Melt Rheology of Sodium and Zinc Ethylene Ionome

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Abstract

The ionic bonding is one of parameters to control melt rheology. Ethylene poly-(ethylene-co-methacrylic acid)(5.4mol% of MAA, EMAA) which is partially neutraliz zinc. There have been several reports about melt rheological properties of sodiu However, few reports have been published to examine the melt rheological propertie spite of their some industrial commercial applications.

Rheological characterizations were carried out under shear in terms of li oscillatory shear. The ionomer blends here have 60% of neutralization and variou Time-material superposition was applicable among sodium, zinc ionomers, and their i viscosity as a function of blend composition unexpectedly showed that the zero sh 80% is almost constant with that of sodium ionomer. However, ionomer blends surpri damping than each ionomer, depending on the composition. The unexpected zero shear from acid-cation exchange mechanism, which is observed only in sodium ionomers, not

1. Introduction

Poly(ethylene-co-methacrylic acid) (EMAA) partially neutrali ions such as sodium or zinc is one of the most widely used and mechanical properties in the solid state of these eth been extensively investigated.[1)] Ionic cross-links and the aggregatio groups impart a dramatic increase in mechanical propertie properties are essential for sodium and zinc of EMAA to variety of industrial applications viscoelastic properties o ionomer melts have also been studied to clarify the role state.[2-4)] Especially, Vanhoorne and Register[5)] studied the effect of the of unneutralized acid groups on the melt rheology of partia ionomers. By removing the protons by esterification of th have found that the role of the protons in sodium ionomers in zinc ionomers.[5)]

In this paper, in order to get deeper insight into the rheology, we have studied dynamic shear properties for blend and zinc ionomers as a function of the blend ratio. In th blends, the zero shear viscosity as a function of composit additively rule, while a strong negative deviation from th was observed in the latter blends. A possible explanation given.

2. Experimental

Poly(ethylene-co-methacrylic acid)(EMAA,Mw=94,500 Mn=19,200) a methacrylic acid content of 5.4mol% was used. Ethylene ba

EMAA partially neutralized by zinc or sodium ion, that i
(EMAA-59Zn, EMAA-54Na). The samples were mixtures of these
ionomers. The blends were prepared by double-screw kneader °C. The
blend ratio of two cation ionomers were written in Tab
abbreviations are designated as EMAA-Zn(x)/Na(y), where x
blend ratios of two cations. All of these samples were
Mitsui-DuPont Polychemicals. The melting temperature was °C for these
samples. All samples were treated with vacuum oven at 80 °C for at least on
week to eliminate water before measurements.

Dynamic shear measurements were conducted using a rotat
(Rheometrics, ARES) under nitrogen atmosphere. These exp
conducted in the range from 0.01 to 100 rad/s and 140 °C to 200 °C, which
are substantibially above their melting point.

3. Results and Discussion

Oscillatory shear experiments for samples shown in T
strain (less than Hencky strain 0.04) were performed. Stor
loss modulus G" were obtained as a function of angular f w in the
range from 0.01 to 100 (rad/s). Firstly it was comfirmed tha
superposition principle is applicable for EMAA-Zn(33)/Na(67
in measured conditions. Secondly the resulting master curv
EMAA-Zn(33)/Na(67) at temperature of 140 °C were horizontally shifted
master curve of 140 °C. It was shown in Figure 1 that the successfu
(i.e. Super master curve[3)]) of G′ and G′′ for EMAA-Zn(30)/Na(67) was
at the G′ and G′′ of EMAA as the refference. For the othe
time-material[3)] superposition principle was also applicable.
construction of super master curve can be interpreted as th
must have the same shape of relaxation spectrum with differ
expressed by material shift factor[3)]. This shift factor value is importa
it is well satisfied following relation to the zero-shear v h_o.

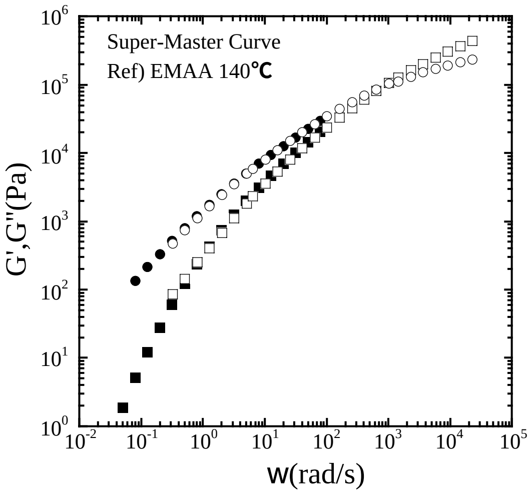
$$h_o(\text{EMAA-X}) = a_T{}^* \, h_o\,(\text{EMAA}). \quad (1)$$

Here a_T* is the time-material shift factor for EMAA-X rel
and h_o(EMAA) and h_o(EMAA-X) are the zero-shear viscosity of E
EMAA-X, respectively. Figure 2, it shows a_T as a function of various blends
EMAA-59Zn content These blends are miscible, but a large n
from the linear blending rule was observed. In the case o
acid-cation exchange mechanism is effective because COOH gr
aggregates, resulting in lower viscosity. In EMAA-59Zn, on
acid-cation exchange does not occur because no acid group
aggregates, and the viscosity is relatively high. When EMAA

59Zn were blended, it can be explained by the idea that s
coexisted in the same ion aggregates,[6] where the acid-cation exchange is c

Table 1 The samples for binary blends of EMAA-Na and EMAA-Zn

Sample abbreviation	Zn : Na ion ratio (mol)	EMAA-Zn : EMAA-Na weight ratio (wt%)
EMAA-Na(100)	0 : 1	0 : 100
EMAA-Zn(20)/Na(80)	1 : 4	31.4 : 68.6
EMAA-Zn(33)/Na(67)	1 : 2	47.8 : 52.2
EMAA-Zn(50)/Na(50)	1 : 1	64.7 : 35.3
EMAA-Zn(67)/Na(33)	2 : 1	78.6 : 21.4
EMAA-Zn(80)/Na(20)	4 : 1	88.0 : 12.0
EMAA-Zn(95)/Na(5)	95 : 5	97.2 : 2.8
EMAA-Zn (100)	1 : 0	100 : 0



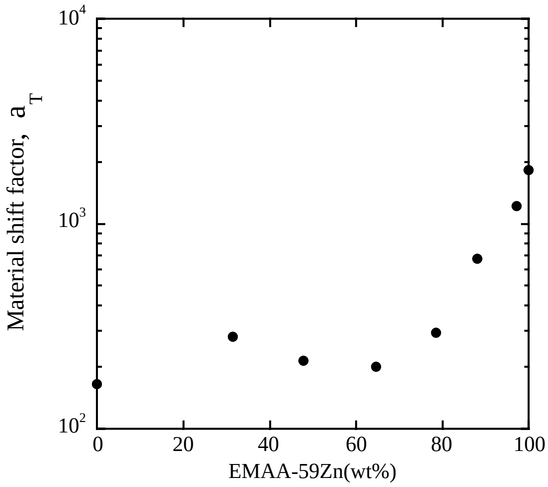


Fig.1 Time-material superposition (
symbols) and G"(circle symbols) fro
curves of EMAA(closed symbols) and
EMAA-Zn(33)/EMAA-Na(67) (open symbo
The reference is the master curves of EMAA
at 140℃

Figure 2 Time-material shift fa
at 140℃ as the reference) as
composition in the blend of EM
and EMAA-59Zn.

4. REFERENCE

1. A.Eisenberg, J.Kim, Introduction to IONOMERS, Wiley-Interscience, New York(1998).
2. T.Takahashi, J.Watanabe, K. Minagawa, K.Koyama, Polymer, 35, pp.5722-5728 (1994).
3. T.Takahashi, J.Watanabe, K.Minagawa, J.Takimoto J, K.Iwakura, K.Koyama, Rheol. Acta, 34, pp.163-171 (1995).
4. A.Nishioka, T.Takahashi, Y.Masubuchi, J.Takimoto, K.Koyama, Polymer, 42, pp.7907-7910 (2001).
5. P.Vanhoorne, R.A.Register, Macromolecules, 29, pp. 598-604(1996)
6. H.Tachino, H.Hara, E.Hirasawa, S.Kutsumizu, S.Yano, Macromolecules, 27, pp.372-378(1994)