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可塑劑와 加工助劑가 PVC의 流性學的特性 및 物性에 미치는 影響

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Effects of Plasticizer and Processing Aid on the Rheological and Physical Properties of PVC

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요 약 : 가소제로 사용되는 DOP와 가공조제로 사용되는 Acryloid K−125가 PVC의 유성학적성질 및 물성에 미치는 영향을 고찰하였다. 점도와 제1법선 응력차는 DOP의 첨가량이 증가함에 따라 감소하였으나 Acryloid K−125를 첨가한 경우에는 증가하였다. DOP와 Acryloid K−125는 모두 PVC의 유동활성화에너지를 감소시켰으며, 전단속도가 증가함에 따라 유동활성화에너지는 감소하였다. DOP를 첨가한 경우 유리전이온도, 항복응력 및 절단신도는 감소하였다. 그러나, DOP의 함유량이 6 phr 까지는 인장강도와 인장탄성율이 오히려 증가하는 경향을 나타내었다. 인장절단시편의 표면미세구조를 보면 DOP의 첨가가 PVC를 brittle하게 변화시킴을 알 수 있다. 밀도의 변화를 관찰한 결과 이 현상은 PVC 분자쇄의 치밀한 배열에 기인한 것이라 사료된다.

Abstract : The effects of dioctylphthalate (DOP), a plasticizer, and Acryloid K−125, a processing aid, on the rheological and physical properties of polyvinylchloride (PVC) were investigated. DOP reduced viscosity and the first mormal stress difference, while Acryloid K−125 noticeably increased them. Both DOP and Acryloid K−125, however, decreased the flow activation energy. Further, the flow activation energy was decreased with increasing shear rate. Over the DOP content tested, DOP reduced glass transition temperature, yield strain, and elongation to break. But incorporation of DOP up to 6 phr slightly increased the tensile strength and the tensile modulus. Investigation of microstructure of tensile fractured surface revealed that DOP makes PVC more brittle. Judging from density variations, DOP seemed to play a role in enhancing the chain orderness of PVC.

INTRODUCTION

Polyvinylchloride (PVC) has long been used in diverse areas due to easy accommodation of additives which makes PVC develop a variety of properties. However, there are little scientific results on PVC processing available due partly to poor thermal stability and to complexities of the components.[1~5] Up to now, the practical fabrication of PVC still remains more of an art than a science. A slit die was set up for rheological measurement. To minimize the thermal decomposition of PVC the experimental apparatus was coated with nickel, and TM−700R, a high temperature resistant tin-mercaptide type thermal stabilizer, was used.

This study examines the effects of plasticizer and processing aid on the rheological and physical properties of PVC. Dioctylphthalate (DOP), the most usual plasticizer of PVC, and Acryloid K-125, a general-purpose processing aid of PVC, were selected. The results were discussed in terms of rheological properties, flow activation energies, and physical properties of PVC.

RHEOLOGICAL BACKGROUND[6]

For a steady, fully developed flow as depicted in Fig. 1, wall shear stress is given by

$$\tau_w = \left(-\frac{\partial P}{\partial z}\right)\frac{h}{2}$$

in which, P is wall normal stress. For a non-Newtonian fluid, apparent shear rate is definded as

$$\dot{\gamma}_a = \frac{6Q}{wh^2}$$

in which, Q is volumetric flow rate.

Within a range of shear rates giving a constant slope on the plots of wall shear stress against apparent shear rate, one may define power-law index by

$$n = \frac{d\ln \tau_w}{d\ln \dot{\gamma}_a}$$

then, wall shear rate is obtained from the equation

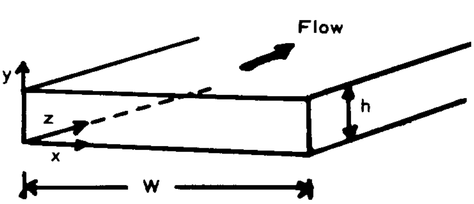


Fig. 1. Schematic description of flow in a rectangular slit.

$$\dot{\gamma}_w = \frac{(2n+1)\dot{\gamma}_a}{3n}$$

Thus, one gets viscosity from the definition

$$\eta = \frac{\tau_w}{\dot{\gamma}_w}$$

First normal stress difference is calculated from the following expression :

$$\tau_{11} - \tau_{12} = N_1 = P_{exit} + \tau_w \frac{dP_{exit}}{d\tau_w}$$

in which, τ_{ij} represents the components of deviatoric stresses, and P_{exit} is exit pressure obtained by extrapolating pressure profile to the die exit.

EXPERIMENTS

Materials and Formulations

A suspension grade PVC (Korea Plastic Industry Co., Korea) was used, whose properties are as follows : Degree of polymerization= 800±50 ; bulk density=min. 0.5g/cm^3, volatiles=max. 0.3%. Dioctylphthalate (DOP, Korea Plasitc Industry Co., Korea) and Acryloid K−125 (Rohm and Haas Co., USA) were tested as plasticizer and as processing aid, respectively. As thermal stabilizer and as lubricant, stearic acid and TM−700R (Songwoun Industrial Co., Ltd., Korea) vere used.

Experimental formulations tested are given in Table 1.

Table 1. Experimental Formulations*

Code	Formulation
P−base	PVC+TM(2)+SA(0.5)
P−AK(5)	P−base+AK(5)
P−AK(10)	P−base+AK(10)
P−AK(15)	P−base+AK(15)
P−AK(5)−DOP(3)	P−base+AK(5)+DOP(3)
P−AK(5)−DOP(6)	P−base+AK(5)+DOP(6)
P−AK(5)−DOP(9)	P−base+AK(5)+DOP(9)

*Numbers in parenthesis are in "phr".
TM : Thermal stabilizer, AK : Acryloid K−125, and SA : Stearic acid

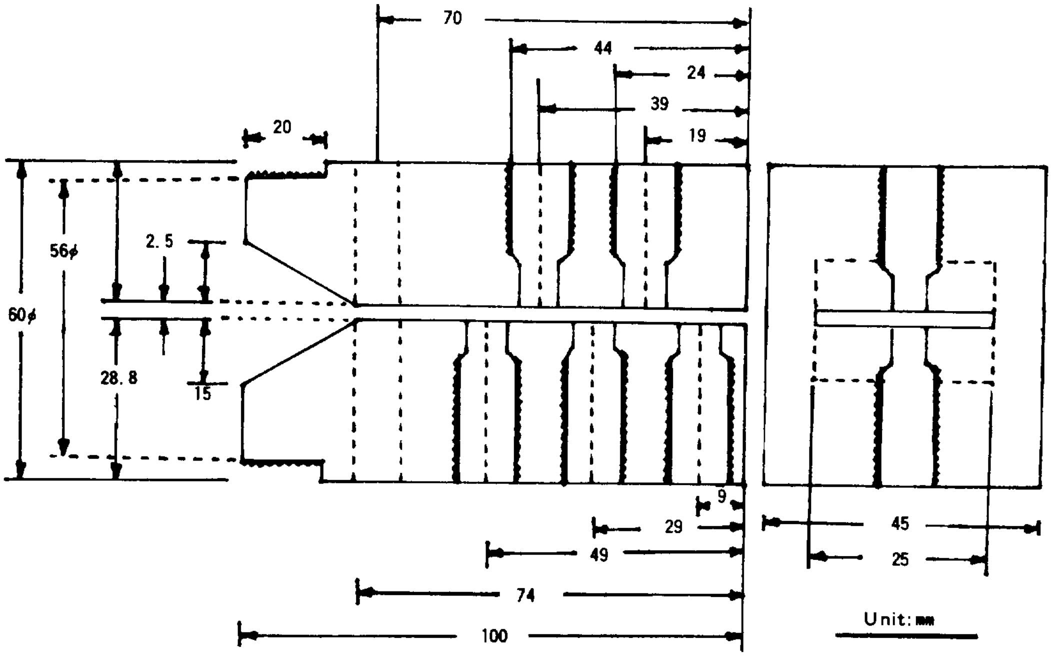


Fig. 2. Detailed layouts of silt die rheometer used.

Apparatus and Experimental Procedure.

The components were compounded in a super-mixer (Kawada Seisakusho, Japan) for 25 minutes at 2,000 rpm. The rheological properties of PVC formulations were measured with a slit rheometer whose detailed layouts are given in Fig. 2.

Glass transition temperature was measured by differential scanning calorimeter (Perkin Elmer System 4, Perkin Elmer Co., USA), and tensile properties were measured by an Instron tester. The cross head speed in tensile testing was 1cm/min. The microstructure of fractured surface of tensile specimen was investigated by scanning electron microscope (Hitachi-S-510, Hitachi Co., Japan). Density was measured by use of a density gradient column built-up with aqueous solution of sodium bromide.

RESULTS AND DISCUSSION

Rheological Properties

Plots of viscosity and first normal stress difference versus shear rate for P-base at three different temperatures are given in Fig. 3. An increase of temperature reduced both viscosity and first normal stress difference. Power-law indices of various formulations at three different temperatures are listed in Table 2. As given in the table, the power-law index was unusually small at low temperautures and noticeably increased with temperature. We had also obtained similar results using a capillary die rheometer for different grade PVC.[7] Further, power-law index was also increased as the usage level of DOP or Acryloid K-125 was increased, which

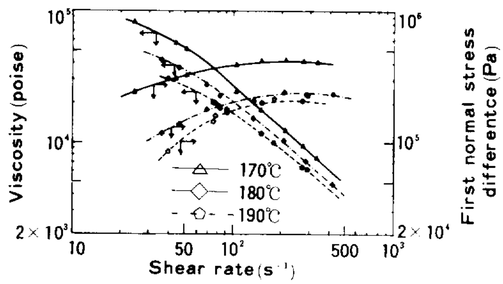


Fig. 3. Viscosity and the first normal stress difference vs. shear rate for P-base.

Table 2. Power−law Index of PVC Compounds

Code \ Temp.(℃)	170	180	190
P−base	0.061	0.110	0.178
P−AK(5)	0.050	0.110	0.208
P−AK(10)	-	0.166	0.265
P−AK(15)	-	0.160	0.260
P−AK(5)−DOP(3)	0.120	0.220	0.360
P−AK(5)−DOP(6)	0.120	0.230	0.380
P−AK(5)−DOP(9)	0.140	0.270	0.390

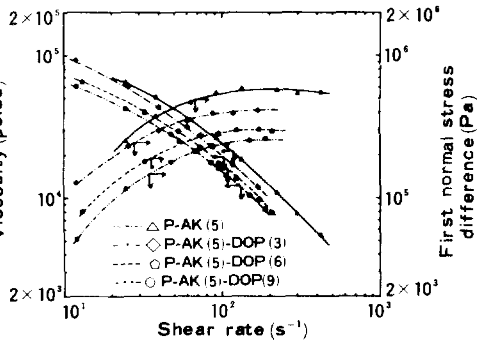


Fig. 4. Effect of DOP on the viscosity and first normal stress difference at 180℃.

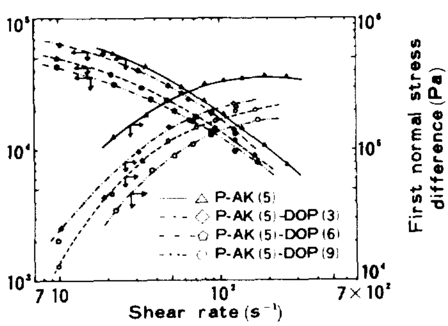


Fig. 5. Effect of DOP on the viscosity and first normal stress difference at 190℃.

may be ascribed to the improved chain mobility.

In a normal PVC processing the use of processing aid is usual for uniform flow and for the better product properties. On the whole the processing aids incorporated are polar components to enhance compatibility with polar PVC. In this experiment, Acryloid K−125, a general−purpose processing aid for PVC, was used.

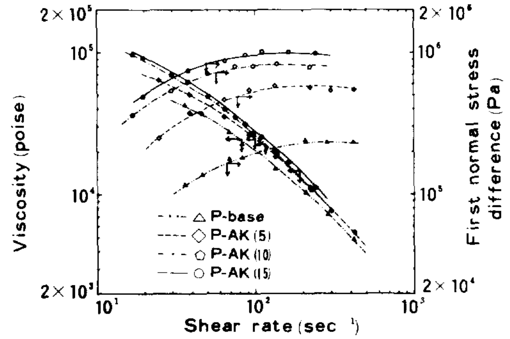


Fig. 6. Effect of AK on the viscosity and first normal stress difference at 180℃.

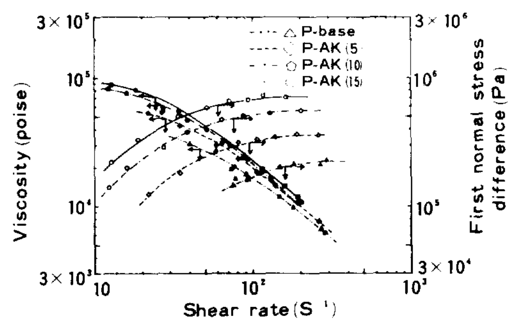


Fig. 7. Effect of AK on the viscosity and first normal stress difference at 190℃.

Although the exact composition of Acryloid K−125 is unknown, the main component seems to be polymethylmethacrylate (PMMA), judged by IR Spectra.

The effect of Acryloid K−125 on the rheological properties of PVC is shown in Figs. 4 and 5. Contrary to one's expectation, both viscosity and first normal stress difference were increased with increasing Acryloid K-125 content. Therefore it should be prerequisite in rigid PVC processing to measure the rheological properties accurately. Fig. 6 and 7 represent the effect of DOP on the rheologioal properties of PVC. Both viscosity and first mormal stress difference were reduced with increasing DOP content as expected. Plots of first nomal stress difference versus shear stress are given in Figs.8 and 9. Although there is some scattering of data points substitution of shear stress for shear rate

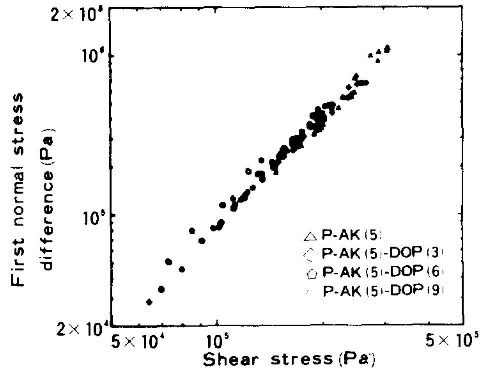


Fig. 8. Plots of first normal stress difference against shear stress showing the effect of DOP.

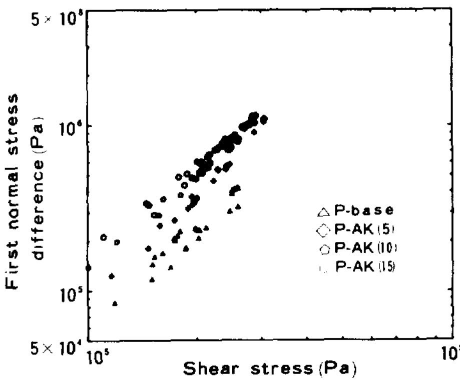


Fig. 9. Plots of first normal stress difference against shear stress showing the effect of Acryloid K−125.

gave almost straight lines independent of temperature. It is interesting to see that Acry-loid K-125 considerably increased first normal stress difference but DOP had little effect on it. The elimination of temperature effect in most elastic parameters such as first and second normal stress differences, exit pressure, die swell ratio, recoverable shear strain and steady state shear compliance by substituting shear stress for shear rate has also been reported by others.[8~10] In an engineering sense, it is advisable to construct a master curve independent of temperature since it makes comparison of elastic properties at different processing temperatures more convenient.

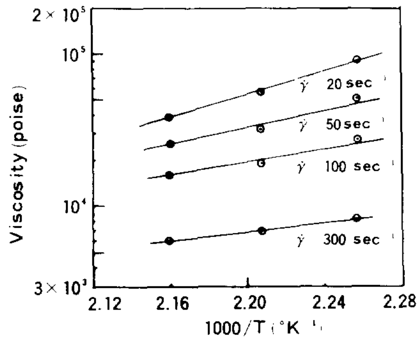


Fig. 10. Polts of viscosity vs. reciprocal of temperature for P−base.

Table 3. Flow Activation Energy of PVC Compounds

Code \ Shear rate(sec^{-1})	20	50	100
P−base	17.57	13.06	11.53
P−AK(5)	13.20	12.00	11.72
P−AK(10)	12.76	10.65	10.21
P−AK(15)	14.35	11.66	10.43
P−AK(5)−DOP(3)	13.24	10.80	9.90
P−AK(5)−DOP(6)	11.33	10.55	9.36
P−AK(5)−DOP(9)	10.44	10.20	9.02

* Dimension of activation energy is (kcal/mol).

Flow Activation Energy

To obtain flow activation energy, viscosity was replotted against reciprocal temperature at a given shear rate. Typical plots for P−base at four shear rates are given in Fig. 10. The flow activation energy was calculated from the slope using Arrhenius−type equation :[11]

$$\eta = A\exp(\Delta E/RT)$$

in which, η is viscosity (poise), A is constant, ΔE is activation energy (kcal/mol) R is gas constant (kcal/mol °K), and T is absolute temperature (°K). The flow activation energy of tested formulations at three different shear rates are given in Table 3. In general the flow activation energy was diminished with increasing shear rate. Further, inclusion of DOP and Acryloid K−125 reduced

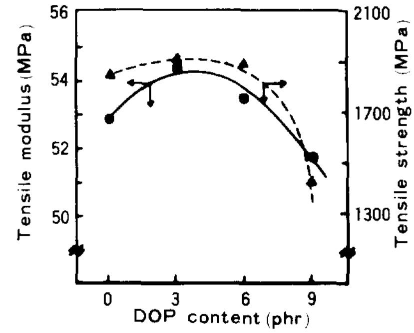


Fig. 11. Variations of tensile strength and tensile modulus with DOP content.

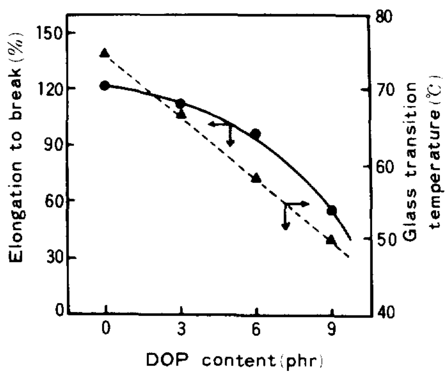


Fig. 12. Variations of elongation to break and glass transition temperature with DOP content.

flow activation energy. This suggests that DOP and Acryloid K−125 enhance chain mobility at higher temperatures, since flow activation energy represents the influence of temperature on the viscosity.

Physical Properties

Variations of tensile strength, tensile modulus, elongation to break and glass transition tempèraute with DOP content are shown in Figs. 11 and 12. It sholud be noted that while the glass transition temperature was lineary decreased with DOP centent, tensile modulus and tensile strength were increased up to DOP content of 6 phr. Further, inclusion cf a small amount of DOP also reduced elongation to break. At first sight, these facts appear to be somewhat contradictory. However, some other re-

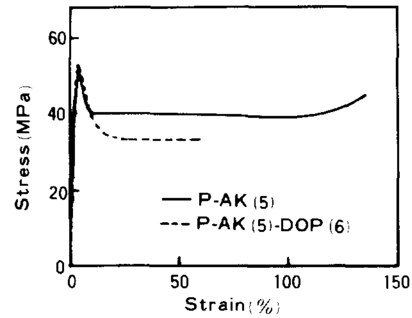
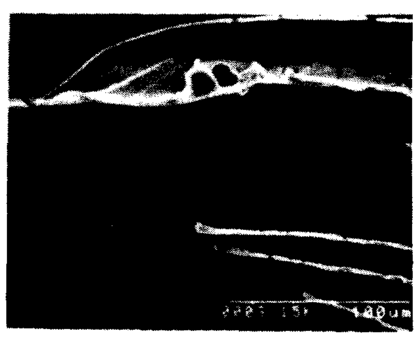


Fig. 13. Typical stress−strain curves showing effect of DOP on embrittlement of PVC.

(a) P-AK(5) : Elongation to break = 138%



(b) P-AK(5)-DOP(6) : Elongation to break = 59%

Fig. 14. SEM photomicrographs of tensile fractured surfaces showing the effect of DOP on embrittlement of PVC.

searchers have also found the similar phenomena for the compatible polar resin−polar plasticizer systems in the glassy state, and they denominated it an "antiplasticization".[12~15] Fig.13 represents typical stress−strain curves of P−AK(5) and P−AK(5)−DOP(6). It clearly shows that DOP reduces ductility of PVC. SEM photo-

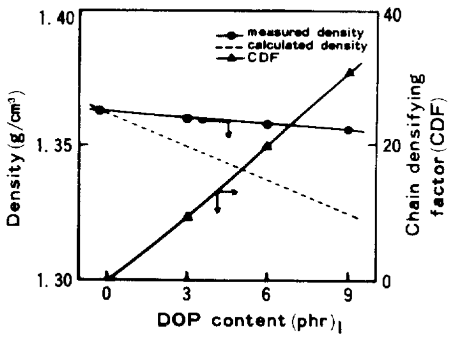


Fig. 15. Plots of density vs. DOP content showing the effect of DOP on the molecular orderness of PVC. CDF=(measured density−calculated density)×1000.

micrographs of tensile fractured surfaces of the two formulations are given in Fig. 14. The microfibril structure is more noticeable with AK(5) than with P−AK(5)−DOP(6). In addition, the fractured surface of P−AK(5)−DOP(6) exhibits some cracks. This also indicates that DOP makes PVC more brittle. The embrittlement may be ascribed to the partial restriction of chain motion. That is, the polar DOP molecules cohere to PVC segment through dipole−dipole interaction and the motion of cohering parts of PVC chain may be greatly hindered. As a result, such a local hindrance of chain motion may develop an embrittlement of PVC in the glassy state.

To trace the change in chain packaging by adding a small amount of DOP, calculated and measured densities are plotted against DOP content in Fig. 15. It is a generally accepted fact that when the temperature is lowered to below glass transition temperature, a non−equilibrium structure is usually observed in a polymer because of long relaxation time required to get a new equilibrium state corresponding to a new lower temperature. An introduction of plasticizer may promote a more compact structure at the temperatures below glass transition temperature due to reduced relaxation time.[15] In addition, the free volume may also be diminished through the polar-polar interaction between PVC chain and DOP molecule. In consequence, the measured densities were higher than the calculated densities as given in the figure.

CONCLUSIONS

1. While dioctylphthalate (DOP) reduced viscosity and first normal stress difference of polyvinylchloride (PVC), Acryloid K−125 increased them.
2. Flow activation energy of PVC was decreased with the increase of shear rate, and both DOP and Acryloid K−125 reduced flow activation energy of PVC.
3. Incorporation of a small amount of DOP reduced ductility of PVC. It increased tensile strength and tensile modulus, and reduced elongation to break of PVC. DOP seemed to play a role in enhancing the chain compactness of PVC.

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