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〈연구논문〉

알킬벤젠술폰산나트륨을 함유하는 폴리프로필렌의 유변학적 성질 및 함유물의 용출성

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Rheological Properties of Polypropylene Containing Sodium Alkylbenzenesulfonate and the Elution Property of the Ingredient

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요 약

Sodium octylbenzenesulfonate(SOBS)와 sodium dodecylbenzenesulfonate(SDBS)를 폴리프로필렌(PP) 용융액에 각각 균일하게 서로 다른 함량으로 섞어 넣은 후에 용융압착법으로 PP 필름을 제조하였다. 저장 점성도(η′), 저장탄성률(G′) 및 손실탄성률(G″)을 진동식 레오미터를 사용하여 170~195℃에서 측정하였다. 실험온도 범위 내에서 첨가제를 함유한 PP와 순 PP간에 Cole-Cole 플롯(G′에 대한 G″의 log-log 플롯)에는 차이가 없었다. 그러나 광범위한 전단속도에서 SOBS의 첨가량이 8%를 넘어서면서 η′과 G′은 증가하였다. 이러한 현상은 PP 중에서의 첨가제의 응집효과로 설명되었으며 이것은 SOBS와 SDBS를 함유하는 PP 필름의 시차 주사열량법 및 주사전자현미경 관찰결과로 확인되었다. SDBS를 8% 미만 함유하는 PP로부터 섬유의 용융방사가 가능하였으나 SDBS 3% 이상 함유 PP 방사섬유는 연신 과정 중에 섬유의 절단이 이따금 일어났다. PP 기질내에 있어서의 SDBS의 뜨거운 물에 대한 견뢰성을 SDBS와 C. I. Basic blue 41 사이의 이온결합 형성 거동에 바탕을 두어 가시분광법에 의하여 검토하였다.

Abstract—Sodium octylbenzenesulfonate (SOBS) and sodium dodecylbenzenesulfonate (SDBS) were added to the polypropylene (PP) melt, and several PP films with different quantities of these additives were prepared by a melt press method. The storage viscosity (η′), storage modulus (G′), and loss modulus (G″) were measured in a temperature range of 170~195℃ on an oscillating rheometer. No differences between the modified Cole-Cole plots (log-log plot of G″ against G′) for the PP containing additives and that for the pure PP were found in the whole temperature range. However, it was recognized that in a wide shear rate region, both the η′ and G′ of the PP containing SOBS increased as the content of SOBS exceeded ca. 8 wt%. This fact was explained as an aggregation effect of the additives in the PP substrate, while the point of view was supported by differential scanning calorimetric and scanning electron microscopic observations for the films of the PP containing SOBS and SDBS. The filament was spun successfully from the polymer melt with the content of SDBS less than 8 wt%, but fracture of the filament occasionally occurred during the drawing of the one with more than 3 wt% SDBS content. Finally, the hot water fastness property of the SDBS in the PP substrate was examined

by a visible spectroscopy on the basis of the ionic bond formation behavior between SDBS and C. I. Basic blue 41.

Keywords: Polypropylene, Sodium alkylbenzenesulfonate, Rheological property, Melt spinning.

1. Introduction

Since the synthesis method of polypropylene (PP) was developed by Natta, numerous studies to improve dyeability have been continued as the demand of PP increased. For this purpose, when the additives containing dyeable sites are added to PP [1, 2], the influence of the additive on the physical properties of the polymer is very important. In general, the filled polymers are multi-component and multi-phase systems. Such systems display a rather complex set of properties owing to the peculiarities of its polymer structure. In particular, rheological properties vary with the property of filled particles as well as the amount of the filler. Consequently, lower spinnability, decreased strength and other problems may occur.

In the present study, the rheological properties of the PP containing sodium octylbenzenesulfonate (SOBS) and sodium dodecylbenzenesulfonate (SDBS) were examined. In addition, the hot water fastness property of the SDBS in the PP substrate was also tested.

2. Experimental

2.1. Materials and reagents

Isotactic PP was supplied by Honam Petrochemical Ind. Co. Ltd. with the following specifications: grade, AR 160; melt index, 38.6 g/10 min.; density, 0.90 g/cc; melting point (m.p.), 160℃. SOBS (m.p., 275℃) and SDBS (m.p., 125℃) were purchased from Aldrich Chem. Co. and Tokyo Kasei Ind. Co., respectively.

2.2. Preparation of samples

SOBS or SDBS was mixed mechanically with PP in a tube and melted under nitrogen flow for 20 min. at 180℃. Several PP films with different amounts of these additives were prepared by a hot pressing method at 180℃ and quenched immediately in a cold water.

2.3. Differential scanning calorimetric analysis

A differential scanning calorimeter (Model 1090; du Pont) was used to obtain the data for the thermal behavior of the PP film containing SOBS or SDBS. The measurements were carried out with a heating rate of 20℃/min. in the temperature range of 25～300℃.

2.4. Rheological property measurements

The rheological properties of the PP films containing SOBS or SDBS were tested by using an oscillating rheometer (Rheometrics Dynamic Spectrometer Model 7700). The measurements were carried out at 175～195℃ with a temperature interval of 5℃ and a shear rate range of 0.1～100 rad/sec. From these measurements, storage viscosity (η'), storage modulus (G'), and loss modulus (G'') were obtained.

2.5. Scanning electron microscopic observation

The fracture surface of the films were observed by using a scanning electron microscope (JEOL; Model JSM-35).

2.6. Glass transition temperature analysis

Glass transition temperature (T_g) of the film was measured by using a Rheovibron DDV-II-C (Toyo Baldwin Co. Ltd.) with a temperature range of −150～150℃ and a heating rate of 3℃/min. at 110 Hz. From the measurment results, the storage tensile modulus (E') and tanδ were obtained.

2.7. Spinning

SDBS of industrial grade was purified. In order to remove Na_2SO_4 from the SDBS, excess methanol was added to the SDBS and filtered several times using very dense stainless steel meshes. After drying at 80℃ in a vacuum oven, the purified SDBS was mixed with 1.5% (wt.) of liquid

paraffin and treated at 100~110℃ for 5 hrs. to remove water from the SDBS. After PP has been uniformly mixed with the prepared SDBS, the PP fiber with 900 den./90 fil. was spun using the experimental spinning machine with a nozzle of 0.8 mm diameter. The spinning temperature was 220 ℃ and the draw ratio was 4.2. Three kinds of PP filaments with contents of 2.00, 2.75, and 3.00% of SDBS were prepared, respectively.

2.8. Spectroscopic measurement

The PP filament was dyed with C. I. Basic blue 41 at pH 4.5 and in a liquor ratio of 1:50. After completing the dyeing, soaping was performed at 80℃ for 20 min. using 1 g/l of detergent. The absorbance curve of the residual dyeing solution was obtained using a spectrophotometer (Macbeth CE-3000, Kollmorgen Instruments, U.S.A.). The reflectance of the dyed PP filament was also measured.

3. Results and Discussion

3.1. Thermal behavior

The thermal behavior of the PP film containing SOBS or SDBS was followed by differential scanning calorimetry (DSC). From the results of the DSC analysis, the melting temperatures of PP, SOBS, and SDBS were found to be 160℃, 275℃, and 125℃, respectively. In the case of the PP/SOBS mixture, as the content of SOBS exceeds 8%, the melting peak of SOBS appeared at 275℃ in a phase separation behavior (Fig. 1). However, the PP/SDBS mixtures did not show any additional melting peak and it was suggested that since the SDBS has a longer aliphatic chain length than SOBS it was more compatible with PP.

3.2. Rheological behavior

G′, G″, and η′ were measured in a temperature range of 170~195℃ at different shear rates. Fig. 2 and Fig. 3 show the dependence of η′ and G′ on temperature. It was shown that η′ and G′ decreased with increasing temperature independently of the additives, showing the same tendency as the pure PP. However, the PP/SOBS mixture had hi-

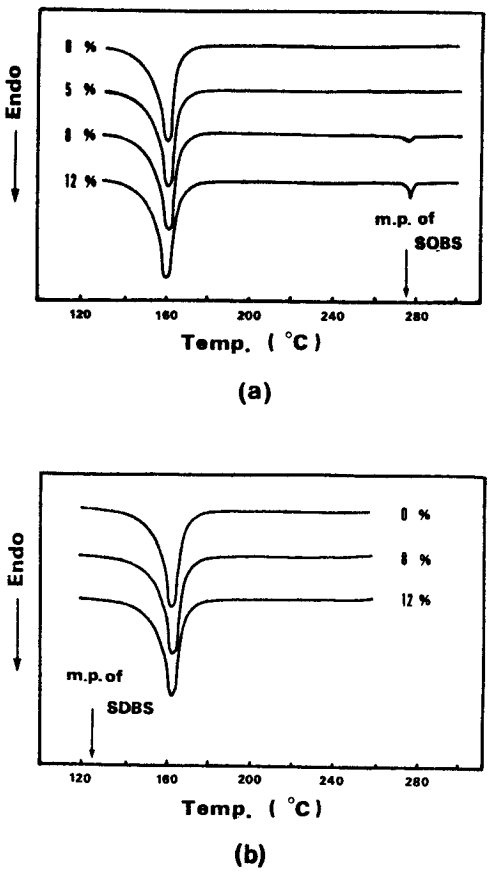


Fig. 1. DSC thermograms for PP, PP/SOBS (a), and PP/SDBS (b).

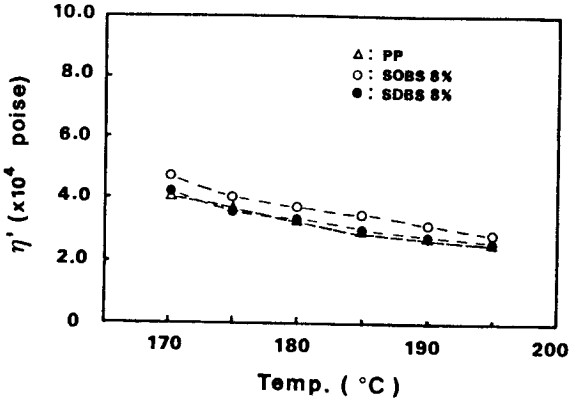


Fig. 2. Dependence of storage viscosity (η′) on temperature for the PP containing sodium alkylbenzenesulfonate at the shear rate of 1.0 rad/sec.

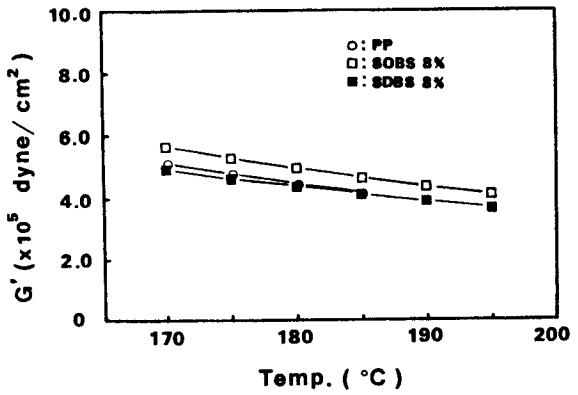


Fig. 3. Dependence of storage modulus (G′) on temperature for the PP containing sodium alkylbenzenesulfonate at the shear rate of 100.0 rad/sec.

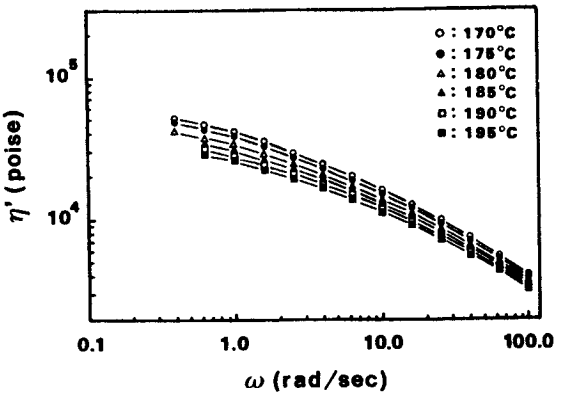


Fig. 4. Dependence of storage viscosity (η′) on shear rate (ω) for the pure PP.

gher η′ and G′ values than those of the pure PP.

In general, to examine the structural characteristics of the filled polymer, the shear rate-viscosity relation and the modified Cole-Cole plot (log G′-log G″) are used. From the shear rate-viscosity relation, the differences in the molecular weight distribution and the degree of the branching of the polymers having similar molecular structure and molecular weight, can be evaluated [3, 4]. The analysis of the molecular weight distribution is based on the concept that the viscosity at low frequencies is dominated by the relaxation process of long chain, while the viscosity at high frequencies corresponds to that of the small molecules [5]. Therefore, the differences in the shape and magnitude of the viscosity curves can be the quantitative description of the molecular weight distribution. On the other hand, using the modified Cole-Cole plot, structural information such as the existence of branch or crosslinking, the variation of the molecular weight distribution, the chain scission, and the formation of branched structure can be easily analyzed by the shape of the plots and the degree of deviation from a straight line, since the plots for linear polymers became a straight line [6, 7]. In Figs. 4-6, it is shown that the η′ of the pure PP, the PP/SOBS mixture, and the PP/SDBS mixture, decrease gradually with an increase in shear rate, and even in the Newtonian

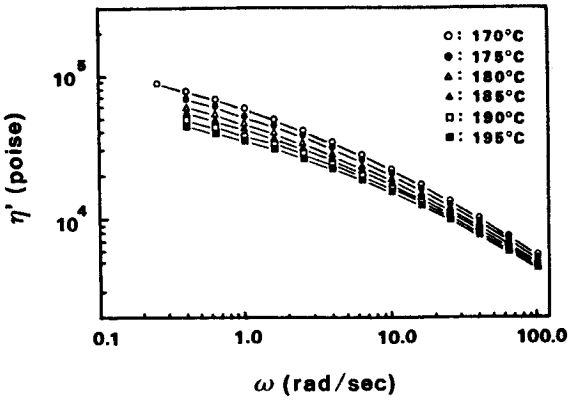


Fig. 5. Dependence of storage viscosity (η′) on shear rate (ω) for the PP containing SOBS 18%.

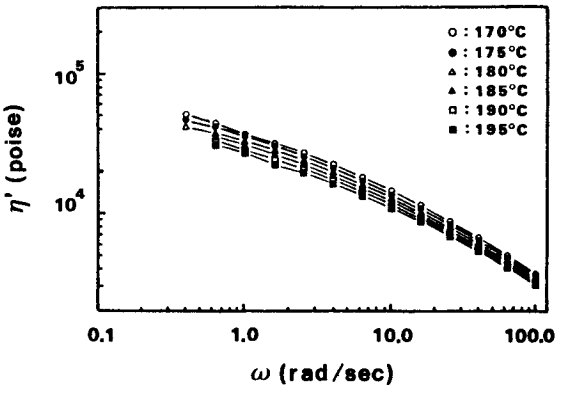


Fig. 6. Dependence of storage viscosity (η′) on shear rate (ω) for the PP containing SDBS 18%.

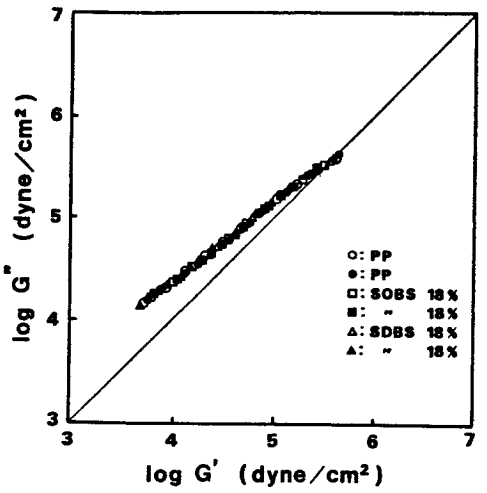


Fig. 7. Modified Cole-Cole plots for the pure PP, PP/SOBS and PP/SDBS at 175℃ (open) and 195℃ (closed).

flow region of a lower shear rate, the flow curves of the PP/SDBS mixture are very similar to those of the pure PP, suggesting that the structural change of the PP/SDBS mixture due to the structure formation of the additive did not occur. Contrary to this, the PP/SOBS mixture showed a somewhat different behavior in the shear rate-viscosity relation from that of the pure PP, exhibiting higher η' values in comparison with those of the pure PP. However, the modified Cole-Cole plots(Fig. 7) showed that all data points including those for the PP/SOBS mixture are found on a straight line.

3.3. Concentration dependence

In the case of a concentrated suspension in the range of sufficiently high concentrations, the rigid filler particles suspended in the polymer form a structure which possesses a certain strength. If there is no specific interaction between the particles, a pseudo-structure may be formed as a result of their mechanical contacts. Therefore, at high rates of shear such a composition behaves as a liquid, but below a certain stress limit the composition behaves as a solid-like body [8]. A direct evidence of the increase of the rigidity of the polymer when it is loaded with a filler is the increase of G', with increasing filler content [9].

The dependence of η' and G' on the concentration of the additive is shown in Figs. 8-13. As shown in figures, the viscosity and the modulus do not change significantly in the lower concentration of the additives. This suggests that the additive in the PP melt does not impede the flow of PP, because of the uniform dispersion of the additive particles. However, in the case of the PP/SOBS composition, as the concentration of the additive exceeds 8%, the viscosity and the modulus increased abruptly. These results imply that the presence of the structural skeleton of the additive particles or its fragment (aggregated particles) impedes the manifestation of the viscoelasticity of PP and induces higher stress than that necessary for the same development of deformation as produced in the pure PP. On the other hand, in the case of the PP/SDBS mixture, the viscosity and the modulus did not change even at the higher concentrations of the additive. It was thought that SDBS dispersed uniformly throughout the PP matrix even at the higher concentrations. These differences between SOBS and SDBS may be explained as the phenomenon due to the difference in melting temperature. Since the melting temperature of SDBS is lower than the mixing temperature, the SDBS in liquid state is mixed uniformly with PP. However, SOBS has a higher melting temperature and the solid particles of SOBS are mixed unevenly with PP. Therefore, the SOBS particles aggregate more easily than that of SDBS.

The surfaces of the PP films with different amounts of SOBS or SDBS are shown in Fig. 14. In the PP/SOBS mixture, with a 8% concentration of SOBS, some aggregated particles of SOBS appeared as a form of a laminated layer which might be caused by the pressure during the film preparation. At higher concentrations, the aggregation of SOBS could be seen throughout the whole surface and the size of the particles became larger. On the other hand, as for the PP/SDBS mixture, the aggregation was not significant even at higher concentration and the phase boundary between PP and SDBS was unclear.

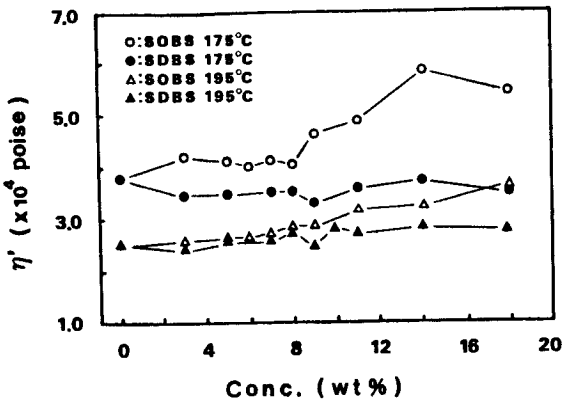


Fig. 8. Dependence of storage viscosity (η′) on the concentration of additive at 1.0 rad/sec.

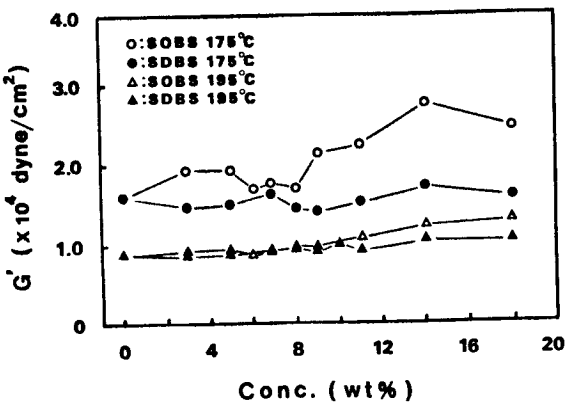


Fig. 11. Dependence of storage modulus (G′) on the concentration of additive at 1.0 rad/sec.

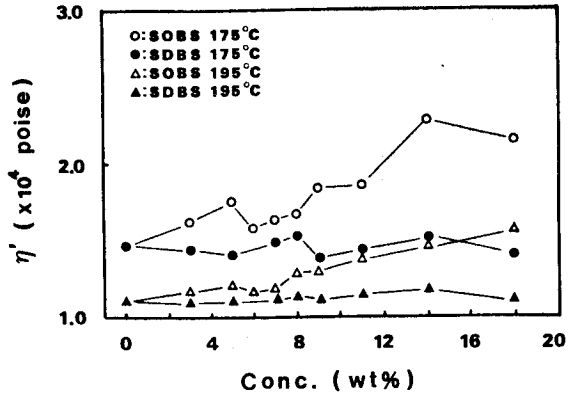


Fig. 9. Dependence of storage viscosity (η′) on the concentration of additive at 10.0 rad/sec.

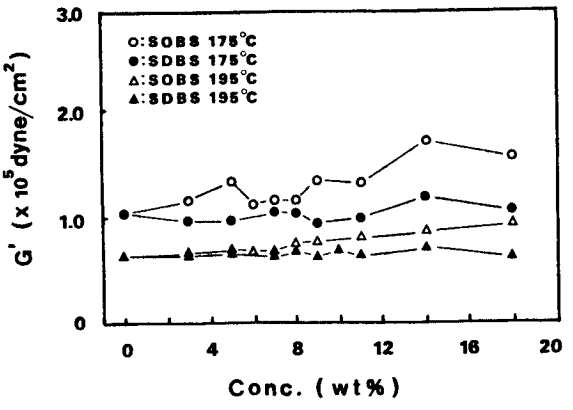


Fig. 12. Dependence of storage modulus (G′) on the concentration of additive at 10.0 rad/sec.

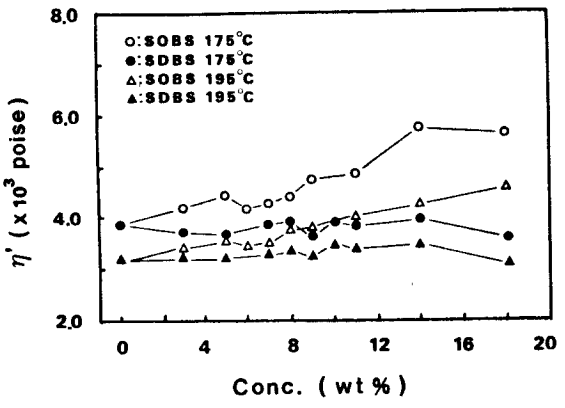


Fig. 10. Dependence of storage viscosity (η′) on the concentration of additive at 100.0 rad/sec.

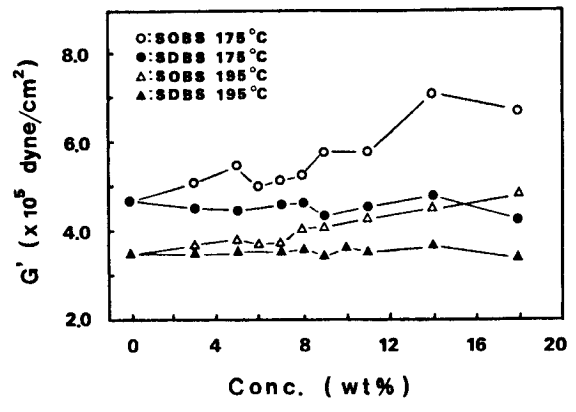
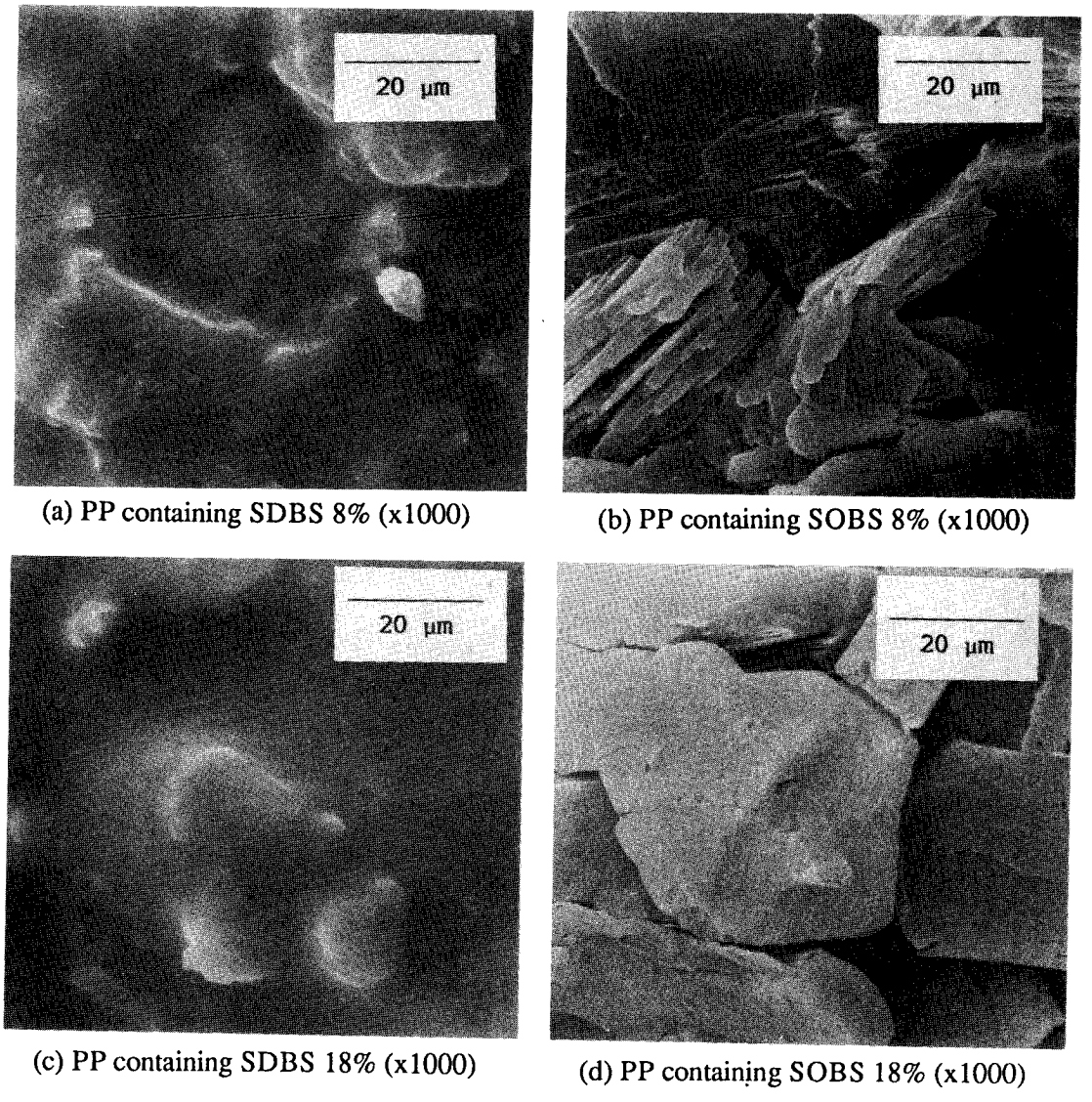


Fig. 13. Dependence of storage modulus (G′) on the concentration of additive at 100.0 rad/sec.



(a) PP containing SDBS 8% (x1000)

(b) PP containing SOBS 8% (x1000)

(c) PP containing SDBS 18% (x1000)

(d) PP containing SOBS 18% (x1000)

Fig. 14. Scanning electron microscopic photographs.

3.4. Glass transition behavior

T_g of a polymer is affected by many factors. In general, some additives in a polymer shift the T_g of the polymer by altering the mobility or chain packing of the polymer [10]. It is a well known fact that the relaxation temperatures of crystalline region (α_c), amorphous region (α_a), and the β part of PP are 110℃, 10℃, and −60℃, respectively. In particular, the α_a relaxation is related to the micro-brownian motion of the amorphous region and it is important in the view point of finishing, dyeing, and other manufacturing process. From Fig. 15 and Fig. 16, in which the points corresponding to each characteristic temperature appeared, it is confirmed that the relaxation behavior of PP containing the additives is not different from that of pure PP, in spite of the partial differences of curves between pure PP and PP/additive mixtures.

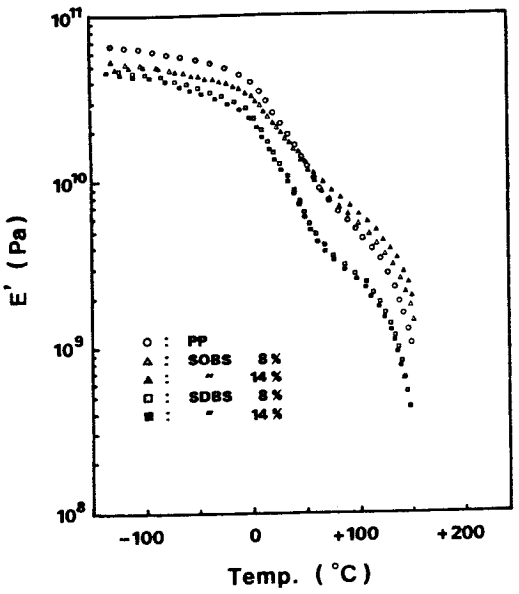


Fig. 15. Effect of additives on the tensile storage modulus (E′) of PP.

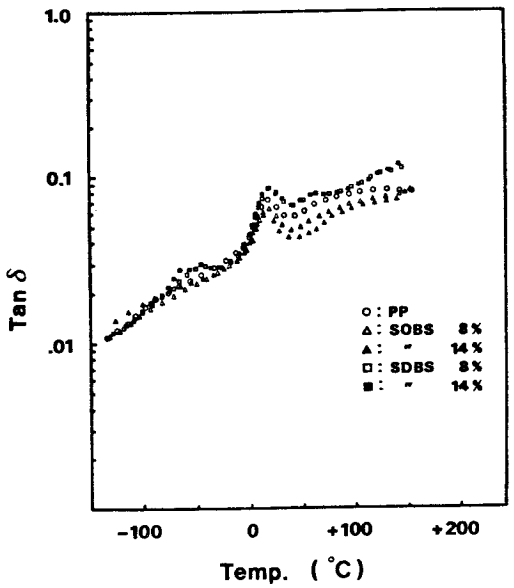


Fig. 16. Effect of additive on the tanδ of PP.

3.5. Spinning

For experimental convenience, the PP fiber spinning was carried out tentatively at 220℃. At any content, the spinning of the PP/SDBS mixture was possible at this temperature. Fig. 17 is a photograph of spinning process of PP containing SDBS 6%. However, some filaments were partially fractured in the case of 3% SDBS content during the drawing. Accordingly, it was thought that the optimum content of SDBS is between 2.75% and 3.00 %. The trial of spinning seemed to be satisfactory, but it was considered that a further systematic examination at the varied temperatures must be necessary in order to obtain the complete spinning results.

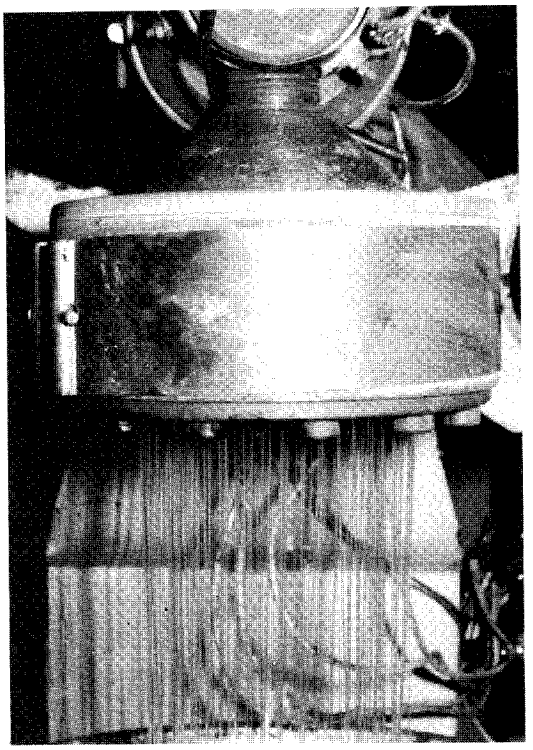


Fig. 17. Photograph of spinning process of PP containing SDBS 6%.

3.6. Elution property of SDBS

Because SDBS is not only soluble in water, but also melted at a low temperature (m.p. 125℃), it is considered that SDBS in PP may be eluted from PP easily into water at high temperatures. Fig. 18 shows the effect of SDBS on the absorbance curve of C. I. Basic blue 41 solution, which has a maximum absorbance peak at 600 nm. However, as the content of SDBS increased, the ab-

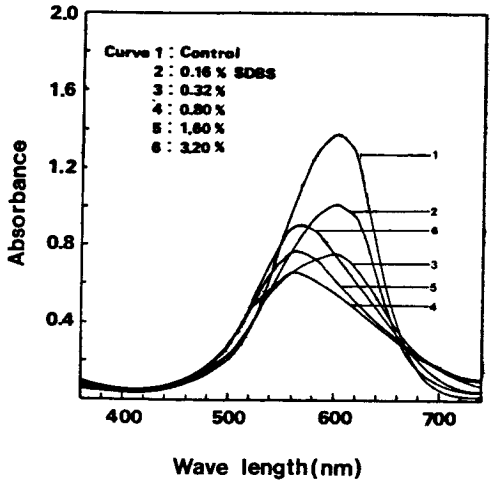


Fig. 18. Effect of SDBS concentration on the absorbance curve of 0.22% C. I. Basic blue 41 solution.

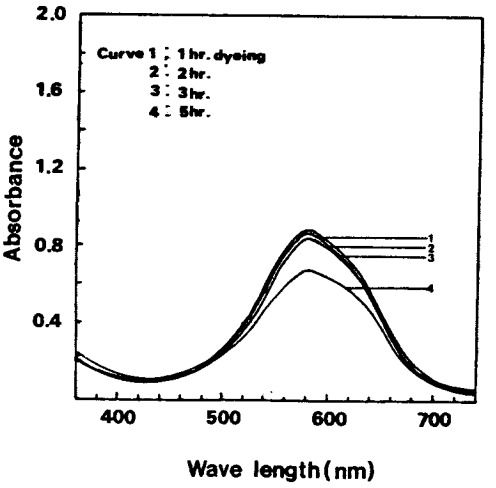


Fig. 20. Absorbance curves of residual dyeing solution of C. I. Basic blue 41 after dyeing with different times at 120℃.

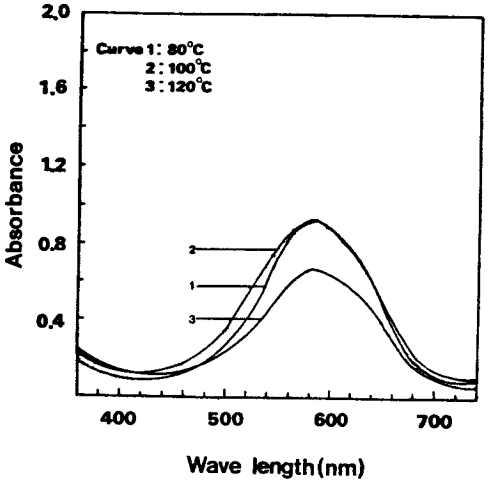


Fig. 19. Effect of dyeing temperature on the absorbance curve of residual dyeing solution of C. I. Basic blue 41 after 5 hrs. dyeing of the PP containing 3% of SDBS.

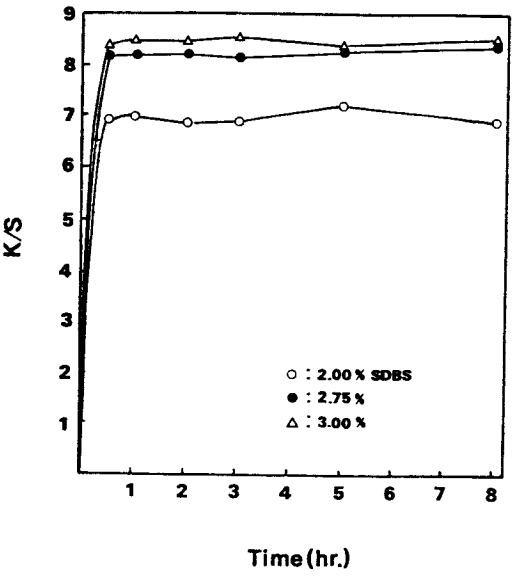


Fig. 21. K/S curves of the PP containing SDBS dyed with C. I. Basic blue 41 at 80℃.

sorbance decreased and the curve became broad. When the content of SDBS increased further, the maximum absorbance peak shifted to the short wave length, 560 nm, and the absorbance increased again. This phenomenon is considered to be attributed to the hypsochromic effect by the ionic bonding between SDBS and the dye. With the increment of the SDBS content, the number of the ionic bonding between SDBS and the dye increases and as a consequent the absorbance increases again.

The absorbance curves of C. I. Basic blue 41 residual solution after the dyeing of PP containing 3% of SDBS are shown in Fig. 19 and Fig. 20. Comparision of Fig. 19 and Fig. 20 with the reference curve, Fig. 18, reveals that at the same dyeing

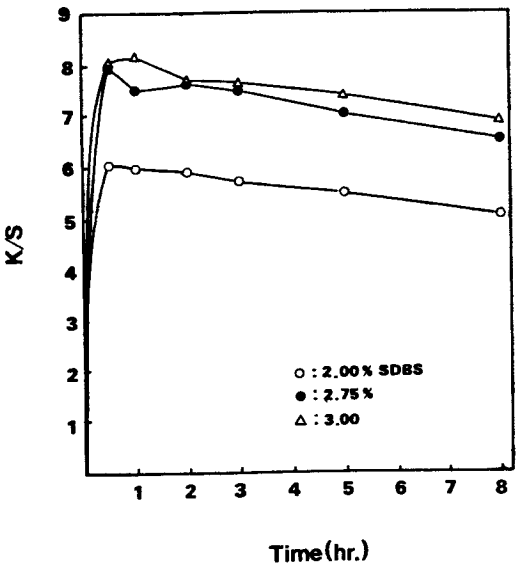


Fig. 22. K/S curves of the PP containing SDBS dyed with C. I. Basic blue 41 at 100℃.

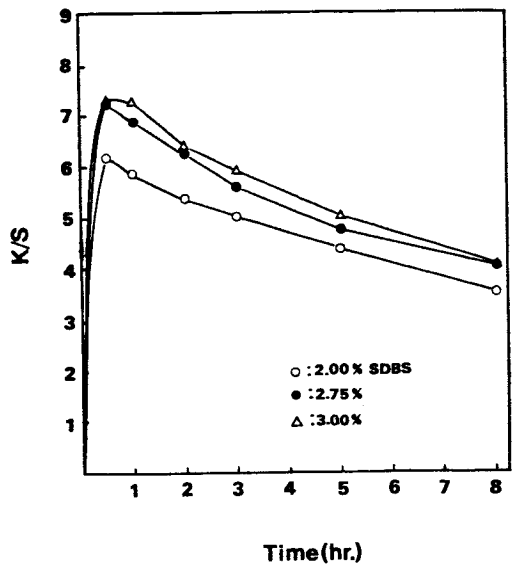


Fig. 23. K/S curves of the PP containing SDBS dyed with C. I. Basic blue 41 at 120℃.

time SDBS in PP easily elutes into the dye bath in proportion to the dyeing temperature, and at the same dyeing temperature SDBS elutes in proportion to the dyeing time. However, considering that in Fig. 19 and Fig. 20 the maximum absorbance peak does not shift, it is thought that the absolute elution rate of SDBS is not very high after dyeing at lower temperature for 5 hrs.

Using the Kubelka Munku equation, K/S values were calculated from the reflectance values of the PP/SDBS filaments dyed with C. I. Basic blue 41, and these were plotted against the dyeing times in Figs. 21-23. It is shown that as the dyeing temperature rises, the K/S value decreases steeply, agreeing with the above absorbance results. Accordingly, it becomes evident that SDBS in PP is able to fully withstand hot water of 80℃.

4. Conclusions

PP was mixed with sodium alkylbenzenesulfonate in order to improve its dyeability. The dependence of the storage viscosity and the storage modulus on temperature for the PP containing a small amount of the additive was almost similar to that of the pure PP. The decreasing behavior of the storage viscosity with increasing shear rate and the modified Cole-Cole plots results suggested that the morphological changes caused by the additives were not large. However, it was characterized by thermal analysis that as the content of the additive increased, the phase separation between PP and SOBS occurred. In addition, beyond a certain concentration of SOBS the storage viscosity and storage modulus of the polymer increased simultaneously, and this was considered to be due to the impediment of the aggregated particles of the additives to the flow of PP. The aggregated particles were observed by using a scanning electron microscope for both the PP/SOBS and PP/SDBS mixtures. The aggregation of SDBS was not significant in comparison with SOBS. The phase boundary between PP and SDBS was more continuous than that between PP and SOBS. This fact suggested that SDBS dispersed more evenly in PP than SOBS due to its lower melting temperature. The glass transition behavior of the PP/additive mixture was not affected by the additive. The spinning of PP some containing SDBS was achieved successfully, but filaments were fractured partially in the case of 3% content of SDBS when

it was drawn. It was found that the SDBS in PP was eluted into water beyond 80℃, and this was verified by the spectroscopic analysis of the PP /SDBS filament dyed with C. I. Basic blue 41 and the exhausted dye bath.

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