together with a report by Kambour[6),7)] that crazing indicates a decreased elasitc modulus in that particular region as compared with that of the base material, thus not only presents an overall interpretation of craze formation generated by highly localized deformation phenomenon, but also reveals the elastic nature of the initial steps of crazing itself as is evaluated quantitatively by whitening ratio measurement. The above finding is an interesting phenomenon which deserves further study.

As clearly seen in Figs. 4 and 5, a larger value of strain rate $\dot{\varepsilon}$ causes the $\phi-\varepsilon$ curves of different temperatures to move closer to one another. That is, the smaller the strain rate, the larger the temperature dependenc of th whitening ratio.

The relationship between ϕ and T with ε as a parameter is shown in **Figs. 6** and **7**. In the temperature region below 60°C in Fig. 6 nearly linear relationships are observed between ϕ and T except for cases where $\varepsilon=0.04$ and 0.05; ϕ decreases with increasing temperature. The slopes of the linear relationships for $\varepsilon=0.02$ and 0.06 are smaller than those for $\varepsilon=0.09$ to 0.16, indicating a larger temperature dependence for the latter cases. For $\varepsilon=0.04$, ϕ remains constant up to around $T=20$°C and then increases in a curve-like manner, while a convex curve is observed

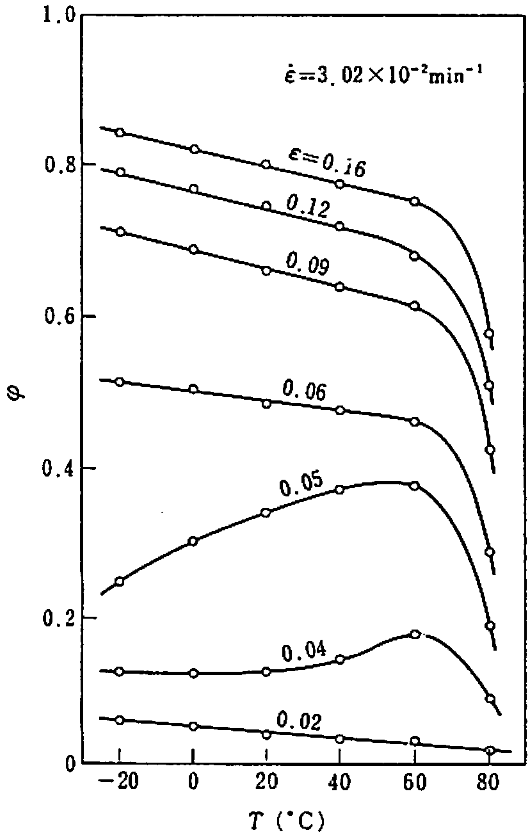


Fig. 6 Whitening ratio (ϕ)-temperature (T) curves at various strains (ε); strain rate ($\dot{\varepsilon}$) $=3.02\times10^{-2}$ min^{-1}.

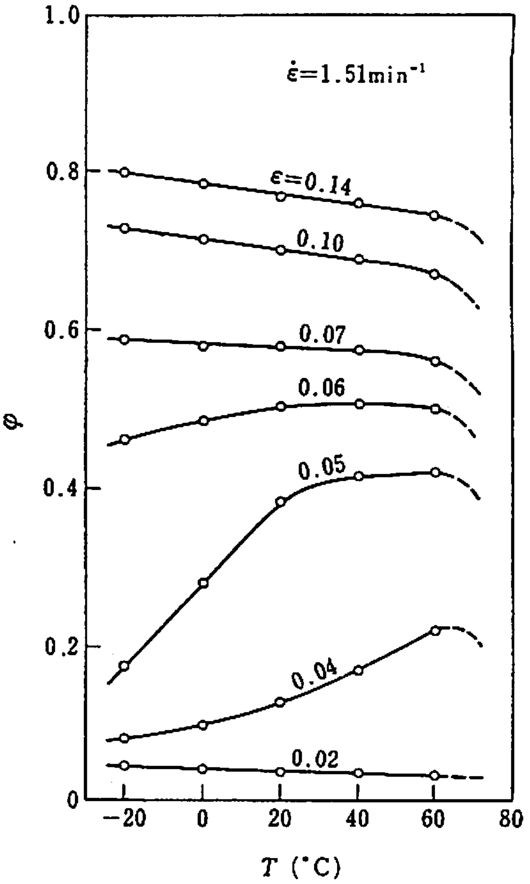


Fig. 7 Whitening ratio (ϕ)-temperature (T) curves at various strains (ε); strain rate ($\dot{\varepsilon}$) $=1.51$ min^{-1}.

with $\varepsilon=0.05$. The above observation is closely related to the fact that the rate of increase of whitening ratio reaches a maximum near the yield strain region, causing whitening to proceed more rapidly than its recovery due to temperature increase. Crazes are known to be removed by heating above the glass-transition temperature or by treating with solvent vapor[2),14)]. Changes of the $\phi-T$ relationship with ε, that is, ϕ increases, then decreases, and again increases with increasing ε, correspond to the inversions of the $\phi-\varepsilon$ relationship as observed with T as a parameter. Except for the case with $\varepsilon=0.02$, ϕ observed at $T=80°C$ is much lower than that observed at $T=60°C$, indicating that when the temperature is close to the glass-transiiton temperature a large reduction of ϕ occurs. When the strain is in the elastic region, i.e., $\varepsilon=0.02$, the large decrease of ϕ in the temperature region of 60 to 80°C is not observed: the $\phi-T$ relationship observed below 60°C is maintained in the higher temperature region.

In Fig. 7, as in Fig. 6, ϕ decreases linearly with increasing T except for $\varepsilon=0.04$ to 0.06; the slope of the linear relationship increases somewhat with increasing ε. With $\varepsilon=0.04$ to 0.06, ϕ increases with T giving convex curves for $\varepsilon=0.05$ and 0.06 and a concave curve for $\varepsilon=0.04$. With $\varepsilon=0.04$ to 0.06, the $\phi-T$ relationship behaves differently from the other strains, and this is again due to the reason mentioned for a similar observation in Fig. 6: the rate of increase of whitening ratio reaches a maximum in the vicinity of yield point. Since the position of the yield point varies with temperature, the above $\phi-T$ relationship is observed regardless of the strain rate. The slopes of the $\phi-T$ relationships in Fig. 7 are, in general, smaller than those in Fig. 6, indicating that the temperature dependence of the whitening ratio decreases with increasing strain rate.

Since the dependence of stress-whitening on ε is expected to differ from that of stress on ε, the relationship between ϕ and σ was examined with T as a parameter, as shown in **Figs. 8** and **9**. At a fixed temperature, ϕ slowly increases with σ up to a certain value of σ. The $\phi-\sigma$ curve then changes its direction toward smaller σ value (except of −20°C), while ϕ increases

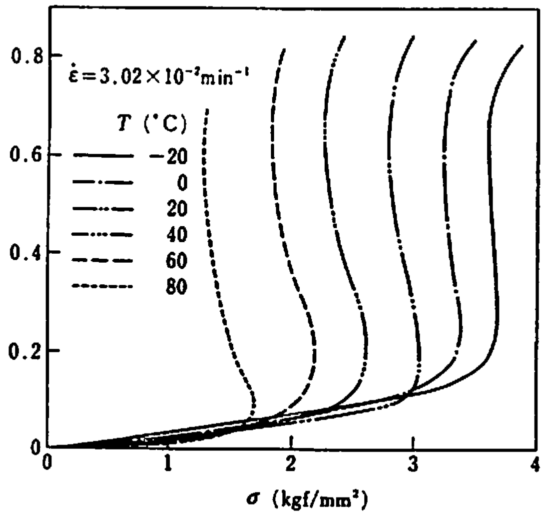


Fig. 8 Whitening ratio (ϕ)–tensile stress (σ) curves at various temperature (T); strain rate ($\dot{\varepsilon}$) $=3.02\times10^{-2}\ \mathrm{min}^{-1}$.

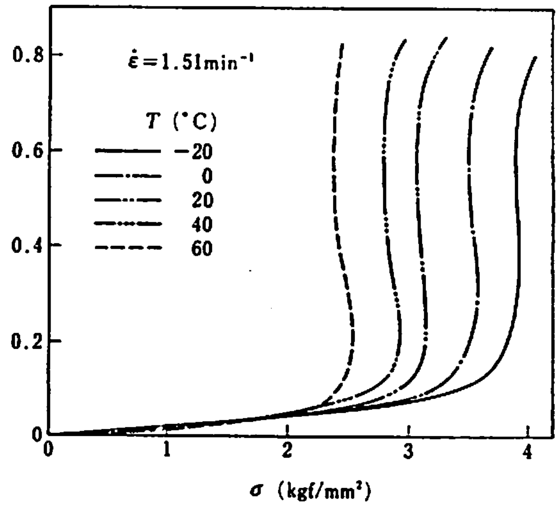


Fig. 9 Whitening ratio (ϕ)–tensile stress (σ) curves at various temperatures (T); strain rate ($\dot{\varepsilon}$) $=1.51\ \mathrm{min}^{-1}$.

rapidly. The maximum value of σ, at which the $\phi-\sigma$ curve changes its direction, corresponds to the yield point. The shape of the $\phi-\sigma$ curve is such that one obtains different values of ϕ for the same σ value in the elastic region near the yield point and in the plastic region: two or even than ϕ values, in some cases, are thus obtained. In the $\phi-\varepsilon$ relationship, the rate of increase of ϕ reaches a maximum in the yield strain region and decreases in the plastic region, while in the $\phi-\sigma$ curve ϕ shoots up almost vertically in the plastic region regardless of temperature. The rate of increase of ϕ thus becomes maximum in the plastic region when examined with respect to σ. The shape of the $\phi-\sigma$ curve after the yield point does not differ so much from temperature to temperature; the curves are arranged in the order of temperature. In the σ region where the $\phi-\sigma$ curve at -20°C enters the plastic region, the stress value giving the same ϕ is found to be larger, as the temperature is lower. At each temperature, ϕ reaches a maximum at rupture point.

The relationship between ϕ and T with σ as a parameter is shown in **Figs. 10 and 11.** For low strain rates and when σ is small, ϕ tends to decrease slightly with increasing T, as shown in Fig. 10. With $\sigma=$ca. 1.85 kgf/mm^2, ϕ decreases with increasing temperature up to around 20°C, and then increases as temperature rises further. With $\sigma=3.24$ kgf/mm^2, ϕ tends to increase with temperature, though only a few data are available on $\phi-T$ relationship at such a large value of σ. As clearly seen in the shapes of $\phi-\sigma$ curves shown in Figs. 8 and 9, fewer

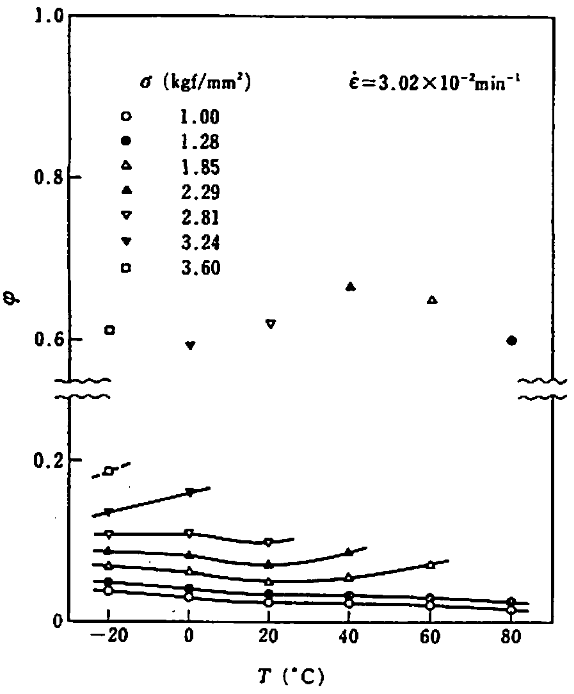


Fig. 10 Relationship between whitening ratio (ϕ) and temperature (T) at various tensile stresses (σ); strain rate ($\dot{\varepsilon}$) = 3.02×10^{-2} min^{-1}.

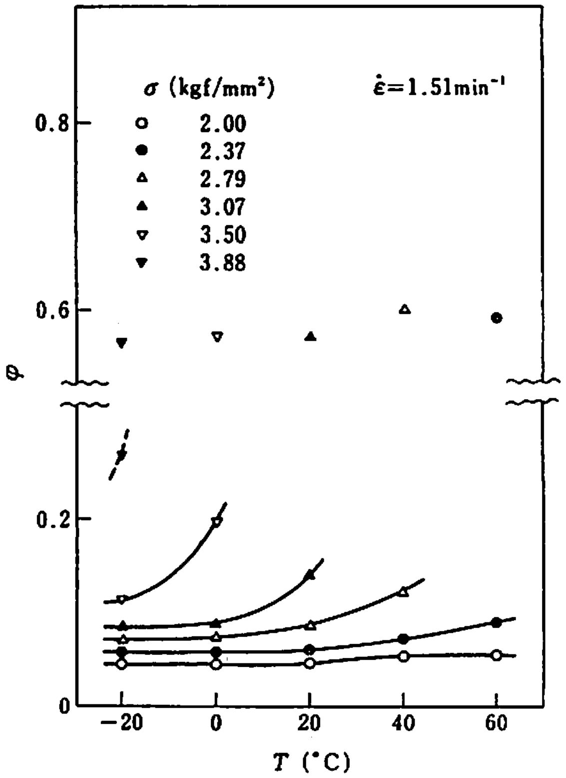


Fig. 11 Relationship between whitening ratio (ϕ) and temperature (T) at various tensile stresses (σ); strain rate ($\dot{\varepsilon}$) = 1.51 min^{-1}.

data on the temperature dependence of ϕ are obtained as σ becomes larger. Fig. 11 shows that for higher strain rates and the elastic region of σ the dependence of ϕ on T is also not very large. However, as σ is increased, ϕ begins to increase with temperature. In both Figs. 10 and 11, values of ϕ with different σ are plotted around ϕ=ca. 0.6 for each temperature; this is due to the shape of $\phi-\sigma$ curve shown previously with T as a parameter, that is ϕ increases rapidly as σ decreases after yield point, giving two ϕ values for each σ value. The larger of the two values is plotted here. Except for $\sigma=1.00$ and 2.00 kgf/mm², the data shown are those obtained when σ reaches a minimum in the plastic region.

3.2 Relaxation behavior of stress-whitening

In **Fig. 12** is shown the relationship between stress (σ) and time (t) as stress relaxation proceeds. The solid line indicates the $\sigma-t$ relationship obtained when tension is applied continuously. Each circle on hte solid line indicates a point where the tensile deformation was stopped to start stress relaxation. Each triangle, on the other hand, indicates the stress value after the strain at the circle was held constant for 10 min. The strain was then reversed and the square indicates the point where σ became zero as tension was removed from the triangle point △ at the same $\dot{\varepsilon}$ as that employed in applying tensile deformation.

The behavior of the stress relaxaiton, from ○ to △ depends on whether the starting point of stress relaxation is in the elastic region or in the plastic region. That is, when stress relaxation is started at the yield point (B) or in the plastic region (C, ..., F), the initial σ decreases fairly rapidly, but then slows down, giving a curve as shown in Fig. 12. Unlike those from B to F, stress relaxation from A in the elastic region gives a slower decrease of σ with t.

The $\sigma-t$ relationship (△ to □) observed as the tensile stress is removed after 10 min stress relaxation also depends on whether stress relaxation is started in the elastic region (A) or in the plastic region (B to F). In the former case, a linear $\sigma-t$ relationship is observed, while in the latter case σ initially decreases linearly with t, but then slows down to give a curve. The length of the linear part of the curve becomes longer as the starting point of stress relaxation moves closer to the yield point. In the $\sigma-t$ relationship starting from point A, no change in σ is observed after the square point is reached, i.e. σ stays zero. In the $\sigma-t$ relationship started

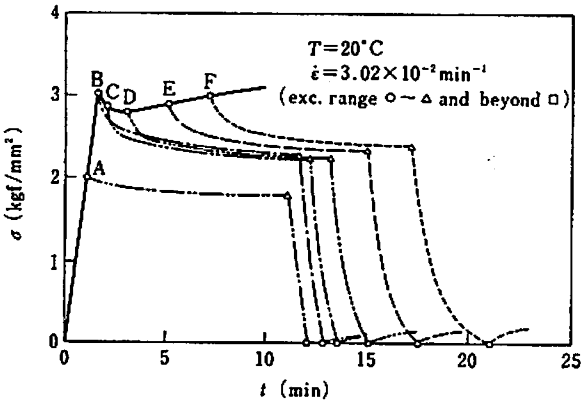


Fig. 12 Stress (σ)–time (t) curves at temperature (T) = 20°C; strain rate ($\dot{\varepsilon}$) = 3.02×10^{-2} min^{-1} (excepting range ○～△ and beyond □).

in the plastic region, on the other hand, σ increases again after having been reduced to zero at point □. The extent of this increase in σ is larger with increasing degree of plastic deformation. The above phenomenon seems to be caused by the "memory effect" of visco-elastic and visco-plastic materials[24].

Fig. 13 shows the relationship between the the whitening ratio ϕ and t during stress relaxation. The marks and letters correspond to those used in Fig. 12. When stress relaxation proceeds in the elastic region (A), ϕ does not change with t. On the other hand, in the post-yield-point plastic region (△ to □), ϕ changes with t. In case deformation is suspended at the yield point for stress relaxation, ϕ initially increases rapidly and then slows down to give a curve as shown. The $\phi - t$ relationship in the post-yield-point plasitc region give a lower rate of increase of ϕ than that starting from the yield point; the slope after the initial rise is also smaller as the deformation is larger, eventually giving a $\phi - t$ curve almost parallel to the t axis.

As seen above, the rise in ϕ just after the start of stress relaxaiton is maximum when relaxation is started from the yield point. At any rate, as relaxation proceeds in the plastic region, ϕ increases with time despite the fact that forced deformation has been suspended. That is, stress-whitening does not stop when deformation stops, but behaves as if it had "inertia". The observed "inertia" of stress-whitening in the plastic region is largest around the yield point and decreases as the plastic deformation increases; in the $\phi - t$ relationship started from F, only a little "inertia" is observed. In the case of elastic deformation, no such inertia of stress-whitening is observed.

The above observation is interpreted as follows: in the post-yield-point plastic region, crazes propagate after suspension of deformation, causing local yielding to be uniform. Thus the response to the suspension of deformation is delayed somewhat, resulting in the inertia-like behavior of stress-whitening. The fact that the increasing rate of ϕ during stress relaxation is maximum around the yield point corresponds to the observation that the $\phi - \varepsilon$ relationship with a continuous application of deformation gives the maximum rate of increase of ϕ around the yield point. The behavior at the yield point is thus extremely important in studying the mechanism of craze propagation in relation to stress-whitening.

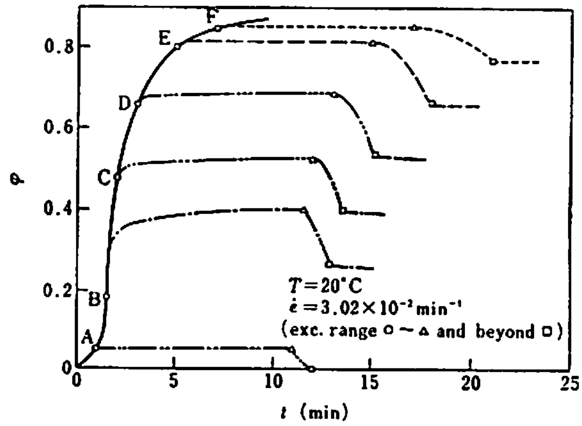


Fig. 13 Whitening ratio (ϕ)–time (t) curves at temperature (T) = 20°C; strain rate ($\dot{\varepsilon}$) = 3.02×10^{-2} min^{-1} (excepting range ○~△ and beyond □),

The shape of the ϕ—t curve, in the region where tensile deformation is removed after stress relaxation (△ to □) depends on the point where stress relaxation is started: the slope of the curve started from the point in elastic region is less than that of the curve started from the yield point, while the slope of the curve started in the plastic region beyond the yield point decreases with increase in amount of deformation at point ○. Thus, the shape of the ϕ—t curve changes around the yield point. After σ is brought to zero at point □, the ϕ—t curves, except for those started in the elastic region, show a slight decrease in ϕ despite the fact that σ increases as seen in Fig. 12. The extent of decrease in ϕ is smaller as the original plastic deformation is larger; the curve started from F shows practically no change in ϕ after point □. Also, no change in ϕ after point □ is observed in the curve started in the elastic region: ϕ just stays zero. Except for the latter case, fairly large amounts of whitening remain in the samples, confirming that stress-whitening can not be removed simple by removing the force applied from outside.

While the data on the time-dependent change of ϕ during stress relaxation up to $t=10$ min are shown in Fig. 13, the question that arises next is how ϕ behaves over a longer period of stress relaiton. This point was examined, and the results are shown in **Fig. 14**. Specimens at various temperatures were subjected to tension at a strain rate of $\dot{\varepsilon}=3.02\times10^{-2}\,\mathrm{min}^{-1}$; deformation was suspended at $\varepsilon=0.151$ to observe the change of stress-whitening with time. As in Fig. 13, an increase in ϕ occurs immediately after suspension of deformation due to the inertia of stress-whitening; this initial rise in ϕ gives a curve in the ϕ—t relationship as shown in Fig. 14. After the above period, the ϕ—t relationship becomes linear, almost parallel to the t axis up to $t=$ ca. 25 min; ϕ then tends to decrease gradually with time. As expected, the value of ϕ obtained in the above period is a function of temperature: the higher the temperature, the lower the value of ϕ. The shapes of the ϕ—t curves, however, are quite similar; when shifted vertically the curves roughly overlap with each other.

In **Fig. 15** is shown the time-dependent change of stress-whitening generated under the following conditions: specimens at various temperatures are subjected to tensile deformaiton at $\dot{\varepsilon}=3.02\times10^{-2}\,\mathrm{min}^{-1}$ up to $\varepsilon=0.151$; after being maintained at $\varepsilon=0.151$ for min, the deformation is recovered at $\dot{\varepsilon}=3.02\times10^{-2}\,\mathrm{min}^{-1}$ until σ becomes zero; then the lower grip is loosened to free the specimen. The shapes of the ϕ—t curves in Fig. 15 are considerably different from those in Fig. 14. In Fig. 15, ϕ decreases fairly rapidly in the initial period, regardless of the temperature. The decrease of ϕ then becomes linear with time. While in Fig. 14 the ϕ—t curves of different

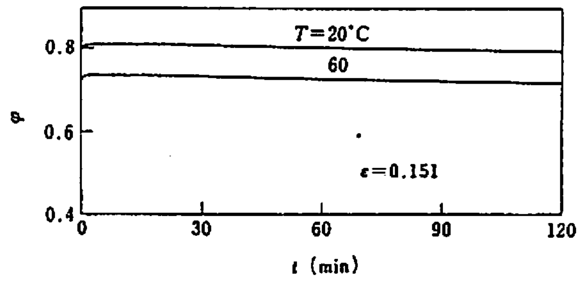


Fig. 14 Change in whitening ratio (ϕ) with time (t) under restrained state ($\varepsilon=0.151$) at various temperatures (T)

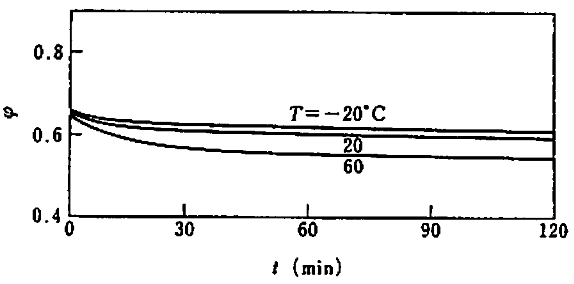


Fig. 15 Change in whitening ratio (ϕ) with time (t) under unrestrained state at various temperatures (T).

temperatures have similar shapes and thus overlap with each other if shifted vertically, the way ϕ behaves with t differs from one temperature to another up to around $t=$ca. 30 min in Fig. 15. After ca. 30 min, the shapes of $\phi-t$ curves become similar, and the curves in this region can be roughly superposed on each other if shifted vertically. The interval between the $\phi-t$ curve of $T=20°\mathrm{C}$ and that of $T=60°\mathrm{C}$ in the above region is small in Fig. 15 compared with the corresponding interval in Fig. 14. The above results indicate that the change of stress-whitening with time under restraint differs from that without restraint, and that the temperaure effect on the former is larger than that on the latter.

Figs. 16 and **17** show changes in ϕ when a stress-whitened specimen is heated. Fig. 16 shows the case where tensile deformation up to $\varepsilon=0.151$ was generated at $\dot{\varepsilon}=3.02\times10^{-2}\,\mathrm{min}^{-1}$ at 20°C to cause stress-whitening. After the deformation was maintained for 10 min, the specimen was heated at rate (v_T) of 1.52°C/min. The case shown in Fig. 17 is the same as that in Fig. 16 except that deformation, after being maintained for 10 min, was recovered at $\dot{\varepsilon}=3.02\times10^{-2}\,\mathrm{min}^{-1}$ till σ becomes zero. The lower grip was then loosened to free the specimen; heating at v_T is then started. Both Figs. 16 and 17 show that ϕ decreases with increasing temperature; in Fig. 16, the value of ϕ at 100°C approximately 0.21, which further decreases to zero in 2 to 3 min. In Fig. 17, ϕ reaches zero at a temperature lower than 100°C. The above observation indicates that the glass-transition temperature is around 100°C. Obtaining the $\phi-T$ curve, and thus the disappearance temperature of stress-whitening, by heating a whitened specimen without restraint seems to be applicable to measurement of the glass-transition temperatures of the micro-composite resins.

In comparison with Fig. 17, Fig. 16 shows a larger decrease in the rate of change of ϕ with respect to temperature up to $T=$ca. 80°C, indicating that stress-whitening disappears faster with respect to temperature increase if the samle is free of restraint. This seems to be due to the fact that an unrestrained specimen has a higher frequency of molecular motion and thus a larger polymer mobility. Stress-crazing is known to disappear at temperatures above the glass-

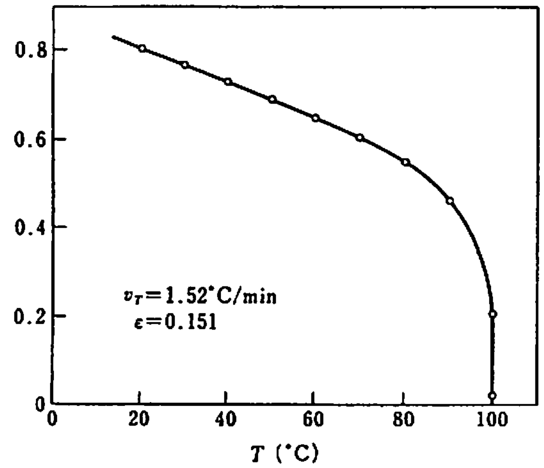


Fig. 16 Relationship between whitening ratio (ϕ) and temperature (T) in test of raising temperature in restrained state ($\varepsilon=0.151$); rate of heating (v_T) = 1.52°C/min.

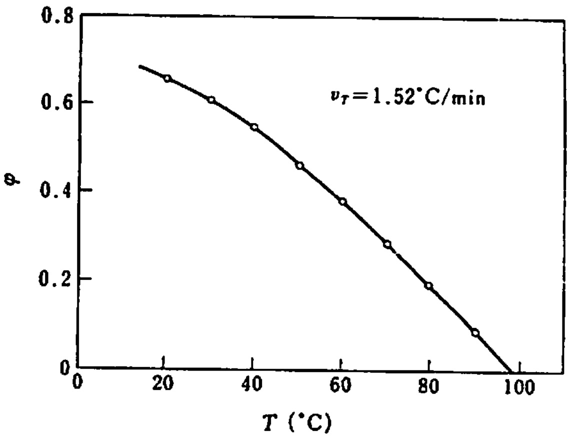


Fig. 17 Relationship between whitening ratio (ϕ) and temperature (T) in test of raising temperature in unrestrained state; rate of heating (v_T) = 1.52°C/min.

transition temperature. On the other hand little or no quantitative studies have been made below the glass-transition. Figs. 16 and 17 now show that stress-whitening decreases significantly even at temperatures below the glass-transition temperature.

In order to study whether or not the mechanical properties of the sample can be restored by heating the sample above the glass-transition temperature and thereby removing stress-whitening, we performed repeated tension application and removal of stress-whitening by the following two methods. The method employed in **Fig. 18**, designated as whitening removal method ①, involves applicaiton of tension to the specimen at 20°C at $\dot{\varepsilon}=3.02\times10^{-2}\,\mathrm{min}^{-1}$ for 5 min to cause deformation of $\varepsilon=0.151$, followed by stress relaxation for 10 min with ε maintained at 0.151; deformation is subsequently removed till $\sigma=0$ at $\dot{\varepsilon}=3.02\times10^{-2}\,\mathrm{min}^{-1}$. The whitened specimen is then taken out, heated at 100°C for 10 min to remove whitening, and then placed in an atmosphere of 20°C for about one hour. The second cycle is then carried out in the same manner; the third and subsequent cycles are also performed likewise. The number of repeated cycles is indicated as N_σ in Fig. 18. The method employed in **Fig. 19**, designated as whitening removal method ②, is the same as whitening removal method ① except for the way stress-whitening is removed. The whitened specimen is heated from 20°C to 100°C at $v_T=1.52$°C/min, maintained at 100°C for 10 min and then left to cool down to 20°C in the furnace.

As shown in Fig. 18, the yield point stress after the second tensile deformation (after whitening removal number $N_\phi=1$) is considerably smaller than that after the first tensile deformation. The curve itself shifts to a lower value of σ. In the post-point-B region, where deformation after stress relaxation is removed, the curves for the first and second tensile deformations are close to each other in the direction of the t axis; they cross each other when σ decreases further. The curve for the third tensile deformation shifts to a lower value of σ compared with that for the second tensile deformation; the degree of shift, however, is not so large as that found between the curves of the first and second tensile deformations. The specimen subjected to the third tensile deformation ruptured in the post-yield point region near point A.

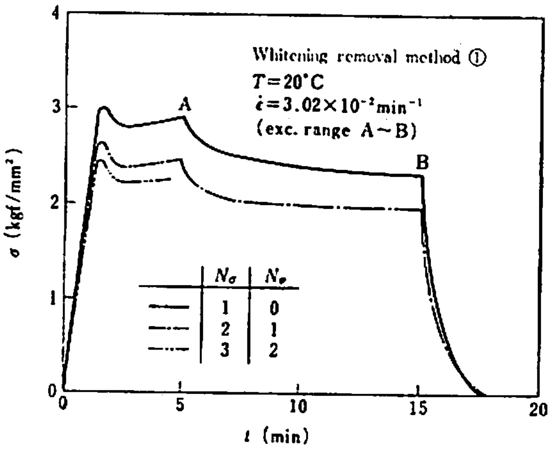


Fig. 18　Stress (σ)-time (t) curves in test of repeated "tension-whitening removal by method ①" at temperature (T) = 20°C; strain rate ($\dot{\varepsilon}$) = $3.02\times10^{-2}\,\mathrm{min}^{-1}$ (excepting range A～B).

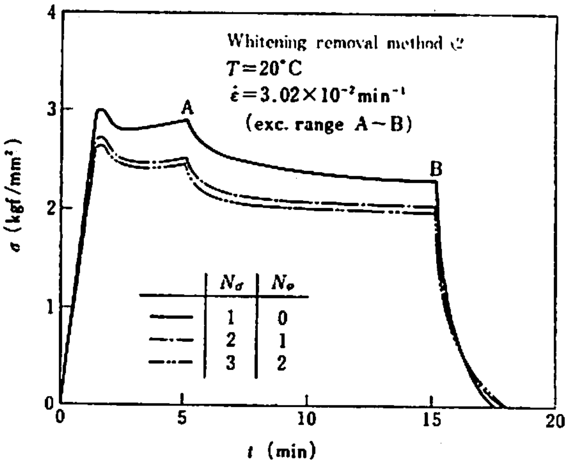


Fig. 19　Stress (σ)-time (t) curves in test of repeated "tension-whitening removal by method ②" at temperature (T) = 20°C; strain rate ($\dot{\varepsilon}$) = $3.02\times10^{-2}\,\mathrm{min}^{-1}$ (excepting range A～B)

In Fig. 19 also, the value of σ decreases considerably on going from the first to the second tensile deformation; the σ—t curve of the third tensile deformation, on the other hand, does not shift so much from that of the second tensile deformation. The specimen subjected to the third tensile deformation did not rupture. Comparison of Figs. 18 and 19 indicates that whitening removal method ① gives a larger dependence of σ on N_ϕ than whitening removal method ②.

As seen above, repetition of tensile application and whitening removal results in a considerable decrease in σ, while prior work[18] has shown that cyclic bending and whitening removal up to ca. 17 cycles does not cause specimen rupture nor lower the bending strength of the specimen. The above difference may be partly due to the difference in the way deformation is generated, i.e., tension vs. bending, but the difference in specimen material may also be responsible for it. It is hoped that future studies will clarify the relationship between the structure of the sample and the results of repetition tests such as those described here.

The ϕ—t curves corresponding to the σ—t curves of Figs. 18 and 19 are shown in **Figs. 20** and **21**. When t is in the elastic region, the value of ϕ for the second or third tensile deformation is smaller than that for the first tensile deformation (Fig. 20). In the region that follows, the ϕ—t curves cross each other, and their relative positions are reversed: the larger the number of tensile deformations, the higher the ϕ—t curves then cross each other for the second time, and arranged, from bottom to top, in the order of increasing number of deformations. These inversions of relative positions, observed also in Fig. 21, are due to the following reasons: the rate of increase of ϕ reaches a maximum around yield point, regardless of the number of tensile deformations; the rate of increase of ϕ becomes larger as the number of tensile deformations decreases; and the position of the yield point varies with the number of tensile deformations. Therefore, even when the σ—t curve of a larger number of tensile deformations reaches its

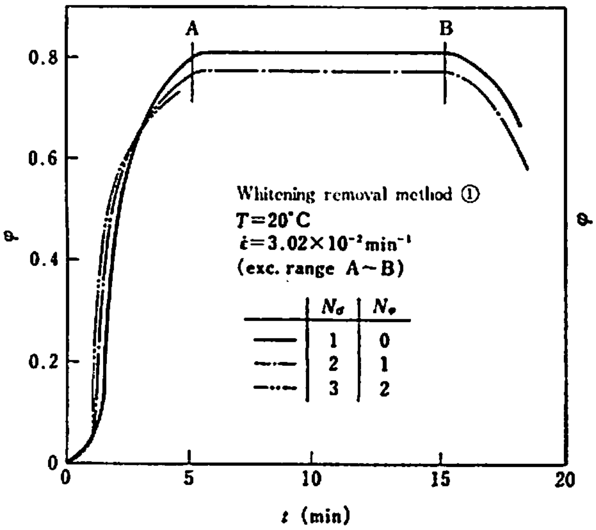


Fig. 20 Whitening ratio (ϕ)-time (t) curves in test of repeated "tension-whitening removal by method ①" at temperature (T) = 20°C; strain rate ($\dot{\varepsilon}$) = 3.02 × 10^{-2} min^{-1} (excepting range A～B).

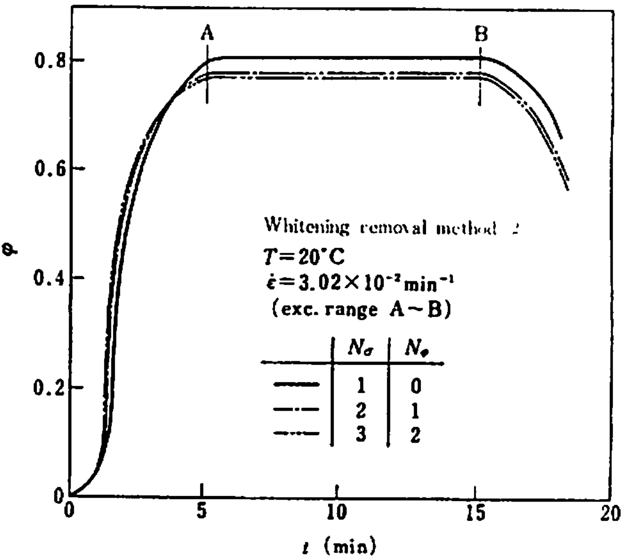


Fig. 21 Whitening ratio (ϕ)-time (t) curves in test of repeated "tension-whitening removal by method ②" at temperature (T) = 20°C; strain rate ($\dot{\varepsilon}$) = 3.02 × 10^{-2} min^{-1} (excepting range A～B).

yield point, that of fewer number of deformations has not reached it yet. Accordingly, the $\phi - t$ curve of a large number of tensile deformations rises ahead of that of fewer number of tensile deformations and locates itself above the latter, causing the first inversion of relative positions. The rate of increase of ϕ after the yield point, on the other hand, is larger as the number of tensile deformations is smaller: ϕ of a smaller number of tensile deformations eventually exceeds that of a larger number of tensile deformations, giving the second inversion of relative positions. As seen above, the yield point has a great significance in stress-whitening behavior. Similar inversion phenomena in the $\phi - \varepsilon$ relationship with temperature as a parameter can be interpreted similarly; a higher temperature in the $\phi - \varepsilon$ relationship corresponds to a large number of tensile deformation in the $\phi - t$ relationship.

As seen in Figs. 20 and 21, ϕ changes little with time during stress relaxation (A to B) except in the initial period; the value of ϕ during this period is smaller for the sample with a larger number of tensile deformations. The same is observed after point B. Fig. 21 gives $\phi - t$ curves similar in shape to those of Fig. 20; however, in the elastic region, practically no change of ϕ with the number of tensile deformations is observed, and the $\phi - t$ curves in the post-yield-point region are more closely arranged than those in Fig. 20. Further comparison of Fig. 20 and 21 indicates the following difference between the two whitening removal methods ① and ②: a larger decrease of ϕ for each tensile deformation cycle is obtained with a specimen rapidly heated to the glass-transition temperature to remove stress-whitening and then rapidly cooled down to room temperature (20°C) (method ①) than with a specimen gradually heated and then gradually cooled (method ②). Also, the number of the tensile deformaiton cycles repeatable before rupture occurs seems to be larger with method ② than with method ①.

4. Conclusions

The following points have been brought to light as a result of our quantitative measurement of whitening ratio in a microcomposite thermoplastic, high impact polystyrene.

(1) There are changes in the whitening ratio not observable with the naked eye in the elastic region. The whitening in the elastic region disappears when the stress and strain are reduced to zero.

(2) The rate of increase of whitening ratio increases with strain and reaches a maximum around the yield point (the peak) for each temperature. The rate of increase of whitening ratio becomes larger as the temperature is lowered. At a fixed temperature, the whitening ratio reaches its maximum at the rupture point.

(3) In the low strain region, below the yield point, the whitening ratio-strain curve for a lower temperature is located above that for a higher temperature. As the curve enters the corresponding yield strain region, which occurs earlier for a higher-temperature specimen, an inversion of the relative positions of the curves takes place. As strain is increased further, yet another inversion is observed. These inversions are due to the following: the ract of increase of whitening ratio becomes maximum in the yield strain region, the increase rate is higher as temperature is lower, and the position of the yield point varies with temperature.

(4) As strain rate is lowered, the temperature dependence of whitening ratio becomes larger. The dependence of whitening ratio on strain differs greatly from that on stress.

(5) When tensile deformation in the elastic region is subjected to stress relaxation, no change in ϕ is observed. When stress relaxation is started in the post-yield-point region, stress-whitening does not stop with deformation, but behaves as if it had "inertia". This stress-whitening "inertia" is maximum with the original deformation around the yield point and decreases as the deformation increases.

(6) The change of stress-whitening with time varies in shape depending on whether the specimen is restrained or free the temperature dependence is larger with a specimen under restraint.

(7) Whn a whitened specimen is heated, a decrease in whitening ratio is observed even at temperatures below the glass-transition temperature. Up until ca. 80°C, the rate of decrease of stress-whitening is higher with an unrestrained specimen than with a restrained specimen.

(8) The decrease of stress-whitening for each tensile deformation-whitening removal cycle is smaller with a specimen gradually heated to the glass-transition temperature to remove whitening and then gradually cooled down to room temperature than with a specimen rapidly heated and rapidly cooled.

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