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Measurement of the Flow of Thermosetting Molding Compound*

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I. INTRODUCTION

Various test methods and procedures[1-25] have been devised and carried out in the past[1] on the rheological flow of thermoplastics at constant temperature. The extrusion method[6-15] as specified by A.S.T.M.[12,13] is a reasonable measuring method, and the flow of thermoplastics in the extrusion rheometer has been investigated in the author's previous papers.[14-17] The parallel plate compression rheometer[18-22] is another typical measuring apparatus for this purpose, and it can be compared to the extrusion rheometer from the standpoint of the rate of strain.[16-17]

On the other hand, thermosetting plastics whose internal molecular structure forms a three-dimensional network have no plastic strain,[26] even though metastable strain may be frozen by secondary bonding forces. Therefore, the flow of thermosetting plastics can usually be measured in the curing process from the not-fully-cured state to the cured state, and thus it is not tested with the same consistency as thermoplastics because of the chemical reaction occurring during the curing process. The measuring method is therefore considerably difficult and complicated. Measurement has been attempted by some investigators, e.g., the cup method[23] by Sontag and Borro,[26] and the method of rushing into minute holes by Burns.[25]

Considering the relationship between thermoplastics and thermosetting plastics, the author measured the flow of the thermosetting plastics by the same extrusion rheometer which had been previously used for the flow of thermoplastics, and experimental results were compared to each other under certain conditions.

II. TEST SAMPLES AND EXPERIMENTAL METHOD

Allyl polyester molding compound (unsaturated alkyd resin[27] containing diallyl phthalate monomer) was used as a test sample in the flow of thermosetting plastics. Because diallyl phthalate monomer acts as a crosslinking component in radical reaction and its curing reaction is not by condensation, this compound has no volatile by-product in the curing reaction as do other thermosetting molding compounds, such as phenol, urea, melamine resins, and other polyester resin containing styrol,[27] even at an elevated temperature. Therefore breathing during the molding process is not needed for these test samples. Their flow curves in the extrusion rheometer can be measured relatively easily after the insertion of preformed cylindrical test samples into the mold cavity.

This allyl polyester compound contains 4% Luperco ATC (benzoyl peroxide paste dispersed in TCP), which acts as a catalyzer, and 50% asbestos, which acts as a filler. The extrusion mold, shown in Figure 1, is heated and kept at a constant temperature by the thermo-regulator in the same manner previously used for the flow of thermoplastics. Both the diameter and the length of the hole in die are 1 mm. The test sample of the thermosetting molding compound which has been preformed in a cylindrical shape (initial height h_0 = 10 mm., initial diameter d_0 = 10 mm.), at a room temperature of 20°C. is inserted into the mold cavity, applied by extrusion pressure after the insertion, and then extruded through the die in the mold. The flow curves experimentally measured in this case are not as simple as those of thermoplastics, because the test sample of thermosetting compound is heated from the

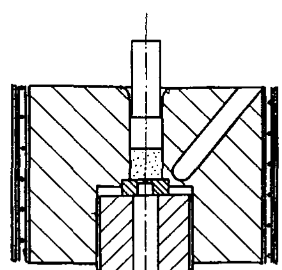

Fig. 1. The extrusion mold in the extrusion rheometer.

* Researches on the flow of polymeric substances by means of extrusion rheometer: 4th report.

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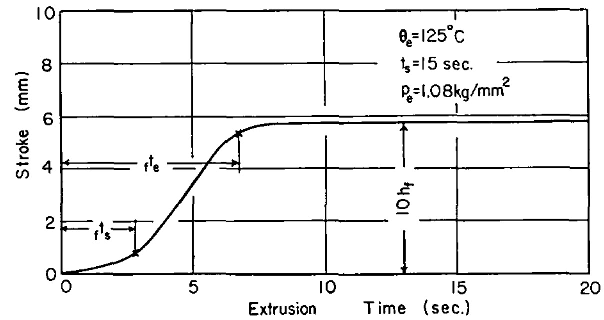

Fig. 2. A representative flow curve of allyl polyester thermosetting molding compound in the extrusion rheometer.

surrounding mold cavity and its consistency varies every second due to the curing chemical reaction.

One representative flow curve of the above test sample by the above test procedures is shown in Figure 2, taking the time in application of extrusion pressure as zero in the abscissa and multiplying the extrusion stroke by 10 in the ordinate. As shown at the beginning of the flow curve, the volume discharge of the test sample through the die is small for a short period after the application of the extrusion pressure. This is because the test sample has a low thermal conductivity and still remains in a powdery state. The volume discharge increases quickly after some time ${}_ft_s$ when the test sample has been considerably heated. The mean velocity v_d in the die in this flow process is one of the factors specified in the flow characteristics of thermosetting resins. After some more time ${}_ft_e$, the volume discharge of the test sample decreases very quickly because of the development of the curing reaction of the thermosetting resin. Even though the same amount of test molding compound may still remain in the mold cavity, the flow of the test sample finally stops due to the completion of the curing reaction.

Thus, the flow characteristics of the thermosetting molding compound can be measured by the relative comparison of the following factors which were obtained experimentally.

(*a*) Flow ratio:

$$R_f = \frac{h_0 - h_f}{h_0} \times 100\ (\%)$$

where h_f and h_0 are the final and initial heights of the cylindrical test specimen, respectively.

(*b*) The time at which flow increases rapidly: ${}_ft_s$ (sec.).

(*c*) The time at which flow decreases rapidly: ${}_ft_e$ (sec.).

(*d*) The mean flow velocity in die in fast flow process: v_d (mm./sec.).

III. PRELIMINARY INQUIRY OF SEVERAL INFLUENCING FACTORS

1. Determination of Time t_s at Which Application of Extrusion Pressure on Test Specimen in Mold Cavity Begins

After insertion into the mold cavity, the preformed test specimen is quickly heated from the surrounding mold. Therefore the time period t_s between the insertion of the specimen into the mold cavity and the application of the extrusion pressure influences the flow characteristics of the test specimen greatly. The experimental results concerning the influence of t_s are shown in Figure 3. In this test the mold cavity was kept at constant extrusion temperature θ_e = 125°C., which is considered to be most suitable for the curing of the allyl polyester molding compound. As is clearly shown in Figure 3, the test sample can hardly flow in the case where t_s is as long as 60 sec. because of the considerable development in the curing reaction before the application of extrusion pressure. On the other hand, the flow is small in the case of as small a t_s as 5 sec. because the part near the surface of the test specimen, which is first heated and extruded in the neighborhood of the hole in the die, hardens in the die and prevents the flow of the remaining part. Nevertheless, almost all of the test specimen in the mold cavity does not as yet have a soft enough consistency to flow. Consequently, the flow is at its maximum at the middle value of t_s, as shown in Figure 3. The change of v_f has the same tendency as that of R_f. The latter experiment was performed under the same conditions of t_s = 15 sec., in line with the above experimental results and their relations to such practical moldings as compression and transfer molding in which external pressure is applied rapidly after the insertion of the molding compound into the cavity.

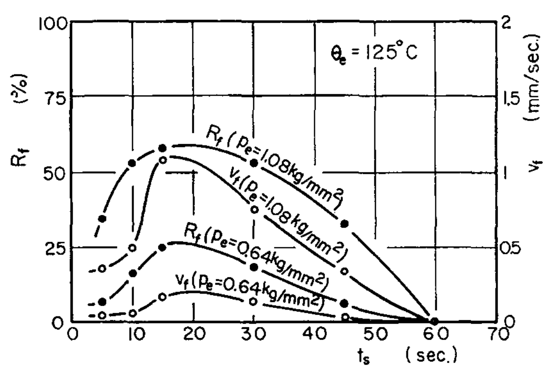

Fig. 3. The relationship between t_s and the flow characteristics of allyl polyester molding compound.

2. Influence of Extrusion Pressure p_e

The influence of extrusion pressure p_e on the flow characteristics was measured at θ_e = 125°C. and t_s = 15 sec. and is shown in Figure 4. It is natural

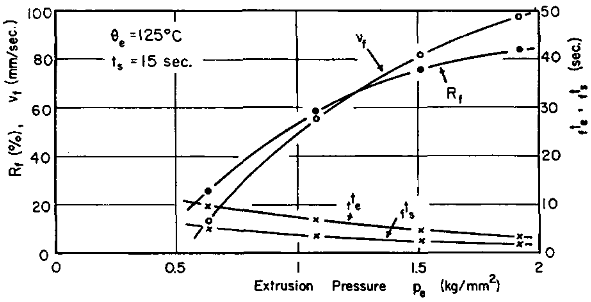

Fig. 4. The influence of extrusion pressure p_e on the flow characteristics of allyl polyester molding compound.

that R_f and v_f increase with the increase of extrusion pressure p_e. However ${}_ft_s$ and ${}_ft_e$ decrease slightly with the increase of p_e. The latter experimental result is interpreted by the rapid increase in flow due to the increase of thermal conductivity coupled with the increase of p_e.

3. Influence of Extrusion Temperature θ_e

Extrusion temperature θ_e must be evaluated while considering the curing of the thermosetting test samples. A low extrusion temperature must be avoided because of full curing and the efficiency in molding. However, a high extrusion temperature which may induce the chemical decomposition of the test specimen is also not desirable. Extrusion in the former experiment was tested at constant extrusion temperature of 125°C. Experiments at extrusion temperatures from 115 to 135°C., at which the curing reaction is expected to be suitable, were performed in the same way. The results ob-

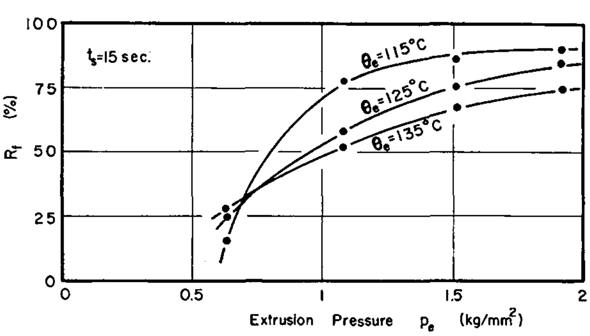

Fig. 5. The relationship between extrusion temperature θ_e, extrusion pressure p_e, and R_f.

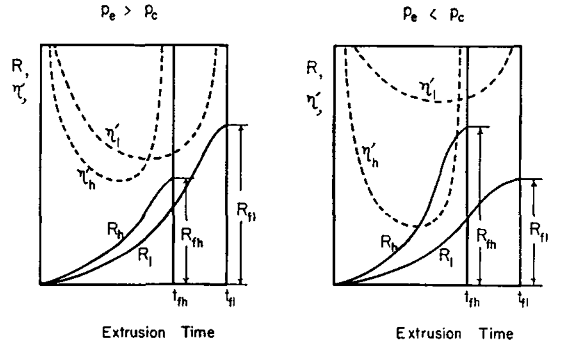

Fig. 6. Schematic interpretation of the influence of extrusion temperature θ_e on R_f. The suffix "h" means a high extrusion temperature; "l" means a low extrusion temperature.

tained are shown in Figure 5. It is reasonable that R_f increases at the same time that p_e increases.

However, the influence of extrusion temperature θ_e is complicated. Specifically the order in the magnitude of R_f in different extrusion temperatures θ_e is reversed when the extrusion pressure p_e is more or less than the critical extrusion pressure p_c, and these results must be interpreted in relation to the extrusion pressure p_e. In general, R_f is predominantly determined by the value of ${}_ft_e$ and the time dependence of the coefficient of apparent viscosity η'. The higher the extrusion temperature θ_e, the smaller the value of ${}_ft_e$. In the case of $p_e < p_c$, however, R_f in the higher extrusion temperature θ_e is larger than R_f in the lower extrusion temperature θ_e, because the decrease of η' in the high extrusion temperature is very large despite the small value of ${}_ft_e$ in the high extrusion temperature. The influence of the decrease of η' at the higher extrusion temperature on R_f is larger in the case of $p_e < p_c$ than that of the decrease of ${}_ft_e$ in the higher extrusion temperature on R_f. On the other hand, the influence of the decrease of η' in the higher extrusion temperature on R_f is smaller in the case of $p_e > p_c$ than that of the decrease of ${}_ft_e$ in higher extrusion temperature on R_f. These relationships are shown schematically in Figure 6.

Such phenomenon is often observable in the extrusion flow of a thermosetting molding compound. For example, the results of some melamine molding compound containing rayon pulp as a filler in the amount of 40% (weight ratio) is shown in Figure 7. The breathing which is usually necessary for the molding of melamine compound was not performed in this experiment for comparison with the flow results of allyl polyester compound. From these results it was found that the extrusion temperature θ_e must be most suitable for various thermosetting molding compounds through consideration of the conditions of both rapid curing and full flowing.

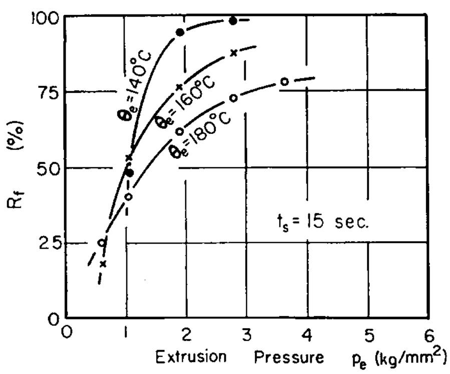

Fig. 7. The flow characteristics of melamine molding compound.

IV. RECOMMENDABLE MEASURING CONDITIONS AND TESTING EXAMPLES OF THE FLOW

From the preliminary investigation of several factors which effect the extrusion flow of the thermosetting molding compound, the recommended measuring conditions for the flow of thermosetting molding compound by extrusion rheometer are as follows.

(*1*) The extrusion temperature θ_e is the most suitable temperature for the curing of thermosetting test samples.

(*2*) The time at which the application of extrusion pressure begins, t_s, is 15 sec.

(*3*) The extrusion pressure p_e is the mean compressive molding pressure (transfer molding pressure is too high to use as an extrusion pressure although extrusion rheometer may be more similar to transfer molding than compression molding).

Then the flow characteristics of thermosetting resins can be compared mainly on the basis of the factors v_f, R_f, ${}_ft_s$, and ${}_ft_e$, measured experimentally.

As mentioned previously, allyl polyester molding compound is very suitable as a sample for measuring the flow of the thermosetting resin because of the polymerization reaction during curing. Therefore allyl polyester molding compounds having different treatments and ingredients were used as test samples for further flow tests for thermosetting compounds.

1. Measurement of Time-Aging Effect of Life of Thermosetting Resins

Even in storage at room temperature the flow of the thermosetting molding compound decreases step by step because of the time-aging effect through the gradual advance of the internal molecular structure to a three-dimensional network. This problem is very important in relation to the life of the thermosetting molding compound, and consequently the influence of time-aging on the flow of allyl polyester molding compound was investigated in the extrusion rheometer.

If the test compound samples are kept at room temperature, a very long storage time is necessary for the measurement of the above time effect by the extrusion rheometer. Hence, test samples were kept at 50°C. for varying time periods. The results obtained are shown in Figure 8. Even at so low a temperature as 50°C. in storage, Lupereo ATC has considerable action on allyl polyester compound as a catalyzer.

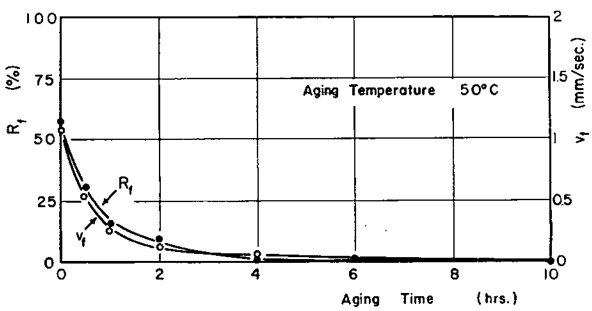

Fig. 8. The relationship between the flow characteristics and the time-aging effect of allyl polyester molding compound. (p_e = 1.08 kg./mm.^{2}, θ_e = 125°C., t_s = 15 sec.)

2. Influence of Various Fillers

The quality and quantity of filler[28] in the thermosetting molding compound not only strongly influence the mechanical, electrical, and physical properties of molded plastics, but also their flow characteristics. Several allyl polyester molding compounds having various kinds of filler in various amounts were examined in the investigation of the influence of filler on flow characteristics. The experimental results obtained are shown in Table I. Except for cost problems, rayon pulp is recommended as a filler from the standpoint not only of mechanical properties and color problems, but also because of its flow characteristics.

Thus the flow of the thermosetting molding compound in the curing process, which is more compli-

TABLE I
The Influence of Fillers on the Flow Characteristics of Allyl Polyester Molding Compound
(p_e = 1.08 kg./mm.^{2}, θ_e = 125°C., t_e = 15 sec., Luperco ATC = 4%)

		Flow characteristics			
Filler	Wt. ratio, %	v_f, mm./sec.	R_f, %	${}_ft_s$, sec.	${}_ft_e$, sec.
Rayon pulp	29	1.3	80	2.1	6.7
Diatomaceous earth	18				
Diatomaceous earth	50	0.1	8	1.0	2.2
Asbestos	50	1.1	58	2.8	6.9

cated and difficult to evaluate than that of thermoplastics, can be measured under recommended testing conditions by the use of an extrusion rheometer and compared on the basis of the factors R_f, v_f, ${}_ft_s$, and ${}_ft_e$. Because the extrusion method in which the test specimen usually flows at a high rate of strain is used for the measurement of the flow of the thermosetting compound, these experimental results become a useful guide for such practical applications as transfer and compression molding of the thermosetting compound.

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Synopsis

The extrusion rheometer, suggested by the author, is used for the relative measurement of the flow of thermosetting molding compounds in a curing process which is more complicated and difficult to measure than that of thermoplastics. Allyl polyester molding compound, which contains asbestos as a filler in the amount of 50% and Luperco ATC as a catalyzer in the amount of 4%, is used as a test sample of the thermosetting compound. Because the unsaturated polyester which is used as a resin in the test sample of the thermosetting compound contains diallyl phthalate monomer, which acts as a crosslinking component in the radical polymerization reaction, there is no volatile by-product in the curing reaction. Therefore, breathing during the molding of this test sample is not needed, and this allyl polyester molding compound is considered to be most suitable to use as the test sample of the thermosetting molding compound. Several factors which exert an influence on the flow of the thermosetting compound in the curing process are investigated, and recommended testing conditions are determined. Although the flow curve of the thermosetting molding compound in the extrusion rheometer is not as simple as that of thermoplastics, the flow characteristics of the thermosetting molding compound can be evaluated and compared by the factors R_f, v_f, ${}_ft_s$, and ${}_ft_e$, which are obtained from the flow curve. As an example, the influences of time-aging effect and various fillers on the flow of the thermosetting molding compound are examined by the above method.

Résumé

Le rhéomètre d'extrusion, proposé par l'auteur est utilisé pour la mesure relative de l'écoulement de composé fondu thermodurcissable durant le processus du durcissement qui est plus compliqué et difficile à mesurer que dans le cas des thermoplastiques. Un polyester d'allyle fondu contenant 50% d'asbeste comme charge et 4% de Luperco ATC comme catalyseur est employé comme substance témoin de composé thermodurcissable. Puisque le polyester non saturé, utilisé comme résine dans l'échantillon test de la substance thermodurcissable, contient du phthalate de diallyle monomère, jouant le rôle d'agent de pontage dans la réaction de polymérisation radicalaire, il n'y a pas de produit volatil formé en cours de la réaction. Par conséquent l'aspiration pendant le fonte de cet échantillon n'est pas nécessaire et ce polyester d'allyle fondu est le plus adapté pour servir de test de substance thermodurcissable. Plusieurs facteurs qui exercent une influence sur l'écoulement du composé thermodurcissable au cours du traitement sont examinés et les conditions d'essai sont déterminées. Bien que la courbe d'écoulement du composé thermodurcissable dans le rhéomètre d'extrusion n'est pas aussi simple que celle des composés thermoplastiques, les caractéristiques d'écoulement du composé thermodurcissable peuvent être évaluées et comparées par les facteurs R_f, v_f, ${}_ft_s$ et ${}_ft_e$, qui sont obtenus à partir de la courbe d'écoulement. Par exemple, les influences du vieillissement et des diverses charges sur l'écoulement du composé thermodurcissable sont examinées par la méthode ci-dessus.

Zusammenfassung

Das vom Autor vorgeschlagene Extrusionsrheometer wird zur Relativmessung des Fliessens von wärmehärtenden Pressmassen während des Härtungsprozesses benützt. Dieses ist komplizierter und schwieriger zu messen als dasjenige von thermoplastischen Stoffen. Ein Allylpolyesterpressharz, das 50% Asbest als Füllstoff und 4% Luperco ATC als Katalysator enthält, wird als Testprobe für wärmehärtende Pressmassen benützt. Da der ungesättigte Polyester, der als Testharz für wärmehärtende Pressmassen benützt wird, monomeres Diallylphthalat enthält, das als Vernetzungskomponente bei der Radikalpolymerisation wirkt, entstehen bei der Härtungsreaktion keine flüchtigen Nebenprodukte. Daher ist eine Entlüftung während des Pressens dieser Testprobe nicht notwendig und dieses Allylpolyesterpressharz wird als am besten geeignete Testprobe für wärmehärtende Pressmassen betrachtet. Es werden die Faktoren, die einen Einfluss auf das Fliessen einer wärmehärtenden Masse haben, untersucht und empfehlenswerte Prüfungsbedingungen festgelegt. Obwohl die Fliesskurve des wärmehärtenden Pressharzes im Extrusionsrheometer nicht so einfach, wie die von thermoplastischen Substanzen ist, kann die Fliesscharakteristik des wärmehärtenden Pressharzes ermittelt und ein relativer Vergleich mittels der Faktoren R_f, v_f, ${}_ft_s$ und ${}_ft_e$ durchgeführt werden, die aus der Fliesskurve erhalten werden. Als Beispiel werden die Einflüsse der zeitlichen Alterung und verschiedener Füllstoffe auf das Fliessen der wärmehärtenden Pressmasse mit der oben angegebenen Methode geprüft.

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