The Effect of Shear on the Properties of Rigid PVC

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ABSTRACT:

The rheological and fusion behavior of polyvinyl chloride (PVC) compounds plays a dominant role in the processing operations and in the development of physical properties in the processed material. A comprehensive study was made in this work to evaluate the effect of shear and thermal history on stability, mechanical and rheological properties of rigid PVC compounds. Different samples of Rigid Poly vinyl chloride including dry blend powder, granules, and bottles molded from both were examined. A study was also made on recycled RPVC where 25% of reclaimed material was continuously blended with fresh dry blend and processed for 15 cycles. Results showed that compaction of the PVC material took place in the brabender plastograph at constant temperature and shear stress. Correlations were given to explain results concerning residual stability and rheological behavior. Furthermore, it was seen that elongation and tensile impact are dependent on shear history.

KEYWORDS: stability, rigid polyvinyl chloride, rheology, apparent viscosity, recycling, and shear stresses.

تأثير قوى القص على خواص مادة متعدد (كلورايد الفاينيل) الصلب

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خلاصة البحث :

حيث ان لخواص الانصهار والانسياب لبوليمرات متعدد (كلورايد الفاينيل) الصلب دورا حيويا في عمليات التصنيع وفي عمليات تطوير الخواص الفيزياوية للمنتج النهائي ؛ تمت اجراء دراسة شامله تناولت تاثير قوى القص والاجهاد الحراري المسبق على كل من الثبوتية وخواص الانسياب والخواص الميكانيكية لهذا البوليمر. شملت الدراسة اربع انواع من متعدد (كلورايد الفاينيل) الصلب هي : مسحوق البوليمر الجاف ، حبيبات مصنعة من نفس المسحوق، وقناني مصنعه من كلا الفقرتين السابقتين. كذلك تمت دراسة تاثير رفع نسبة (المثروم البلاستيكي للقناني : نسبة المسحوق الجاف) الى ٢٥% وذلك باعادة تدويره ١٥ دورة متتالية .

اظهرت النتائج ان عملية الرص والانصهار للبوليمر حصلت في جهاز البرابندر بدرجة حراره واجهاد قص ثابتين. وكذلك تم اعطاء ارتباطات لتوضيح النتائج التي تتعلق بالاستقرارية وخواص الانسياب. علاوة على ذلك ، تبين ان الاستطالة والصدم تعتمد على قوى القص المسبقة.

INTRODUCTION:

Poly (vinyl chloride) (PVC) is one of the most explored polymers in the world, bearing a wide range of properties. It is very durable and strong, abrasion and moisture resistant; withstands rust and corrosion, is electrically nonconductive and has excellent fire resistance properties. Moreover, it is cheap, easily produced, and light weight [Charles, 2000].

In 1996, about 6.5 million pounds of post-consumer vinyl were recycled in the U.S. An estimated additional 300 million pounds of vinyl post industrial scrap was diverted from landfills and recycled into second-generation products. More than 3,500 communities accept vinyl products in their recycling programs, which is about 25 percent of all communities that recycle [PACIA & Nolan-ITU, 2004]. A recent directory published by vinyl institute lists nearly 50 companies that make commercial products out of recycled vinyl [Directory of Companies, 1994].

It is known that rigid PVC is the most sensitive thermoplastic to the effect of shear and heat [Owen et al, 1984 and Ivan et al, 1989]. Noticeable changes in the structure could occur and therefore some physical and chemical properties would consequently changes such as melt viscosity [Villemaire, 1983], mechanical properties and long term performance [Yarahmadi, 2001].

Rigid PVC microstructure strongly depends on processing conditions. Under both shear and heat influence, gelation process occurs, and the resulting morphology can be characterized by gelation level parameter [Fillot et al, 2007].

Hattori [1972], Marshall [1983], and Gilbert [1985] showed that PVC powder consisted of grains which were 50-150 microns in size. These grains were converted into smaller micro domains of 0.3-1.0 micron in diameter after the plastic material has melted. Sieglaff [1981] reported that the small grains of 100-1000°A network structure were developed during processing within the PVC micro grains. According to Truss [1985], these grains could not be destroyed completely in the melting process. Allsopp [1982] reported the predominance of Van Der Waals forces, entanglements and crosslinking could also contribute to couple these particles. Teriellus [1981] postulated the formation of crystallites and/or entanglements, which can be destroyed by increasing temperature, and stated that balancing the properties of rigid PVC products requires an optimization of the gelation level.

Furthermore and according to Summers et al [1996] the primary particles fused when the crystallites started to melt, freeing polymer chains for interdiffusion between the primary particles. Covasa and Gilbert [1992] studied the behavior of RPVC during single screw extrusion and observed both the breakdown and internal fusion of the grains, depending on the location of the material around the screw.

Moghri [2004] examined the effect of processing temperature on fusion in the Brabender Plasticorder. Chen et al [1995] pointed that the starting temperature of the brabender, rotor speed, and totalized torque are the three major factors that affect the fusion level of PVC compounds. Tomaszewska et al [2007] discusses the transitory stage between the minimum and the maximum of the torque, which corresponds to an inflection point on the torque curve.

Wenguang et al. [1996] compared the mechanical and processing properties of recycled polyvinylchloride from bottles and pipes with those of virgin pipe grade PVC, and concluded that recycled PVC didn't reduce the modulus and tensile strength.

Yarahmadia et al [2001] examined recycling RPVC profiles by re-extrusion and noticed an improvement of mechanical properties after the second extrusion, due to an increase in the degree of gelation of the PVC material.

Melt processing is one of the best methods of reutilizing plastics, but particular care is required in the recycling of PVC due its thermal and shear sensitivity [Scheirs, 1989]. There are several poly vinyl chloride plants which produce pipes, bottles, and containers from rigid PVC dry blend material. PVC compounds develop optimum bottle properties, impact and chemical resistance when they are highly fused (melted) during processing. These plants consume several thousand tons of this material. Hundreds of tons per year of processed PVC waste are accumulated. This waste is added to the fresh material at certain concentrations not exceeding 10%. In the present work, a comprehensive study was made to evaluate the effect of the shear and thermal history on stability, mechanical and rheological properties changes in three different probes, viz. rigid PVC dry blend, granules obtained thereof and bottles molded from both materials. Moreover, in order to

examine a higher recycling percent, 25% of a previously processed dry blend was mixed with fresh material and then reprocessed for 15 cycles to study and correlate rheological properties for industrial applications.

2. EXPERIMENTAL WORK:

2.1 Materials:

PVC resin (Geon) with K-value 57 was used in this study. Irgastab BC103 (Ciba-Geigy) (100:3 parts by weight) was used as a stabilizers and (Epolene E-20) (100:0.5) as lubricants.

2.2 Sample preparation:

The dry blend mixtures were prepared using a mixer type Henschell FM4, fitted with temperature indicator mounted inside the mixing chamber. An industrial pelletizer and blow molding machine were utilized for producing granules and bottles respectively.

2.3 Rheological properties:

The shear flow properties of polymers are frequently used to characterize polymer melts and to distinguish their processing performance. The measurements of RPVC systems were carried out using a Brabender torque plastograph heated at 190°C. Temperature of the melt was continuously measured and recorded using Fe/Co thermocouple, fitted in the test chamber. The speed of the rotors was 60 rpm. Density was measured for PVC during the Brabender measurements at several periods of time.

It is useful to mention that the measured torque is a function of the melt viscosity, which related to the flow property of the plastic melt

High pressure capillary rheometer, type Rheoscope 1000-CEAST, was also used. Flow properties were conducted at 190°C, the L/D of the capillary was 10.

2.4 Measurements of mechanical properties:

The mechanical properties were specified by measuring the tensile and tensile impact properties.

2.4.1 Tensile properties:

Specimens for mechanical testing were cut out from bottles and then tested according ASTM D-638 for tensile properties. A Zwick testing machine was used to perform the tensile strength test at a crosshead speed of 50 mm/min, and each test was performed until tensile failure occurred. The elongation was also measured [ASTM 1989].

2.4.2 Tensile impact:

Impact is a very important phenomenon in governing the life of a structure. This test was performed according to DIN 53448 (ASTM D1822). A tensile-impact test is a uniaxial tensile test with a high deformation speed. The pendulum device has a working capacity of 7.5 J, at maximum falling angle (150°). For the test, a specimen was fixed between a stationary clamp and a cross head. The pendulums hammer hit the cross head which is fixed to the specimen. In this way, the specimen is deformed in the direction of its longitudinal axis until fracture occurs.

2.5 Recycling evaluation:

For recycling experiments, 25% of already processed dry blend was mixed again with a fresh material and reprocessed. This procedure was repeated for 15 cycles in the same conditions, without adding new additives. Extrudate Samples from each cycle was tested in a high pressure capillary rheometer.

3. RESULTS AND DISCUSSION

The fusion rate plays an important role in the processing of RPVC, especially in blow molding technique, and is defined as the required time to convert a cold formulation of PVC when introduced in an extruder to a melt.

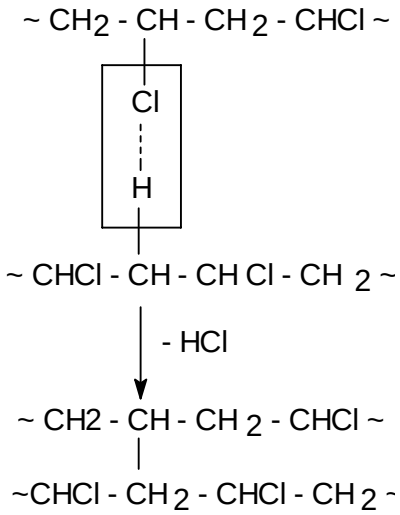
Plots of torque-time and temperature-time curve obtained from Brabender measurements for PVC dry blend and granules are represented in **Fig. 1**. It is seen that the thermal stability of the granules was reduced by 6% and the value of minimum torque was increased by ca.4%. This can be due to the heat and shear that the dry blend was subjected to in the pelletizing machine, therefore, stability and viscosity were slightly affected.

Point E in **Fig.1** represents the end of stability period. Behind this point, the polymer started to degrade and HCL – libration reaction come off very fast.

As shown in **Fig.1**, the melt took 10 minutes to obtain the set temperature and the minimum value of the torque. Thereafter, temperature and torque remained unchanged for about 14 minutes, after which they increased slightly. This could indicate an increase in melt viscosity of the system. In polymer melts, temperature increase is known to cause decrease in the viscosity, but in this work an opposite trend was obtained which could be due to the predominant effect of densification. This observation underlines the possibility that

crosslinking reaction took place. The consequent increase in density values supports such reaction (see density values in **Fig. 1**).

Compaction was attributed in literature [Truss, 1985] as a consequence of the increase in pressure and /or temperature. However, in this work, these parameters in the brabender were constant, yet compaction took place. Therefore, this could be due to the time dependency of the process where the following irreversible crosslinking reaction might occur:



It is worth to mention, that mixing of the melt and metallic surfaces of the mixer would accelerate this reaction. IR data obtained for the samples taken near point E in **Fig. 1** showed no evidence to the presence of conjugated double bonds which give another support of a suggested formulation of the crosslinking reaction rather than dehydrochlorination according to zipper mechanism.

Table 1 shows data obtained from brabender measurements, namely: minimum torque, stability period, and percentage reduction in stability reference to the dry blend. These measurements were conducted on the dry blend, granules, bottles from both and a mixture of dry blend with 25% chips from reclaimed bottles. The bottles which were molded from granules showed the maximum reduction in stability period followed by the bottles molded from the dry blend. The addition of 25% reclaimed bottles to the dry blend caused 7.2% reduction in stability. These results proved that the blow molding process has stronger effect on the reduction of thermal stability than the pelletizing process.

Gelation involves the conversion of the initial PVC particle structure into an increasingly homogeneous melt and therefore the rheological properties of PVC at low temperatures are very different from those at higher ones.

Fig. 2 demonstrates the correlations between apparent viscosity and shear rate obtained from high pressure capillary Rheometer for the following system: PVC dry blend, granules produced thereof, and bottles molded from both materials. No noticeable differences in the values of apparent viscosity could be detected in the higher range of shear rates. On the other hand, the apparent viscosity values for the dry blend were a little lower than that of the bottles molded thereof. These results are in good agreement with the results obtained from the torque measurements in the Brabender.

Fig. 3 shows changes in apparent viscosity of the PVC system for 15 cycles, and at three different shear rates, namely: 608, 1216 and 2452 s^{-1}.

The reprocessing of dry blend containing 25% previously molded PVC indicated the feasibility of using a relatively higher percentage of industrial waste in recycling processes without effective deteriorating changes on specifications but would yield more economic revenue. These results coincide with those of Wenguang et al. [1998].

Table 2 represents data obtained from mechanical testing. A slight decrease in tensile strength for bottles molded from the granules could be seen, while elongation and tensile impact had a more pronounced differences, which probably was due to the shear and thermal history. That indicates that the last two properties are dependent on shear history, while the last cause has no big effect on tensile strength. These results are in agreement with previous studies [Covasa et al. 1992 and Tersilus and Janson 1981], while Fillot et al. [2007] noticed a decrease in impact strength and stated that it was attributed to partial disorientation of the PVC macromolecular chains and reduction of the molecular mobility.

4. CONCLUSIONS:

- The temperature increase in PVC melt caused increase in the viscosity possibly due to crosslinking reaction in the melt and that is proved by the consequent increase in density values.
- When comparing between the blow molding process and pelletizing process, it was noticed that the later had stronger effect on the reduction of thermal stability than the later.

- A correlations between apparent viscosity and shear rate obtained from high pressure capillary Rheometer, demonstrated no noticeable differences in the values of apparent viscosity could be detected in the higher range of shear rates between PVC dry blend, granules produced thereof, and bottles molded from both materials.
- The reprocessing of dry blend containing 25% previously molded PVC indicated the feasibility of using a relatively higher percentage of industrial waste in recycling processes without effective deteriorating changes on specifications.
- Elongation and tensile impact are dependent on shear history, while this cause has no large effect on tensile strength.

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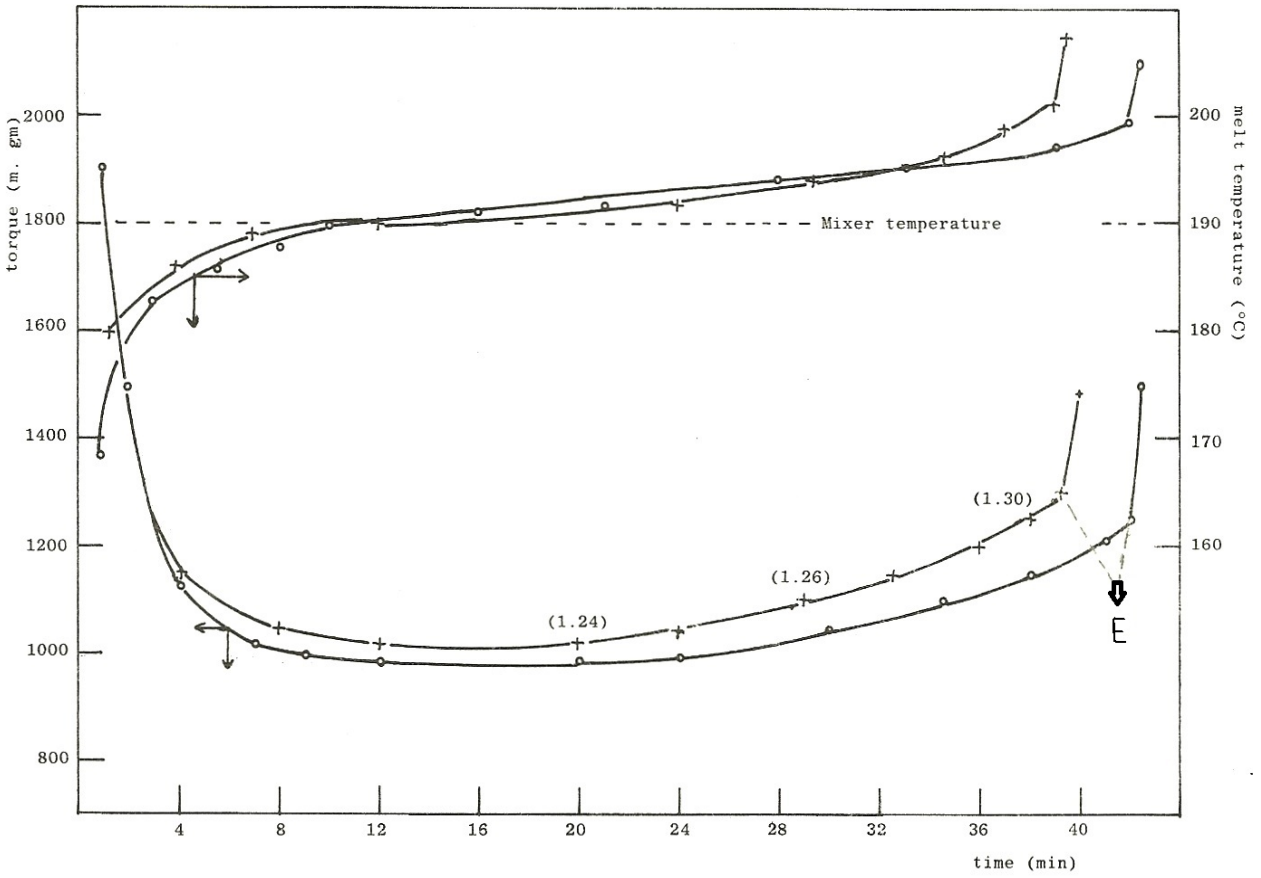

Fig. 1 Torque and temperature vs. time for PVC dry blend (°°°°) and granules (+++)

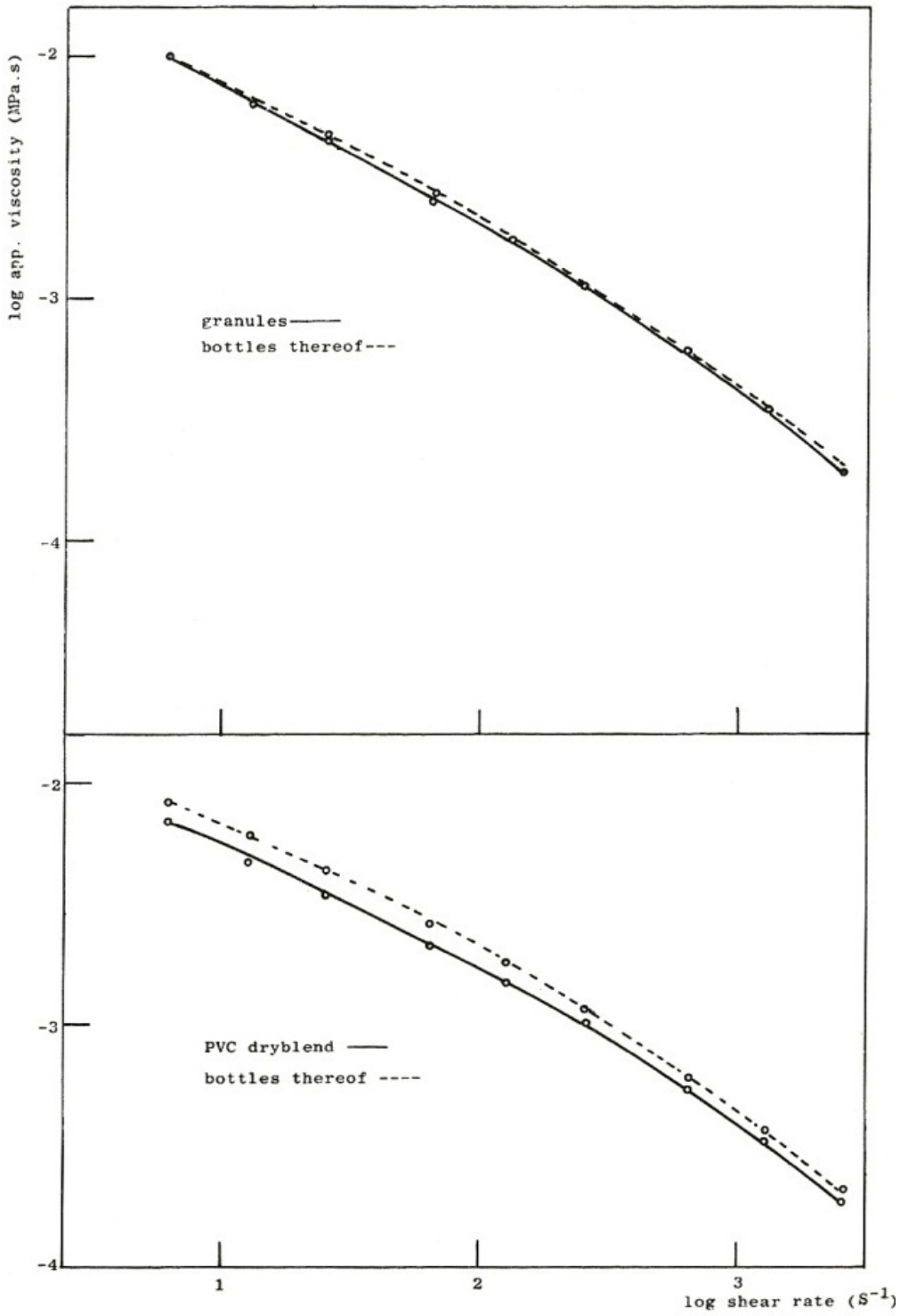

Fig. 2 Log apparent viscosity vs.log shear rate for dry blend, granules and bottles from both.

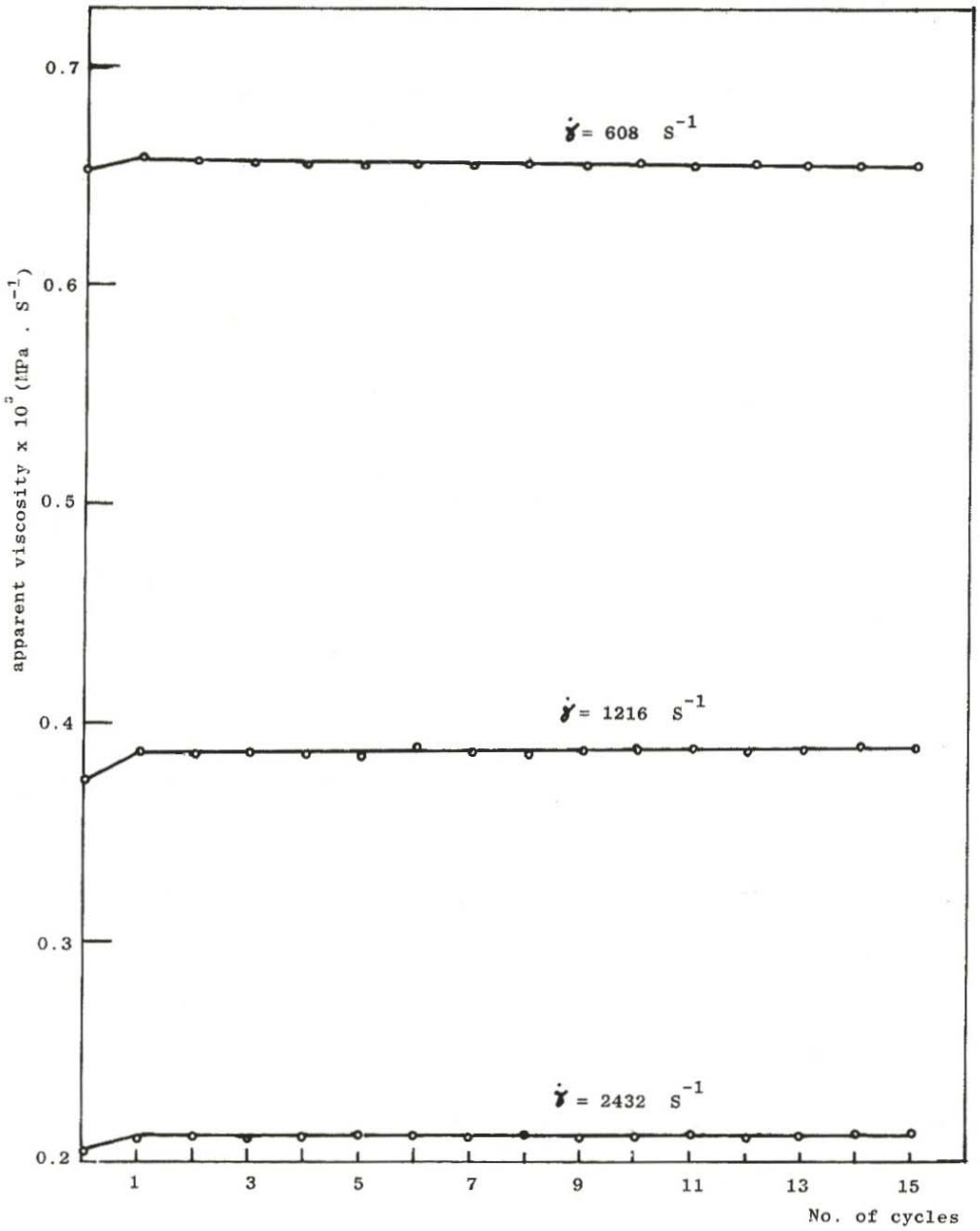

Fig. 3 Apparent viscosity vs. number of cycles at three constant shear rate using 25% waste

Table 1- Thermal stability and torque data on different PVC systems

System	Minimum torque (g .m)	Stability period (min)	Reduction in thermal stability (%)
PVC dry blend(I)	٩٨٠	٤٢	-
sGranule(Π)	١٠٢٠	٣٩,٥	٦
Bottles from(I)	٩٨٠	٣٧,٠	١٢
Bottles from(Π)	١٠٢٠	٣٥,٥	١٥,٥
Dry blend + 25% reclaimed material	٩٨٠	٣٩,٠	٧,٢

Table 2 - Mechanical properties of bottles molded from (I) and (Π)

System	Tensile strength (Mpa)	Elongation (%)	Tensile impact (J/mm^2)
Bottles from (I)	49.0	15	0.48
Bottles from(Π)	48.0	20	0.40