



An Adjustable Gap In-Line Rheometer

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Introduction

The rheological behavior of polymer melts, and structured fluids including emulsions, suspensions and gels can be characterized employing various viscometric flows (1-2). However, off-line rheometers where the fluid is mixed/prepared for characterization and then loaded into a rheometer cannot be always used especially for structured fluids. To alleviate this various devices are proposed (3-7). For example, Nichols and Mathe (3) have proposed an extrusion plastometer type rheometer where the material to be characterized is mixed within the chamber of the rheometer by using a pair of telescopically arranged pistons. However, it is simpler and more accurate to characterize the rheological behavior of a fluid within the confines of the processing equipment used in mixing, compounding devolatilization and/or reaction.

Emery and Herring (4) have suggested that a "slip" stream of melt be pumped from an extruder into a rheometer for monitoring of the shear viscosity of the melt. On the other hand, Blanch et al., (5) have devised a rheometer which involves again diverting a melt stream from an extruder into a capillary rheometer which consists of two metering pumps and a capillary passage in between the two pumps. A one point shear viscosity of the melt is measured by controlling the rate of flow of the melt to maintain a constant pressure drop along the capillary passage thus virtually mimicking the operation of a dead weight plastometer i.e., a melt indexer.

Eswaran et al., (6) connected a slit die with a constant gap with flush mounted pressure transducers to a flood fed extruder for measurement of the shear stress of the melt at the flow rate that the extruder would generate. Springer et al., (7) used a dual slit geometry with a double valve (with again flush mounted transducers) where the flow rates are measured by weighing polymer exiting from each slit and wall shear stresses are calculated from the axial pressure profiles. The utility of such rheometers would increase significantly if it were possible to alter the deformation rate systematically without changing the corresponding volumetric flow rates. In

an extrusion apparatus changes in flow rate may lead to changes in temperature and in the cases of structured fluids, changes in the microstructure of the fluid.

Dealy and co-workers, on the other hand, presented an elegant in-line rheometer (8) which is based on pure drag flow and a novel shear stress transducer. This rheometer is suitable for in-line sensing and process control (9). However, this apparatus measures the shear stress and corresponding shear rate at one point and may not allow structured fluids to reach a fully-developed flow and achieve an equilibrium microstructure at the imposed shear rate.

In the following, we describe a new slit in-line rheometer which is especially designed to characterize structured fluids including blends, emulsions, suspensions, and gels (10). The in-line rheometer contains the mechanism for continuous and remote adjustment of a gap thus providing the facility to alter the deformation rate over a range for a melt fed into the rheometer at constant flow rate. Furthermore, the rheometer allows fully-developed conditions to be reached over a broad range of shear rates, allowing the shear viscosity material function of non-Newtonian fluids to be characterized by employing various corrections including Rabinowitsch and wall slip.

Description of the Rheometer

A schematic diagram of the rheometer in the slit mode is shown in Figure 1. This rheometer consists of a slit die with a movable plate which allows the gap separation, H , between the two plates to change. As shown in Figure 2, the rheometer is equipped with a series of equally-spaced pressure and temperature sensors which are installed flush with the inner surface of the rheometer. The gap adjustment mechanism is coupled to a remotely-controllable stepper motor.

The rheometer is typically connected to a single or twin screw extruder which is starve-fed. The starve feeding is accomplished by the use of gravimetric or loss-in-weight feeders which feed the extruder at a constant volume flow rate, Q . The extruder has multiple feeding ports and multiple feeders to allow complete formulations to be processed and prepared for characterization.

The apparent shear rate, $\dot{\gamma}_a$, for the slit die at a given flow rate is given by:

$$\dot{\gamma}_a = \frac{6Q}{WH^2} \quad (1)$$

where W is the width of the slit rheometer and H is the adjustable gap. The dependence of the shear rate to the square of the gap, H , renders the device sensitive to small changes in gap (high gain for shear rate). The ability to measure the wall shear stress, τ_w , stems from the ability to measure the pressure, P , distribution in the axial direction along the length of the die, z , and to determine the pressure gradient $-P/z$, which remains constant over the fully-developed region of

the slit die:

$$\tau_w = \frac{H}{2} \frac{\partial P}{\partial z} \quad (2)$$

For one dimensional flow to hold the width, W, over the gap, H, ratio i.e., W/H needs to be greater than 10-20. Since shear stress data at multiple gap separations and hence apparent shear rates can be collected, the true shear rate at the wall, $\dot{\gamma}_w$, can be determined:

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

$$\text{where } n = \frac{d \ln \tau_w}{d \ln \dot{\gamma}_a} \quad (4)$$

Thus, determination of τ_w versus $\dot{\gamma}_a$ behavior at multiple shear rates provides the slope n allowing the wall correction (for fluids which do not exhibit wall slip) to be made. For fluids which exhibit wall slip the Mooney procedures (11-13) may be enacted and adopted to determine the Navier's wall slip coefficient, β , for slip flow. For the in-line rheometer this procedure consists of running the rheometer at constant shear rate but at different surface to volume ratios by modifying both the flow rate, Q, and gap separation, H, to generate constant apparent shear rate values, $\dot{\gamma}_a$. The wall slip velocity U_s can be determined from the slope of apparent shear rate, $\dot{\gamma}_a = 6\bar{v} / H$ versus $1/H$ at constant wall shear stress, τ_w , starting from:

$$\frac{6\bar{v}}{H} = \frac{6U_s}{H} - \frac{3}{2} \frac{\tau_w}{\tau_w} \int_0^{\tau_w} \dot{\gamma} d\tau_{yz} \quad (5)$$

Thus, the derivative:

$$\left. \frac{\partial \left(\frac{6\bar{v}}{H} \right)}{\partial (1/H)} \right|_{\tau_w} = \left. \frac{\partial \dot{\gamma}_a}{\partial (1/H)} \right|_{\tau_w} = 6 U_s \quad (6)$$

Here \bar{v} is the mean velocity in the slit die channel i.e., $Q = WH \bar{v}$. If the wall slip velocity, U_s , versus wall shear stress, τ_w , data are used to determine Navier's wall slip coefficient, β :

$$U_s = \beta \tau_w \quad (7)$$

the shear rate data then can also be corrected for wall slip. The wall slip and Rabinowitsch corrected wall shear rate, $\dot{\gamma}_w$, becomes (14),

$$\dot{\gamma}_w = \frac{2(Q - Q_s)}{WH^2} \left[2 + \frac{d \ln(Q - Q_s)}{d \ln \tau_w} \right] \quad (8)$$

where Q_s is the volumetric flow rate due to slip i.e., $Q_s = U_s W H$. This expression becomes the Rabinowitsch correction, Equation 3, for the no-slip condition. It should be noted however, that although the procedure is doable, in practice changes in volumetric flow rate also result in changes in microstructure and temperature of the fluid. To rectify it is necessary to have the in-line rheometer be preceded by a straight conduit, preferably another slit, to allow heat transfer and temperature control under fully developed conditions. This was not done for the prototype rheometer used here and hence in this report wall slip corrections will not be demonstrated.

Typical Results

A set of results obtained with a thermoplastic elastomer (HyTemp available from Zeon Chemicals mixed with a plasticizer, DOA and a KCl solid filler) will be used to demonstrate the operation of the rheometer. This elastomer is extremely difficult to handle in plasticized form. For example, it cannot be molded without fillers for characterization in a rotational rheometer. It is also very difficult to be loaded into a barrel of a rheometer.

The thermoplastic elastomer, the plasticizer and the filler were fed into a Baker-Perkins 50.8 mm co-rotating twin screw extruder using gravimetric and loss-in-weight feeders and a Zenith gear pump. The extruder was used to masticate and plasticize the elastomer and to compound with the filler. A devolatilization section and vacuum were used to deaerate. The adjustable gap rheometer was then connected to the twin screw extruder as shown in Figures 1 and 2.

The typical pressure versus distance data for one run is shown in Figure 1. The linear portion of pressure versus distance data were used to determine $\partial P / \partial z$ and hence the wall shear stress (Eq'n (2)). For comparison purposes, capillary flow experiments were also carried-out for the filled and plasticized TPE.

Typical comparisons of the shear stress versus shear rate behavior of the plasticized TPE (Fig.3) and filled TPE (Fig.4) as collected with the in-line rheometer versus data collected with a capillary rheometer at the same temperature are shown in Figures 3 and 4. The agreement is acceptable.

The utility of the in-line rheometer is further shown in Figure 5 where the shear stress versus the shear rate behavior of the thermoplastic at different plasticizer concentrations is included. The practicality of the instrument and the techniques are demonstrated here. A series of measurements on multiple materials could be collected with the experimental set-up involving the in-line rheometer and extruder within a reasonable period of time. Using such measurements the formulation of the elastomer can be tailored conveniently to provide the desired rheological and processability behavior.

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Key words: In-line rheometer, elastomer, adjustable gap.

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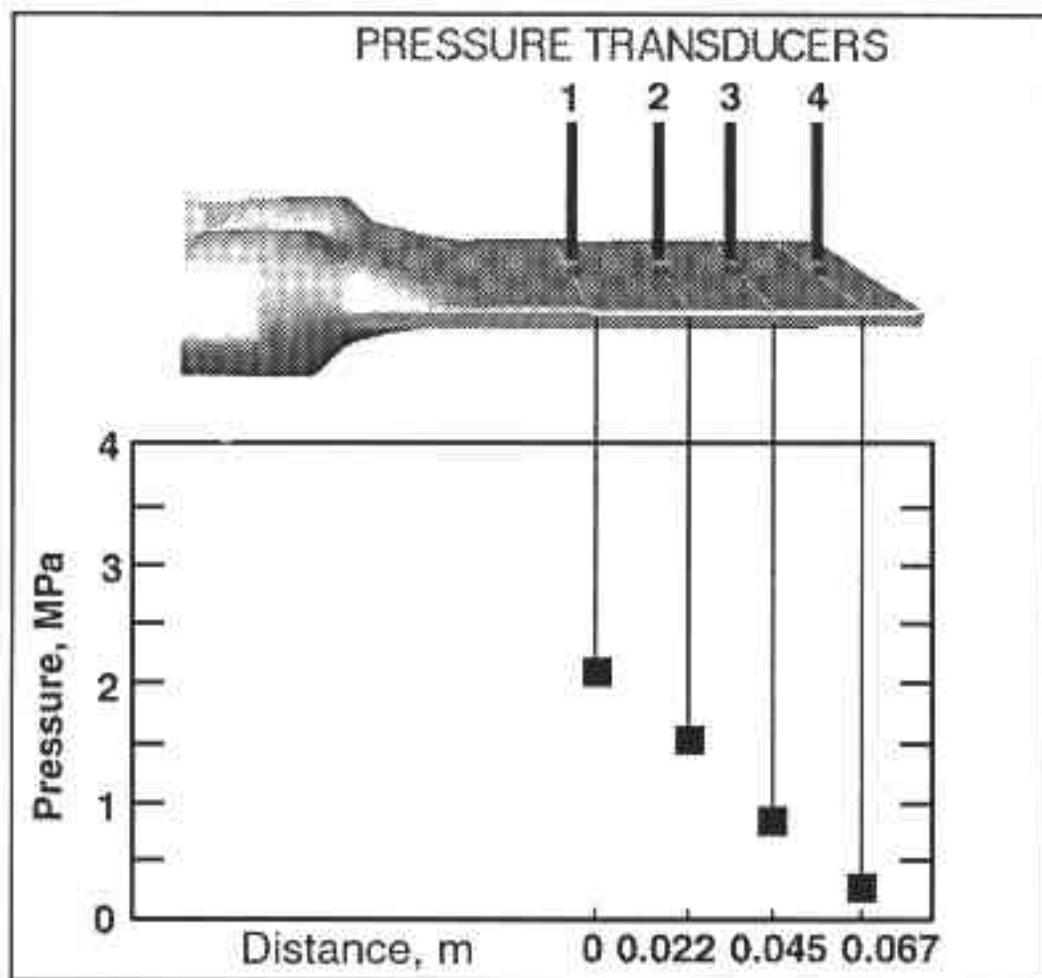


Fig. 1. Schematic representation of in-line slit die and pressure data collected during one run with a filled elastomer

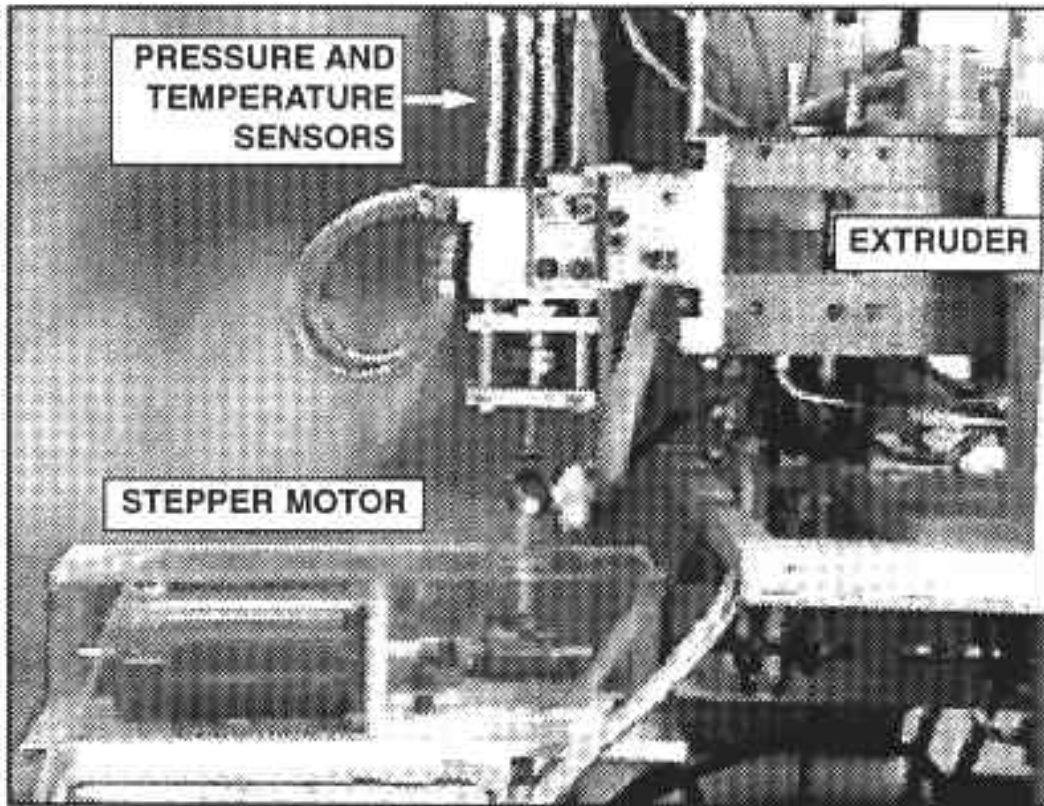


Fig. 2. In-line slit rheometer.

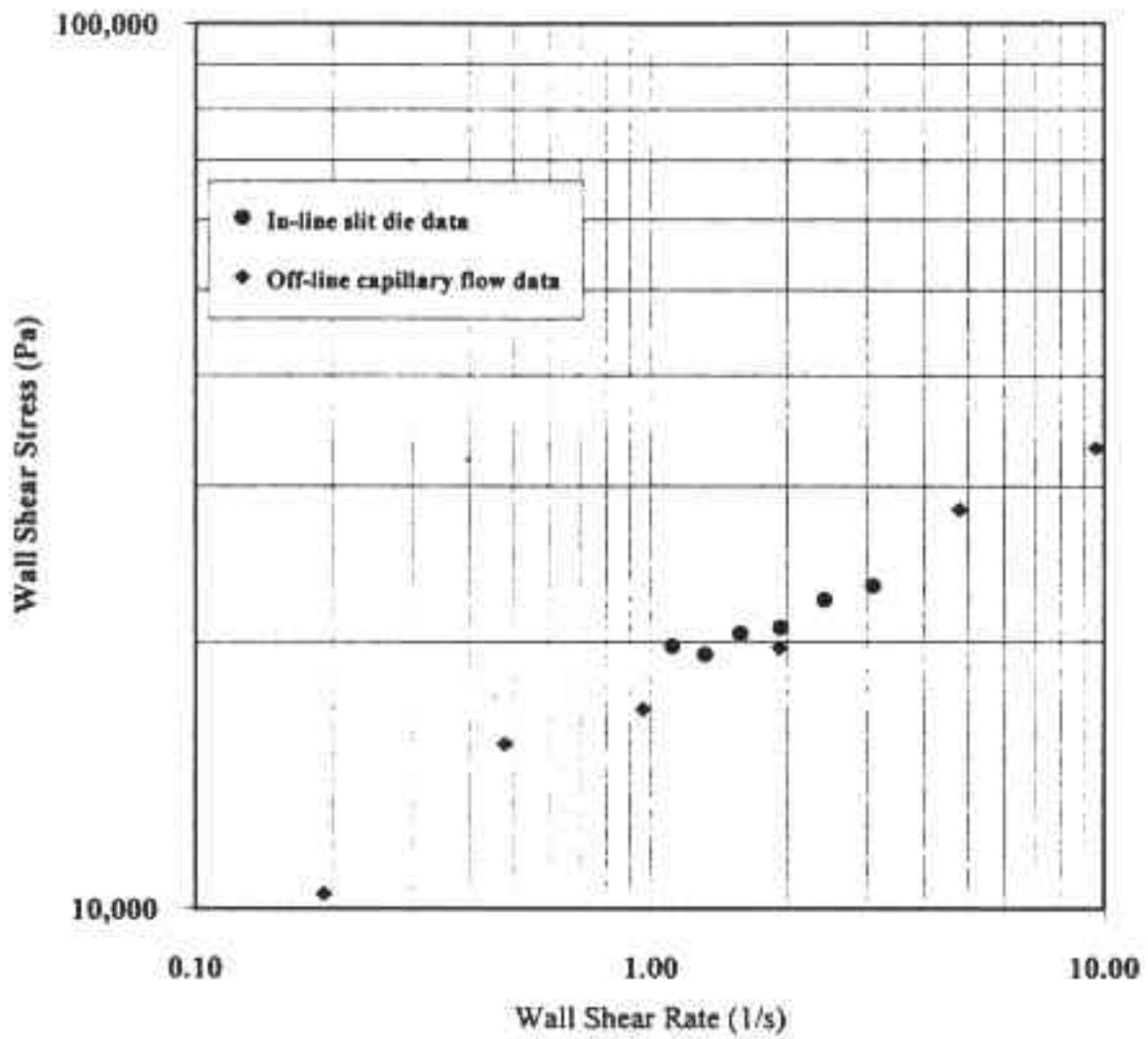


Figure 3: Comparison of data collected with in-line rheometer and off-line capillary flow data for a plasticized TPE at a plasticizer/TPE ratio of 0.275

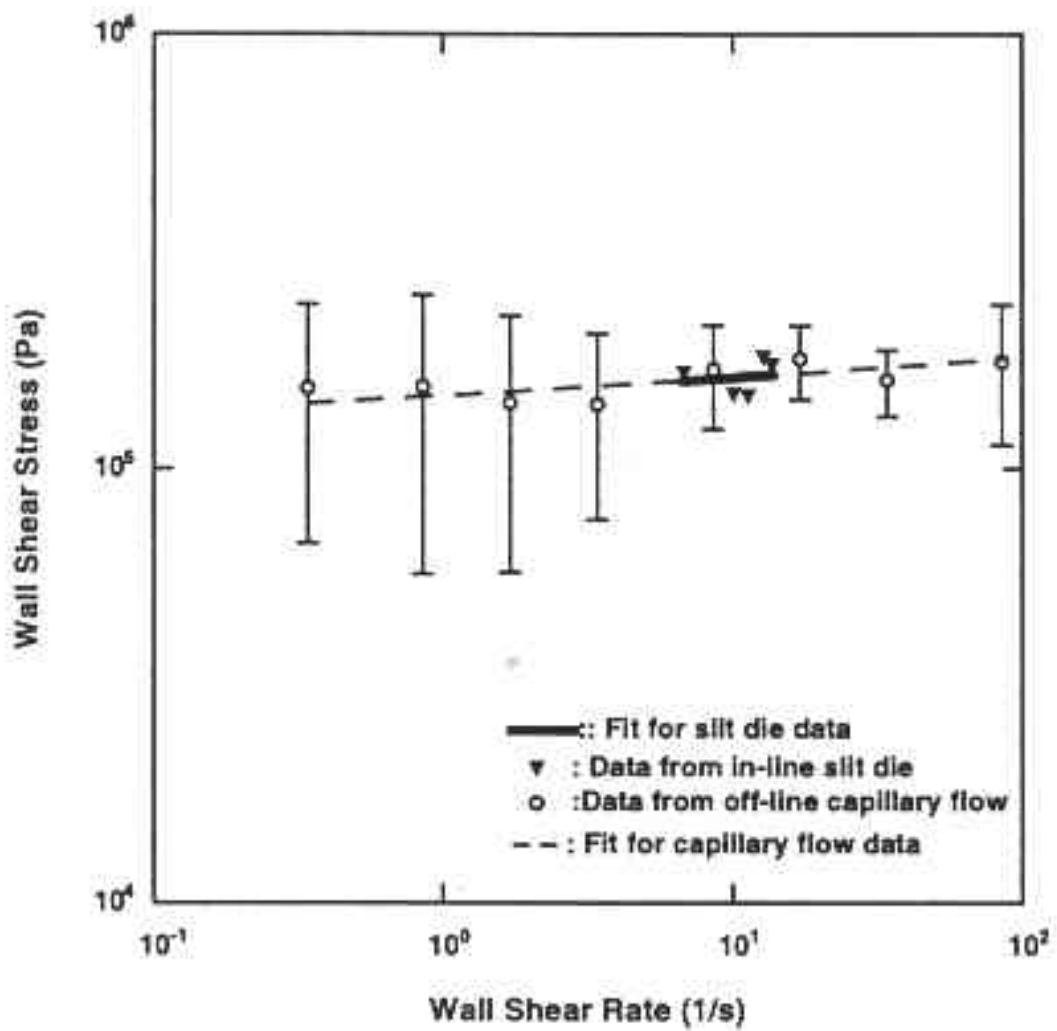


Figure 4: Comparison of data collected with in-line slit rheometer and off-line capillary flow data for a filled elastomer

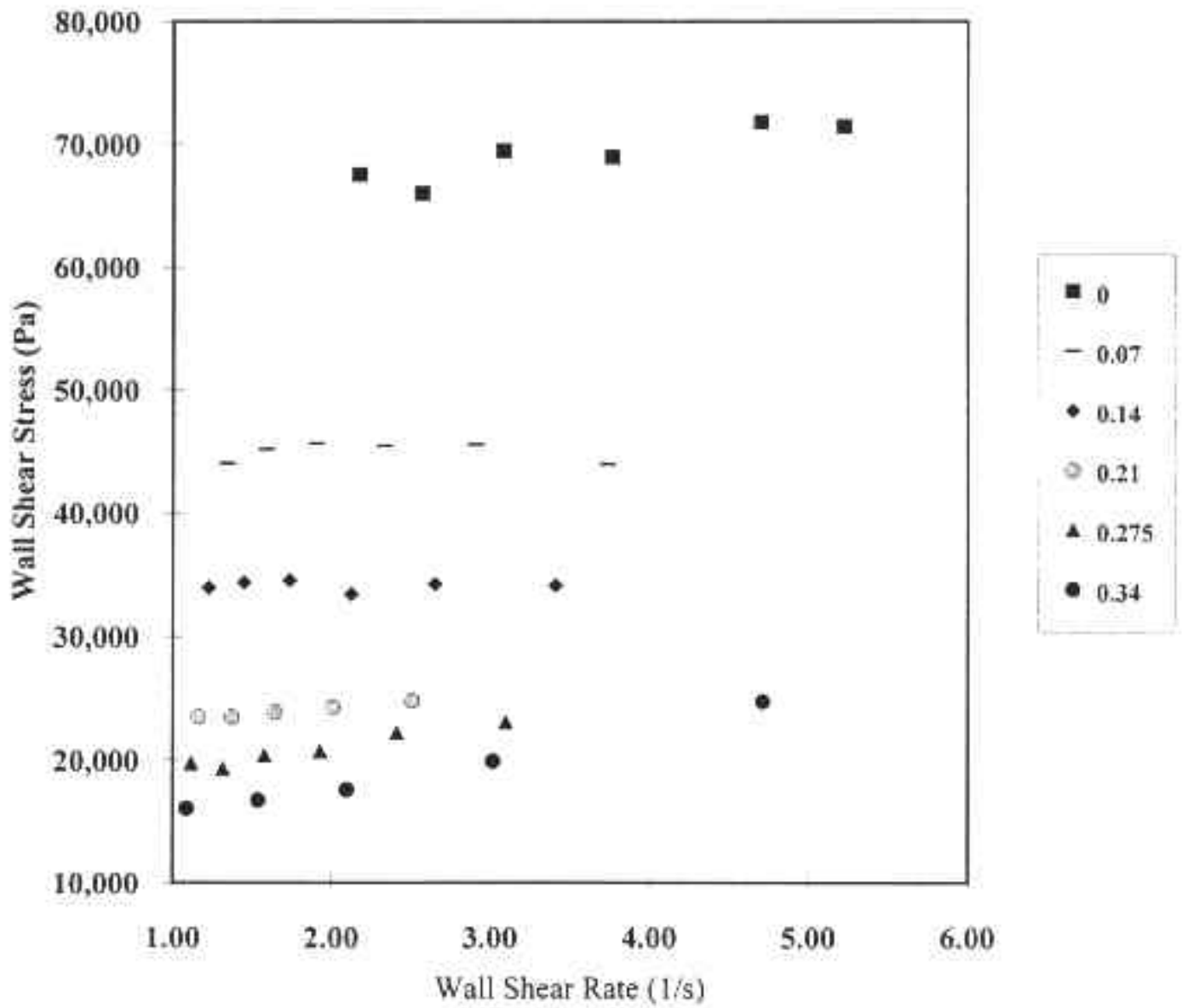


Figure 5: Shear stress versus shear rate behavior of the plasticized elastomer at different values of the plasticizer (DOA) to elastomer ratio by weight as collected with in-line rheometer