CHEMISTRY LETTERS, pp. 1157-1160, 1982.

ELUCIDATION OF REACTION BETWEEN POLYESTERS WITH MAGNESIUM OXIDE BY TITMETRIC METHOD AND FT-IR

Hitoshi NOMURA and Yuzi TAKAYAMA*

Materials Science, Toyohashi University of Technology, 1-1, Hibarigaoka, Tempaku-cho, Toyohashi-shi, Aichi 440

Studies on the states of MgO added into the carboxylic group terminated polyester resins were performed to clarify a mechanism of thickening. Contrary to some literatures, it was confirmed that the MgO was used to form the neutral salt of the polyesters and there was little tendency for the MgO to exist in the form of the basic salt in the system.

SMC(sheet molding compound) is one of typical molding compounds for fiber reinforced plastics. The key step in the production of SMC is "thickening", which means to increase the viscosity of the compound by some interaction between MgO and the unsaturated polyester contained in SMC. Vancso-Szmercsanyi[1,2] found that this interaction was consisted of two factors: the formation of the basic Mg salt of carboxylic group terminated polyester, and the complex formation between the basic salt and the carbonyl oxygen of the ester groups. Thus, she proposed a thickening mechanism, where the cause of thickening was the cross-linking effect of the esters-basic Mg salt complexes. In contrast, Burns *et al.*[3,4] found from the results of moisture content measurement by infrared spectroscopy that neutral salt was formed in the reaction of terminal caboxylic groups with MgO. They concluded that the amount of basic salt present in the reaction mixture was small and hence the thickening appears to be due to neutral salt, that is, thickening would occur by the chain entanglement of the polymer of high molecular weight which was produced by the ionic linkage of the neutral salts. We have investigated to make clear whether the basic salt exists in the reaction

mixture or not.

Since SMC is consisted of various components, there may be many factors which impede the detailed investigation. Thus, the investigation has been carried out on a very simple system which consists of only two components, *i.e.*, MgO and saturated polyesters. The polyesters were prepared from ethylene glycol and the equimolar amount of succinic acid and adipic acid. The analytical results of the polyester are listed in Table 1.

Table 1. Saturated polyesters for the reaction with MgO

No.	Acid Value Va [meq/g]	Hydroxyl Value Vh [meq/g]	Mn*	Comments
1	0.003	0.582	3420	Hydroxylic-terminated
2	0.189	0.446	3150	Hydroxylic- and carboxylic-terminated
3	0.519	0.003	3830	Carboxylic-terminated

* Number average molecular weight, Mn, was determined by following equation.

$$Mn = 2000/(Va + Vh)$$

These polyesters were thickened by storing in a box thermostated at 32°C after the addition of a given amount of MgO. With appropriate time intervals viscosity was measured at 32°C using the Brookfield viscometer model HBT. At the same time, sampling was carried out. The sample was dissolved in benzene-methanol (7:3), and titrated with 0.1N KOH ethanol solution to determine the change in the acid value, from which the amount of reacted terminal carboxylic groups were calculated. Further, the sample was dissolve in dichloromethane, and then centrifuged to remove unreacted MgO. IR spectrum was measured for this solution using a JEOL JIR-40X FT-IR spectrophotometer, and the amount of reacted MgO was determined by EDTA method.

Figure 1 shows the viscosity increase of the polyesters listed in Table 1. It is clear that terminal carboxylic groups are necessary for thickening. The viscosity increase comparable to that of a practical polyester for SMC was obtained in polyester 3. Thus, carboxylic group terminated polyester would play a main role in thickening. This type of polyester should show very large

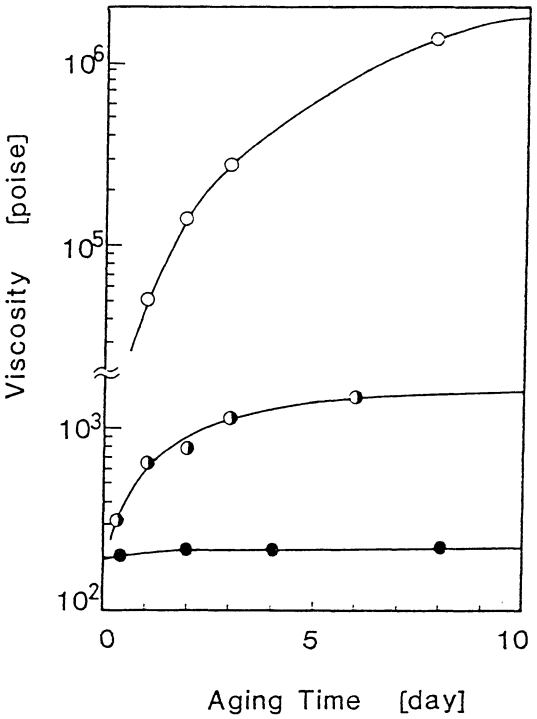

Fig. 1 Thickening curves. ●: polyester 1 in Table 1, MgO/COOH = 2.0[eq/eq], ◑: polyester 2 in Table, MgO/COOH = 1.5[eq/eq], ○: polyester 3 in Table 1, MgO/COOH = 1.4[eq/eq].

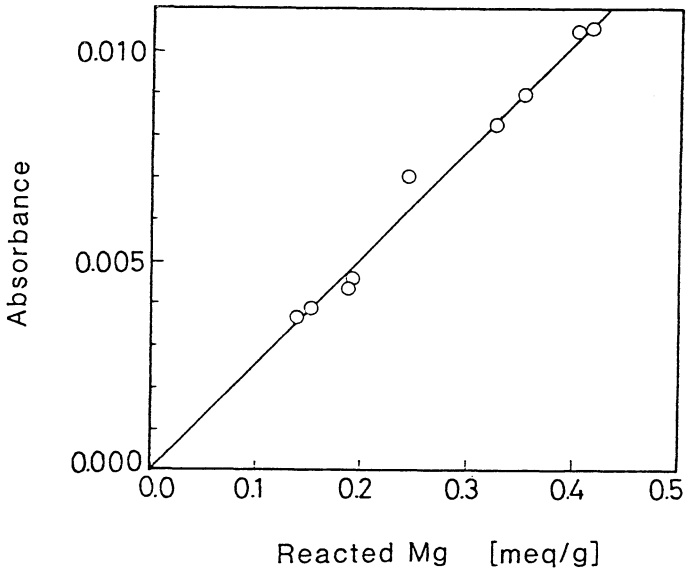

Fig. 2 The change in the absorbance of the peak at 1606cm.$^{-1}$

increase in molecular weight when reacted with MgO.

In Fig. 2, the absorbance of the peak at 1606cm^{-1}, which was brought by the reaction between the added MgO and the terminal carboxyl group of the polyester 3 listed in Table 1, was plotted against the amount of reacted MgO. The peak at 1606cm^{-1} is presumably assighned to the antisymmetric vibration of carboxylate ions. Then, the absorbance should be proportional to the amount of reacted terminal carboxylic groups. It is considered that either of two, neutral salts or basic salts, would be formed irrespective of the amount of reacted magnesium.

Figure 3 shows the plot of the amount of reacted terminal carboxylic groups, of the same polyester as used in Fig. 2, determined by the change in the acid value against the amount of reacted magnesium. It is clear that neutral salts are formed. However, a tendency to approach the basic salt composition in the case of reacted magnesium over 0.3meq/g is apparently

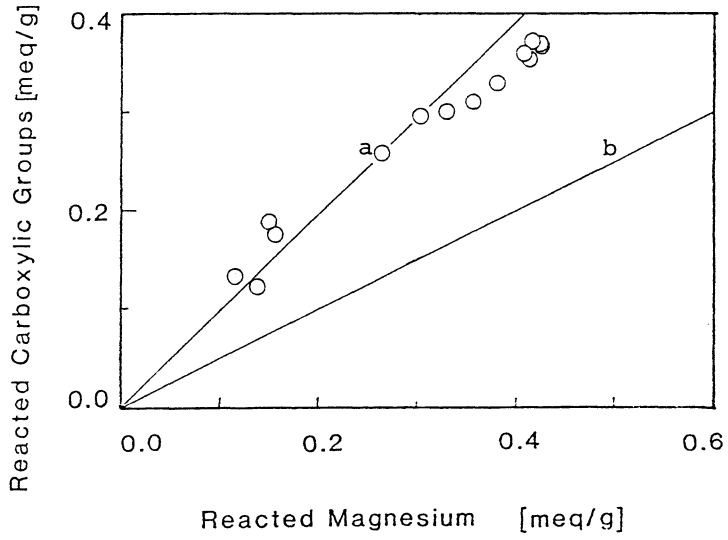

Fig. 3 The ratio of reacted terminal carboxylic groups vs. reacted magnesium. a: the theoretical line for the neutral salt formation, b: the theoretical line for the basic salt formation.

observed at first sight. This fact is contrary to the linear relationship in Fig. 2. The tendency to approach the basic salt composition would be induced by the hydrolysis of the salts during titration, since the amount of unreacted carboxylic group is considerably small compared with that of the salts in the region I. Thus, it can be concluded that the reaction of terminal carboxylic groups with MgO yields neutral salts.

From these results, it is concluded that the main cause of thickening should be the increase in molecular weight due to the formation of neutral Mg salts.

References

1) I. Vancso-Szmercsanyi, Kunststoffe, 58, 907(1968).
2) I. Vancso-Szmercsanyi, Kunststoffe, 60, 1066(1970).
3) R. Burns, K. S. Gandhi, A. G. Hankin, and B. M. Lynskey, Plast. Polym., 43, 228(1975).

(Received April 28, 1982)