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KASAJIMA, Masayuki

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Flow Behaviors of Two Phase Polymer Melts

Masayuki KASAJIMA*

Abstract

Flow characteristics of blended samples of polymethyl methacrylate and polystyrene as two phase polymer melts were measured for various blend ratios by the capillary rheometer, and flow behavior was investigated.

The flow characteristic curves for the blended samples do not intersect each other and are located, in order of the value of blended fraction, between the curves of mono-component samples. The additive property does not hold. The flow characteristics of blended samples are strongly dominated by the fluidity of polystyrene. The correction-factor of blended-fraction is a decreaseable-function with respect to shear rate, when the blended fraction is small, and the correction factor of blended fraction becomes an increaseable-function with respect to the shear rate, when the blended fraction is large.

1. Introduction

With a view not only to improving quality of thermoplastic materials but also of recycling the waste materials, the processing and utilization of blended polymers have been practiced extensively for the past several years. Many studies^{1),2)} on the solid mechanics of the blended materials have been made. The number of studies^{1),3)} on mixing (kneading) and of investigations^{4)~10)} of flow behavior in this field of blends is not more than the number of studies on homogeneous polymers. Investigations have been made of mixture rules¹¹⁾ and mixture theory¹²⁾ for the blended polymer melts. However, the flow mechanism of the blended polymer melts still seems to be not completely clear. Therefore, obtaining information on the flow characteristics of the blended polymer melts is very important in the field of practical polymer processing. When incompatible resins are combined, the blended materials have the properties of the respective mono-components, and, furthermore, there is a possibility of finding compounds with novel and/or different properties.

This paper reports on the flow characteristics of various blend ratios of mechanically blended samples of polymethyl methacrylate (PMMA) and polystyrene (PS), which are combinations of incompatible resins, and the flow behavior is analyzed and relationships among effective blended fraction, correction factor of blended fraction, blended fraction and shear rate etc. are investigated.

2. Experimental

The blended samples used in this study were prepared by mixing PMMA (SUMIPEX-B MH011 of Sumitomo Kagaku Kogyo) and PS (ESBRITE 2V-62 of Sumitomo Kagaku Kogyo).

The blended samples were prepared by the following procedure. Respective resins

* Department of Mechanical Engineering

in pellet form were weighed and blended before mixing in a cylindrical type rotary mixer. Then the blended samples were kneaded until made as homogeneous as possible, extruded through a laboratory-scale extruder and, finally, crushed finely for compounding. The same compounding procedure was applied to the respective mono-components of resin used for blending, so that both kinds of samples would have the same processing history. The flow characteristics of the thus prepared blended samples were measured. Blended fraction c in this paper is defined as the weight fraction of the component having low fluidity. That is, the component having low fluidity is PMMA.

The flow characteristics were measured by a capillary rheometer so called Koka type flow tester. Methods used to induce the values representing the flow characteristic curves are abbreviated here, because the methods were reported in a previous paper⁶⁾. The measuring temperature was 220°C.

3. Results and Discussion

Relationships between shear stress τ_w at the wall and apparent shear rate $\dot{\gamma}_{wa}$ at the wall, which express flow characteristics of PMMA·PS two phase polymer melts, are shown in Fig. 1. The characteristic curves for the blended samples having a different value of c do not intersect with other curves and are located, in order of the value of c , between the τ_w - $\dot{\gamma}_{wa}$ curves of the mono-component samples. These matters mean that the blended sample of smaller c has better fluidity. The curves of apparent viscosity η_{wa} at the wall versus $\dot{\gamma}_{wa}$ are shown in Fig. 2. It is seen from Fig. 2 that the samples used in this experiment have structural viscosity properties. In the τ_w - $\dot{\gamma}_{wa}$ curves, τ_w increases with increasing $\dot{\gamma}_{wa}$. However, η_{wa} decreases with increasing $\dot{\gamma}_{wa}$. The η_{wa} - $\dot{\gamma}_{wa}$ characteristic curves for the respective blended samples are located, in order of the value of c , between the curves of the mono-component samples. This behavior is similar that of the τ_w - $\dot{\gamma}_{wa}$ characteristic curves.

τ_w - c curves and η_{wa} - c curves, having a parameter $\dot{\gamma}_{wa}$, are shown in Fig. 3 and Fig. 4 respectively. Fig. 3 indicate that τ_w increases with increasing $\dot{\gamma}_{wa}$ and c . Conversely, Fig. 4 indicate that η_{wa} decreases with increasing $\dot{\gamma}_{wa}$ and c . From these figures, it is proved that the additive property does not hold for the PMMA·PS two phase

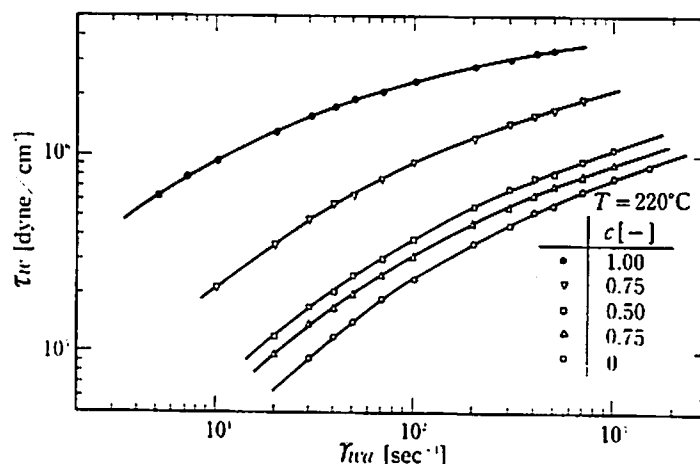


Fig. 1 τ_w - $\dot{\gamma}_{wa}$ flow characteristic curves

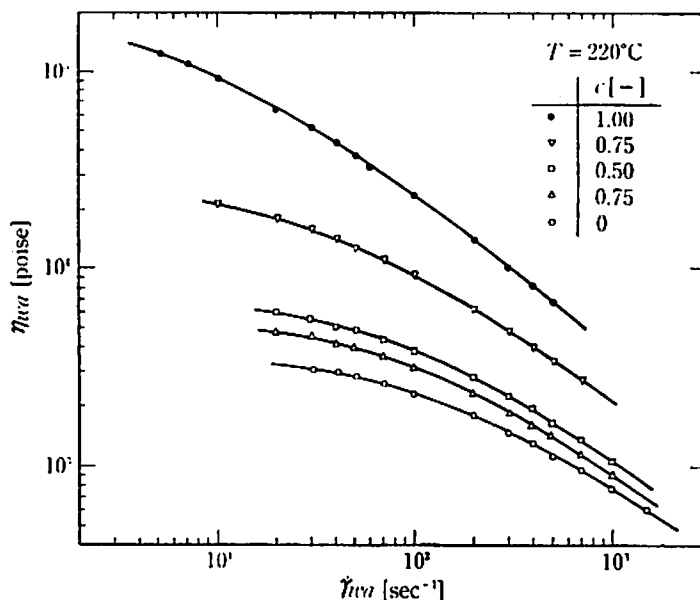


Fig. 2 $\eta_{wa}-\dot{\gamma}_{wa}$ flow characteristic curves

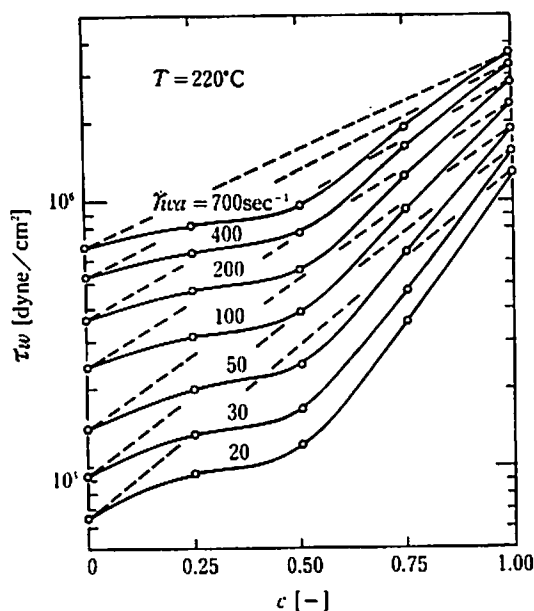
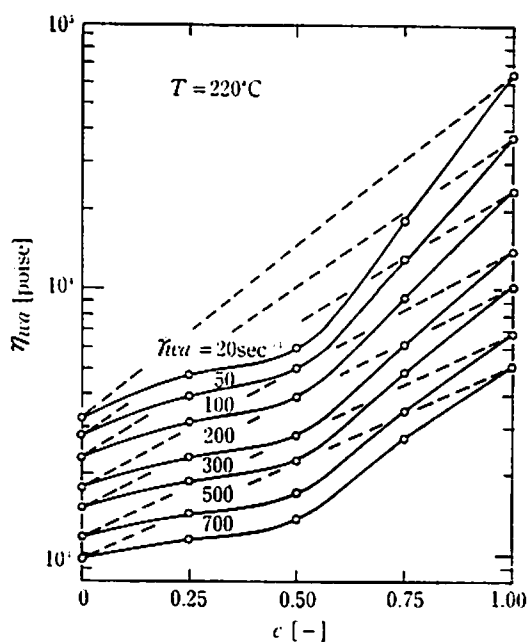


Fig. 3 τ_w-c curves

polymer melts. That is, the increase of η_{wa} to c is not a proportionate increase. The $\eta_{wa}-c$ curves deviate from the broken line which represent Arrhenius' equation¹³⁾ (Eq. (1)). Additionally, this broken line indicates that the additive property holds.

$$\ln \eta_{1 \cdot 2} = c \ln \eta_1 + (1-c) \ln \eta_2 \quad (1)$$

where subscript 1·2 means the blended sample, subscript 1 and 2 mean the mono-component respectively, Eq. (2) is induced from Eq. (1) and Newton law which relates among η , τ and $\dot{\gamma}$. The τ_w-c curves deviate from the broken line indicated by Eq. (2), too. The data shown in Figs. 3 and 4 have

Fig. 4 $\eta_{wa}-c$ curves

$$\ln \tau_{1,2} = c \ln \tau_1 + (1-c) \ln \tau_2 \quad (2)$$

inflection-point, and the degree of deviation from the additive property is remarkable in the vicinity of $c=0.5$.

The effective blended fraction c^* and the correction factor of blended fraction ϕ obtained from Eqs. (3)~(8), which are the expressional formulae^{6),10)} for the flow characteristics of the blended polymer melts, are convenient to investigate the degree of deviation from the additive property.

$$\ln\{\tau_{1,2}(\dot{\gamma}, T)\} = c^*(c, \dot{\gamma}, T) \ln\{\tau_1(\dot{\gamma}, T)\} + [1-c^*(c, \dot{\gamma}, T)] \ln\{\tau_2(\dot{\gamma}, T)\} \quad (3)$$

$$\ln\{\tau_{1,2}(\dot{\gamma}, T)\} = \phi(c, \dot{\gamma}, T) c \ln\{\tau_1(\dot{\gamma}, T)\} + [1-\phi(c, \dot{\gamma}, T)] c \ln\{\tau_2(\dot{\gamma}, T)\} \quad (4)$$

$$\ln\{\eta_{1,2}(\dot{\gamma}, T)\} = c^*(c, \dot{\gamma}, T) \ln\{\eta_1(\dot{\gamma}, T)\} + [1-c^*(c, \dot{\gamma}, T)] \ln\{\eta_2(\dot{\gamma}, T)\} \quad (5)$$

$$\ln\{\eta_{1,2}(\dot{\gamma}, T)\} = \phi(c, \dot{\gamma}, T) c \ln\{\eta_1(\dot{\gamma}, T)\} + [1-\phi(c, \dot{\gamma}, T)] c \ln\{\eta_2(\dot{\gamma}, T)\} \quad (6)$$

$$c^* = \phi(c, \dot{\gamma}, T) c \quad (7)$$

$$\phi = \sum_{j=0}^i \{\lambda_j(c, T)\} (\ln \dot{\gamma})^j \quad (8)$$

where T means temperature, λ means constant. Results relating to c^* of respective blended samples, calculated from Eqs. (3), (5) and Figs. 1, 2 having parameter $\dot{\gamma}_{wa}$, are shown in Fig. 5. In this figure $\dot{\gamma}_{wa}=20 \text{ sec}^{-1}$ and $\dot{\gamma}_{wa}=700 \text{ sec}^{-1}$ are indicated as representative values of parameter $\dot{\gamma}_{wa}$. The c^* change with changing c and $\dot{\gamma}_{wa}$. That is, the curves with parameter $\dot{\gamma}_{wa}$ have inflection-points, and deviate downwardly from the straight line $c^*=c$. The degree of deviation indicates a tendency similar to the results discussed relating to Figs. 3 and 4. The c^* deviates remarkably from the straight line $c^*=c$ at near $c=0.5$, with the large downward convexity. The curves of $\dot{\gamma}_{wa}=20 \text{ sec}^{-1}$ and $\dot{\gamma}_{wa}=700 \text{ sec}^{-1}$ intersect each other in the vicinity of a value somewhat larger than $c=0.5$. The curves of $\dot{\gamma}_{wa}=20 \text{ sec}^{-1}$ are located over the curve of $\dot{\gamma}_{wa}=700$

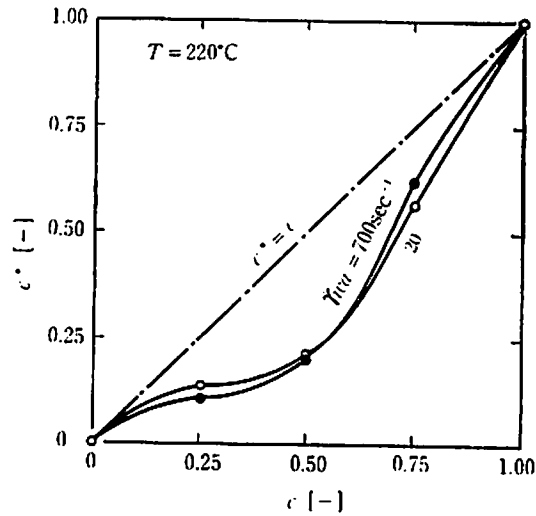


Fig. 5 Relationship between c^* and c

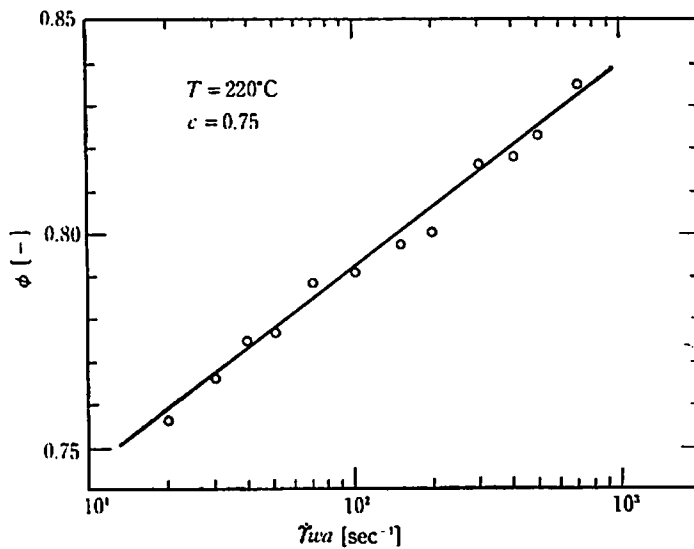


Fig. 6 Relationship between ϕ and $\dot{\gamma}_{wa}$

sec^{-1} in the region of c , and the curve of $\dot{\gamma}_{wa}=700 \text{ sec}^{-1}$ is located over the curve of $\dot{\gamma}_{wa}=20 \text{ sec}^{-1}$ in the region of large c . In other words, we can say these phenomena may be explained by using Eqs. (3) and (5) as follows. When the region of c is small and the value of $\dot{\gamma}_{wa}$ is large, the degree of influence of secondary component sample such as PS sample becomes large, while the region of c is large and the value of $\dot{\gamma}_{wa}$ is small, the degree becomes small.

Partial results with respect to ϕ , calculated from Eqs. (4), (6) and experimental data, are plotted in Fig. 6 taking $\dot{\gamma}_{wa}$ as abscissa. From Fig. 6 the $\phi-\ln\dot{\gamma}_{wa}$ curve may be indicated with a nearly straight line, and can be approximated by the formula of Eq. (8) at $i=1$. The $\phi-\ln\dot{\gamma}_{wa}$ curves of other blended samples can be indicated similarly with a straight line. The ϕ obtained by using Eq. (8) for respective blended samples are shown in Table 1. From Table 1 it is proved that values of ϕ are a decreaseable

Table 1 Correction factor of blended fraction

c [-]	ϕ [-]
0	1
0.25	$-0.03042 \ln \dot{\gamma}_{wa} + 0.6316$
0.50	$-0.00398 \ln \dot{\gamma}_{wa} + 0.4357$
0.75	$0.02051 \ln \dot{\gamma}_{wa} + 0.6976$
1.00	1

function with regard to $\dot{\gamma}_{wa}$ at region of c being small, that the degree of decrease becomes smaller with an increase in c , and that the ϕ change increasable function with regard to $\dot{\gamma}_{wa}$ at more increasable c . Additionally, the values of ϕ are smaller than 1 at measuring range in this study.

The flow characteristics of blended PMMA·PS samples are strongly dominated by the fluidity of PS component which has better fluidity. This phenomenon seems to occur in accordance with the fact that the mono-component fills the role¹¹⁾ of "sea" or "island", and allows slipping at the interface between different polymers.

When the degree of deviation of the additive property in Figs. 3 and 4 is expected, the values can be obtained by using Eq. (9) and the data. If the degree of deviation from the additive property is a_A , Ep. (9) with a function of τ is obtained from Eqs. (2) and (4).

$$\ln a_A = [1 - \phi(c, \dot{\gamma}, T)] c \ln \left\{ \frac{\tau_2(\dot{\gamma}, T)}{\tau_1(\dot{\gamma}, T)} \right\} \quad (9)$$

Replacing τ in Eq. (9) by η , the a_A with a function of η can be obtained.

4. Conclusion

The following conclusions are reached on the basis of the measuring regions for the blended PMMA·PS samples used as two phase polymer melts in this study.

1) The characteristic curves for the blended samples having a different value of the blended fraction do not intersect with other curves and are located, in order of the value of the blended fraction, between the curves of the mono-component samples.

2) The additive property does not hold. And the degree of deviation from the additive property is remarkable in the vicinity of the blended fraction 0.5. The flow characteristics of blended samples are strongly dominated by the fluidity of the PS component which has better fluidity.

3) The correction factor of blended fraction is a decreasable function with regard to the shear rate in the region where the blended fraction is small, and the degree of decrease become smaller with an increase in the blended fraction, and the correction factor of blended fraction change increasable function with regard to the shear rate at more increasable the blended fraction.

Nomenclature

a_A =degree of deviation from additive property	[-]
c =blended fraction	[-]
c^* =effective blended fraction	[-]
T =temperature	[°C]
$\dot{\gamma}$ =shear rate	[sec ⁻¹]
η =viscosity	[poise]
λ =costant	

τ =shear stress [dyne/cm²]
 ϕ =correction factor of blended fraction [-]
 〈Subscripts〉
 a =apparent
 w =at the wall
 1=1st mono-component
 2=2nd mono-component
 1·2=blended

References

- 1) Goto, K. : "Polymer Blend", Nikkan Kogyo Shimbunsha (1970).
- 2) Barentsen, W. M. and D. Heikens : *Polymer* 14, 579 (1973).
- 3) Kasajima, M., A. Suganuma, D. Kunii and K. Ito : *R. P. P. J.*, 21, 105 (1978).
- 4) Hill, A. S. and B. Maxwell : *Polym. Eng. Sci.*, 10, 289 (1970).
- 5) Han, C. D. and T. C. Yu : *Polym. Eng. Sci.*, 12, 81 (1972).
- 6) Kasajima, M. and Y. Mori : *Kagaku Kogaku*, 37, 915 (1973).
- 7) Kasajima, M. : Rheology Kondankai shiryo, 1 (1974).
- 8) Han, C. D. and Y. W. Kim : *J. Appl. Polym. Sci.*, 19, 2831 (1975).
- 9) Han, C. D. : "Rheology in Polymer Processing", p.165, Academic Press (1976).
- 10) Kasajima, M., A. Suganuma, D. Kunii and K. Ito : *Proc. Int. Conf. Polym. Processing*, to be published.
- 11) Takayanagi, M. : *Kobunshi*, 10, 285 (1961).
- 12) Nielsen, L. E. : "Predicting the Properties of Mixtures", Marcel Dekker (1978).
- 13) Arrhenius, S. : *Z. Physik. Chem.*, 1, 285 (1887).