Lead-Acid Battery:

Polyvinyl Chloride Battery Jars and Covers

By T. W. HUSEBY, J. T. RYAN and P. HUBBAUER

(Manuscript received January 14, 1970)

A detailed materials engineering evaluation of a low-cost, high impact, structurally modified rigid polyvinyl chloride (PVC) has demonstrated that battery jars and covers can be molded from PVC in conventional equipment. The battery jars are flame resistant, transparent, and sufficiently tough to withstand considerable abuse without cracking. Although mechanical properties indicate the material becomes slightly more brittle after exposure to 1.220 specific gravity H_2SO_4 at 120°F, the behavior at all times exceeds the currently used styrene-acrylonitrile in toughness. PVC maintains its rigidity beyond 120°F and accelerated tests indicate it will creep less than 1 percent after 20 years at room temperature under all expected loads. Jars weighing 12 pounds and covers weighing 4.5 pounds were each molded in carefully designed molds in a five minute cycle at 400°F without difficulty. The molded parts show very little stress concentration even without expensive annealing treatments and are free of molding defects. The cover diameter is molded 0.005 in. larger than the jar to insure proper fit during assembly. This dimensional accuracy is maintained without requiring special cooling fixtures after molding to restrict uneven shrinkage.

I. INTRODUCTION AND DESIGN CRITERIA

Industrial battery jars historically have been manufactured from either hard rubber or relatively brittle thermoplastics such as styrene and styrene-acrylonitrile copolymer. Each of these materials has a high tensile strength in excess of 10,000 psi. However, they all crack and fracture at very low strains and, although such plastics have a high ultimate strength, they can absorb little energy during impact. The toughness, or work required to bring a material to failure, is related to the area under the stress-strain curve as depicted in Fig. 1. The tough
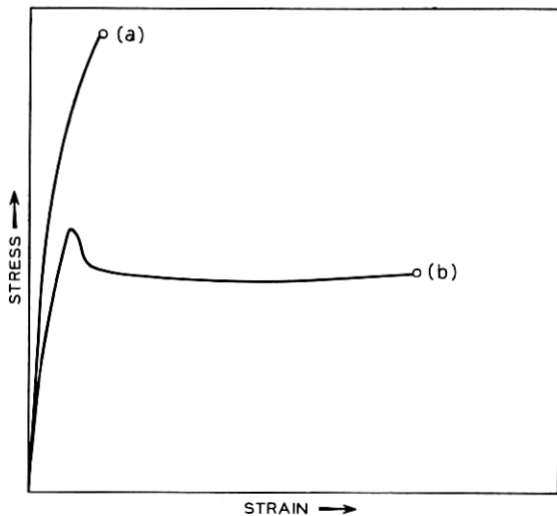
Fig. 1—Typical stress-strain curve for (a) brittle plastic, and (b) tough, ductile plastic.

material illustrated by curve (b) has the ability to yield and dissipate energy prior to breaking. Thus, even after yielding, this material is capable of supporting a load although the deformation may continue to increase. This toughness or impact resistance is gained at the expense of some reduction in rigidity and in failure stress. The rigidity, or stiffness, of a material is related to its modulus of elasticity. The loss in modulus is often due to the introduction of a toughening agent or impact modifier such as a soft rubber well dispersed throughout the hard, brittle matrix. In selecting a plastic for the new Bell System battery jars, emphasis was placed on toughness and impact strength as one of the most desirable and important material improvements.

Clarity for inspection and service convenience is another desirable feature in a battery jar. This is best achieved in heterogeneous, rubber-modified, tough plastics by matching the refractive indices of the two phases. However, since a perfect match is seldom attainable, especially over a sufficiently wide temperature range, it is also beneficial if the size of the dispersed phase remains less than about 0.1 μm in diameter.

In addition, for long-term service, a suitable battery material must have a certain chemical resistance. For example, the material must be free of cracking and mechanical property deterioration in the presence of H_2SO_4 and various other chemicals which might be present in central

offices. It is also important that the material not yield substances that adversely affect the electrochemical performance of the battery. This important property is fully discussed in an accompanying article by A. D. Butherus and W. S. Lindenberger.

Because cells may also be subjected to loads at temperatures as high as 120°F, the long-term creep resistance should also be considered. This is especially important since inclusion of soft impact modifiers into hard plastics increases their tendency to creep.

To reduce the hazard of central office fires, it is desirable for the battery plastic to be flame retardant. Several test methods are available which allow comparisons of this important property to be made. One such method measures the minimum amount of oxygen necessary in a controlled environment to support combustion.[1] Thus, plastics which require an oxygen-rich environment during combustion will be flame retardant in air containing 21 percent oxygen. A comparison is given in Table I of the minimum oxygen concentration necessary to support combustion of most of the common thermoplastics.

Finally, the material must be fabricated by conventional injection molding technology. The molded jars should also not require any annealing treatments to minimize orientation stresses.

II. PROPERTIES OF POLYVINYL CHLORIDE

2.1 General Description

Rigid polyvinyl chloride (PVC) is a commercial, low-cost plastic having a high degree of resistance to solvent crazing and chemical attack. As shown in Table I, no other conventional plastic can match its flame retardancy. Indeed, PVC will support combustion only in environments

TABLE I—OXYGEN INDEX RATING OF COMMON THERMOPLASTICS

Polymer	Oxygen Index (%)
Polyoxymethylene	16
Polyolefins, polystyrene, impact styrene, cellulosics, ABS	17–20
Styrene-PPO copolymers	21–24
Polycarbonate, polyamide	25–28
Polysulfone, PPO, flame retardant polycarbonate copolymers	30–32
Polyvinyl chloride	40
*Polyimide	51
*PTFE	95

* Cannot be processed by injection molding.

containing more than 40 percent oxygen, nearly twice as much oxygen as exists in air. Since it is relatively unstable at high temperatures, its use in injection molding, especially of large or intricate items, has been severely restricted. However, PVC can be stabilized and modified to be processed successfully under many molding conditions. These modified compounds make PVC a material suitable for use in large battery jars.

PVC resin is a high molecular weight polymer containing carbon, hydrogen, and chlorine, whose chemical structure is represented in Fig. 2a. It is transparent and remains very rigid up to temperatures of 160°F. Its glass transition temperature, at 175°F, is closely associated with this loss in rigidity since the modulus decreases rapidly in this temperature range. Its melting temperature is slightly above 400°F. The crystalline fraction is not large, even under the most favorable conditions, owing to polymerization conditions which limit the regularity of the molecular structure. Thus, while the amount of crystallinity may total 10 percent in commerical polyvinyl chloride, especially if samples are carefully annealed, the mechanical behavior of injection molded PVC remains similar to the behavior of amorphous polymers.

2.2 Thermal Stability

PVC resin is unstable at high temperatures and degrades prior to melting. To minimize degradation, it must be stabilized and processed below its melting point at temperatures where its viscosity is quite high. This accounts for the difficulty in molding parts from PVC. When the plastic degrades it gives off corrosive hydrogen chloride vapors and forms a discolored, brittle residue. Dehydrochlorination leads to formation of long segments of unsaturated carbon atoms which are responsible for the color change during degradation.[2] This degradation can be minimized by the addition of a small amount of heat stabilizer, often a combination of organic tin compounds.

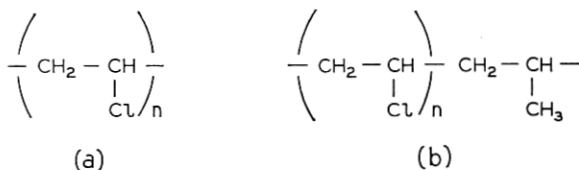A significantly more stable polymer can be made by copolymerizing

$$\left(- CH_2 - \underset{\underset{Cl}{|}}{CH} - \right)_n \qquad \left(- CH_2 - \underset{\underset{Cl}{|}}{CH} - CH_2 - \underset{\underset{CH_3}{|}}{CH} - \right)_n$$

(a)   (b)

Fig. 2—Structural formulae for polyvinyl chloride and vinyl chloride-propylene copolymer.

a small amount of propylene with the vinyl monomer.[3] The resultant vinyl chloride-propylene copolymer (Fig. 2b) contains about 5 weight percent propylene or about one unit for every 15 vinyl chloride units. This structural modification enhances stability by effectively retarding the evolution of hydrogen chloride. The enhanced stability can be demonstrated in several ways. The Brabender method[4] serves to indicate thermal stability under laboratory conditions approximating the molding process where energy is added both as heat and work. A comparison between the vinyl chloride-propylene copolymer and a PVC of equivalent molecular weight is shown in Table II. The processing time relates

TABLE II—THERMAL STABILITY OF PVC BY BRABENDER METHOD*

Material	Processing Time (Minutes)
Polyvinyl chloride	$5\frac{1}{4}$
Vinyl chloride-propylene copolymer	11

* Manufacturing Standard 17000, Section 1171, Method A.

to the time at 375°F required to cause serious degradation in the sample while it undergoes mechanical working. Since these samples have identical heat stabilizers added in the same amounts, the longer time indicates that the copolymer is more stable to heat and work than the homopolymer.

2.3 Processability

Introduction of propylene does not significantly change the processability of PVC. This can be observed from measurements of viscosity at a temperature typical of injection molding. Figure 3 shows viscosity measurements (η) at 392°F over a range of shear rates $(\dot{\gamma})$.

Because polymer melts are viscoelastic, their flow properties change with shear rate. During injection molding, plastic melts are subject to high shear rates usually exceeding 1000 seconds^{-1}. Most plastics are difficult to mold if the viscosity at high shear rates exceeds about 8000 poise; easily processed materials have high shear-rate viscosities of approximately 1000 poise. Figure 3 shows that the copolymer has nearly the same viscosity as an equivalent molecular weight homopolymer over a wide range of shear rates.

Without an impact modifier the PVC battery jar probably could not reliably withstand the shock loading associated with transportation or an earthquake environment. Therefore, a rather large amount of rubbery
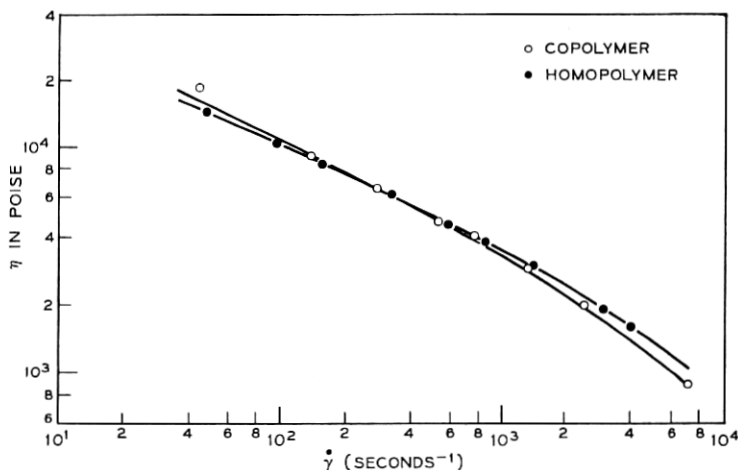
Fig. 3—Melt viscosity versus shear rate for polyvinyl chloride and vinyl chloride-propylene copolymer at 392°F. Weight average molecular weight of both polymers is 80,000.

plastic is used to toughen the PVC compound. The addition of rubber particles to PVC changes its processability. Recent studies of stress relaxation in ABS,[5,6] another impact modified plastic, have shown that above the glass transition temperature of the hard matrix a major effect of the dispersed elastomeric phase is to increase the molecular entanglement. Since entanglement interactions strongly influence the flow behavior, the addition of rubber particles is expected to increase the viscosity. Indeed, an increased viscosity has been observed previously in ABS and in impact modified PVC.[7] Figure 4 illustrates the increase in viscosity due to impact modifier in this compound. Notice, however, that the increase is not so much as to make processing impossible.

Proper dispersion of rubber particles throughout the matrix is a vital factor in developing high impact strength. Figure 5 is a transmission electron micrograph obtained from a sample of the impact modified vinyl chloride-propylene copolymer. Phase contrast is improved by exposing the sample to osmium tetroxide which preferentially stains the rubber particles and thereby increases the electron density.[8,9] The electron staining is also an oxidative process which stiffens the soft rubber particles and aids in the preparation of ultra-thin specimens. The rubber particles in Fig. 5 are largely spherical, well dispersed, and about 0.1 μm in diameter.

To maintain transparency, the rubber particles must have a refractive
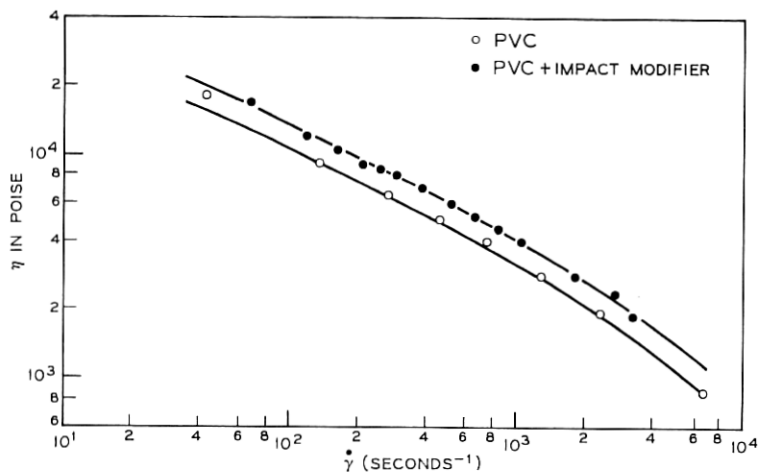
Fig. 4—Melt viscosity versus shear rate for copolymer and impact-modified copoly-
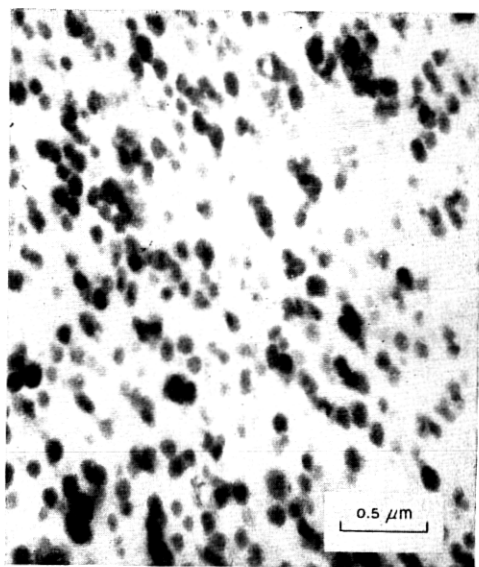mer at 392°F.

Fig. 5—Transmission electron micrograph of impact-modified copolymer.

index close to that of PVC, 1.537 at 25°C. An easily dispersed material having a refractive index of 1.536 at 25°C is methyl-methacrylate-butadiene-styrene polymer (MBS).[10] In such compounds, methyl-methacrylate and styrene polymers are grafted to styrene-butadiene rubber to improve compatibility with PVC. These impact modifiers usually have a butadiene content approximating 50 percent. Most clear, impact-modified PVC compounds contain MBS as the impact modifier. Since the impact modifier is not flame retardant and it increases viscosity and raises cost, it is necessary to balance these considerations against impact strength.

Processability of PVC is also improved by the addition of a wax. This lubricates the molding equipment during processing and enhances processing characteristics.

2.4 *Mechanical Properties*

The properties of the compound developed for cell jars reflect a combination of properties of the described ingredients. Some commonly measured engineering properties appear in Table III. Especially evident is the improvement in impact strength at the expense of modulus and ultimate strength.

2.5 *Effect of Acid Exposure on Modulus and Strength Properties*

Table IV shows values for some of the mechanical properties evaluated

TABLE III—ENGINEERING PROPERTIES OF IMPACT MODIFIED
POLYVINYL CHLORIDE

| | | Value | |
| | ASTM Test Method | With Impact Modifier | Without Impact Modifier |
Property			
Tensile strength (psi)	D-638 Type I	7000	8800
Elongation at break (%)	D-638 Type I	110	36
Impact strength (ft–lb/in notch)	D-256 Method A	28	0.7
Flexural strength (psi)	D-790	9600	13,100
Flexural modulus (psi)	D-790	355,000	416,000
Deformation under load (%) 24 hours at 2000 psi, 50°C	D-621	3.45	1.66
Heat deflection temperature (°K) 264 ps	D-648	144	145
Oxygen index	MS-17000 Section 1226	33	40

TABLE IV—ENGINEERING PROPERTIES OF IMPACT MODIFIED PVC*
AFTER EXPOSURE TO 1.220 SPECIFIC GRAVITY
H_2SO_4 AT 120°F

	Initial	3 Months	6 Months	16 Months
Tensile Strength (psi)	7500	8300	8300	8350
Elongation (%)	50	25	25	18
Modulus (psi)	350,000	350,000	350,000	350,000

* Specimens machined from a battery jar.

at room temperature before and after exposure to battery acid at 120°F for up to sixteen months. Note that the elongation measurements indicate slight embrittlement after exposure to heat and acid. Separate experiments have determined that most of the change is due to heat rather than acid. The tensile strength, for example, increases but levels off after three months. Even after the combination of acid exposure and heat aging, the PVC remains tougher and less brittle than styrene-acrylonitrile is before acid exposure. At no time has the modulus shown any decrease from its initial value. These data show that PVC surpasses in mechanical toughness the plastic currently used for batteries, styrene-acrylonitrile.

2.6 Effect of Temperature on Mechanical Stiffness

Because normal battery service temperatures extend up to 120°F, it is of interest to examine modulus through this temperature range. The dynamic mechanical behavior can be used conveniently to measure the temperature-dependent stiffness properties. This nondestructive test measures the steady-state stress response to a sinusoidal deformation. The response can be resolved into two components, one acting in phase with the deformation and one acting in quadrature. That portion of stress in phase with deformation determines the elastic modulus, E', while the quadrature component gauges the damping modulus, E''. The ratio, E''/E', is defined as tan δ. Figures 6 and 7 show the temperature dependence of E' and tan δ, respectively. This information reveals that the modulus of impact modified PVC remains in excess of 250,000 psi up to the maximum operating condition of 120°F. It should be emphasized that this test measures short-time, temperature-dependent behavior, the time scale being inversely proportional to frequency. This behavior is not quantitatively characteristic of longer time response because the mechanical behavior is time-dependent. It is therefore
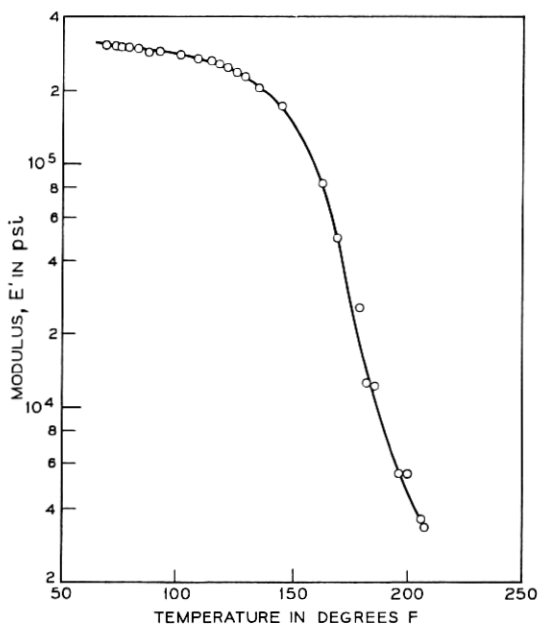
Fig. 6—Dynamic modulus E' versus temperature at 110 Hz for impact-modified polyvinyl chloride.
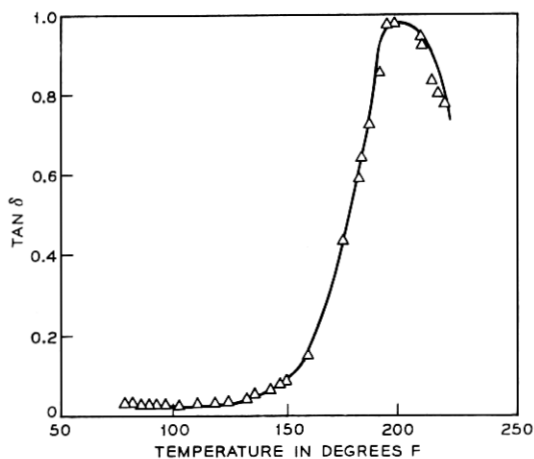

Fig. 7—Loss tangent versus temperature at 110 Hz for impact-modified polyvinyl chloride.

important to inquire into the time-dependent isothermal creep behavior.

2.7 *Long-Term Creep Behavior*

Plastics are known to deform and creep under constant load due to their time-dependent viscoelastic behavior. A characteristic strain-time curve of an amorphous plastic at constant load is shown in Fig. 8. With certain restrictions, the influence of increased temperature is to shift the creep response uniformly along the logarithmic time scale toward shorter times. Thus, the creep response of a plastic at an elevated temperature appears the same in logarithmic time as at a lower temperature, except for a shift in time scale. This relation between temperature and logarithmic time is exploited during accelerated creep testing. Although initially the relationship was exhaustively tested at low loads for amorphous polymers above their glass transition temperatures, it has recently been applied, with good success, to rigid polymers in their glassy state and with higher loads.[11,12]

Figure 9 shows the creep compliance, $J(t) = \epsilon(t)/\sigma$, where $\epsilon(t)$ is the time varying strain and σ is the constant stress, at three temperatures. Note that the compliance appears independent of load at the two lowest temperatures. The master curve in Fig. 10 is obtained by shifting the data at higher temperatures uniformly along the logarithmic time axis to form a continuous curve at 78°F. The displacement in units of logarithmic time is denoted as log a_T, the logarithmic shift factor. The shift in time scale between 78°F and 122°F corresponds to an acceleration by a factor of 300.

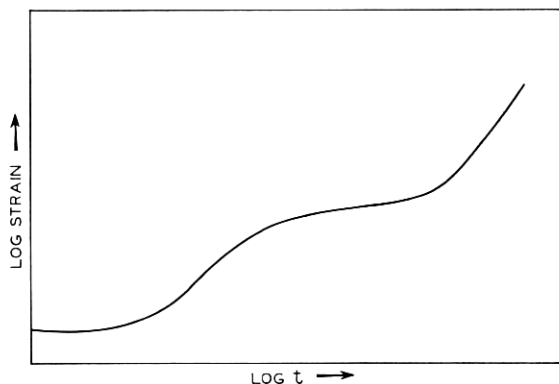Figure 11 shows the creep strain at 122°F under a load of 500 psi,

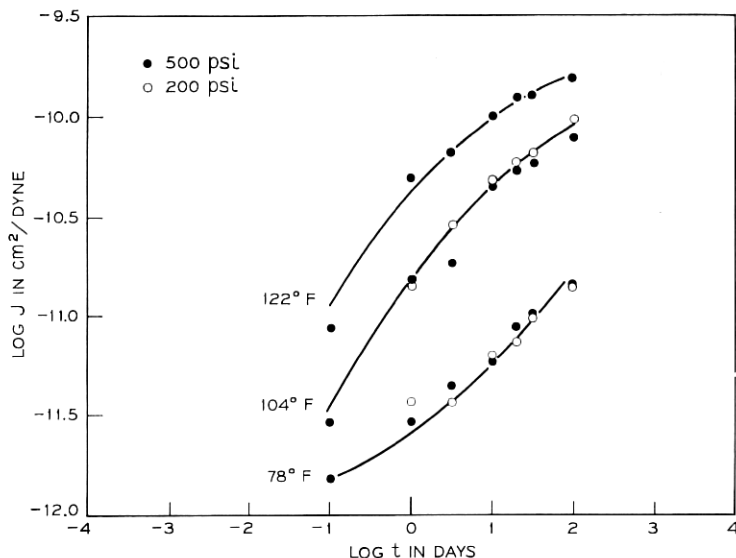Fig. 8—Typical creep curve for amorphous thermoplastics.

Fig. 9—Creep compliance versus time for impact-modified copolymer.

which exceeds the stress likely to occur in practice. The strain after 24 days at 122°F corresponds to a 20-year creep test at 78°F. Note that this acceleration factor pertains only to time-dependent mechanical properties and not to property changes due to aging, chemical change, deterioration in the presence of acid, or to any electrochemical effects. Figure 11 indicates that the creep response to loads of 500 psi or lower for long periods of time is less than 1 percent at 78°F under the most extreme loading conditions. This is a negligible amount. Indeed, even with continuous exposure to 122°F the estimated 20-year creep remains below 5 percent for loads up to 500 psi.

III. MOLDING TECHNOLOGY

Certain aspects of the molding technology required to produce large molded parts from PVC are of interest. In order to assure ourselves that molding PVC in large battery jars was feasible, it first was decided to mold PVC in existing molds of rectangular shape. With the cooperation of one of the battery manufacturers, the material supplier, and the molder, List 508 battery jars were molded from PVC. The molding weighed 17 pounds and is still the largest item ever molded from PVC.

It is significant that the molder, who had no previous experience with PVC, had no difficulties in molding this large jar.

The cylindrical jar, weighing 12 pounds and having a 1/4 inch wall thickness, is not quite so heavy because it is thinner than the square design. It was molded by a second molder without previous experience with PVC on a 1600-ton reciprocating screw injection molding machine (Fig. 12), one commonly found in many large custom molding shops. The parts are molded on a five minute cycle at 400°F under 17,000-psi injection pressure. The covers weighing 4.5 pounds were molded in a smaller machine, also in a five minute cycle at 400°F under 7500-psi.

The molded parts (Fig. 13) are free of bubbles, burn marks, imperfections, and obvious weld lines. The cylindrical geometry permits the necessary dimensional accuracy to be achieved without using special cooling fixtures after molding to restrict uneven shrinkage. These fixtures are necessary to prevent warping in square geometries. The
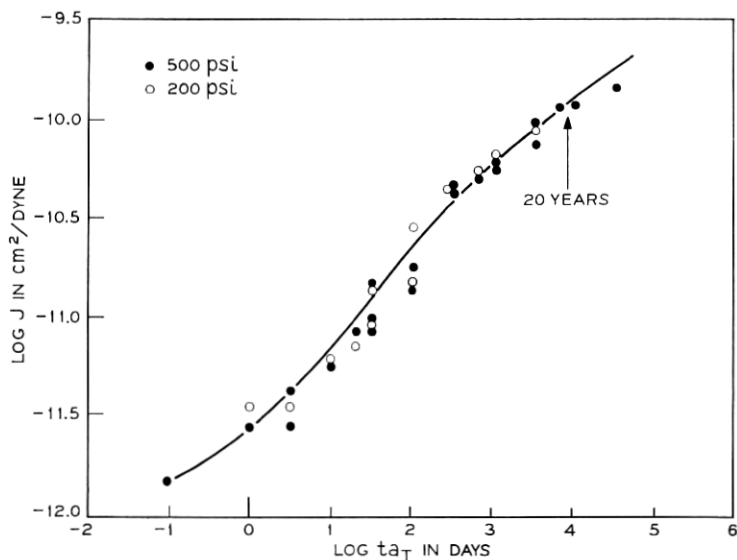

Fig. 10—Master curve of creep compliance versus reduced time for impact-modified copolymer at 78°F.

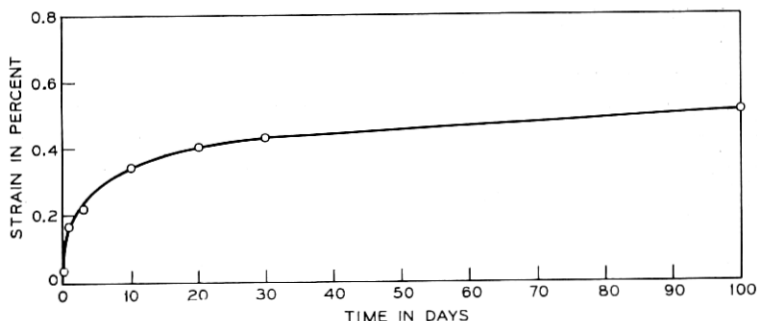| T(°F)	Log a_T
78	
104	-1.5
122	-2.5

Fig. 11—Creep at 122°F and 500 psi of impact-modified copolymer.

parts are also satisfactorily free of stress concentration, even without expensive annealing treatments, as was demonstrated by examination through polarizing films. Use of two films as a polariscope identifies regions of varying orientation which correspond to areas of high residual stress in the molded part. It is noteworthy that, in this case also, the molder has never encountered difficulties in either starting up, running for extended times, or shutting down his machine.

These extremely high quality moldings were achieved by careful design of both cover and jar molds. Several mold design details which contributed to the successful molding can be pointed out in Fig. 14, a schematic of the jar and cover. Both cover and jar molds are made from prehardened tool steel to eliminate the necessity for hardening and subsequent grinding. The jar mold is equipped with an auxiliary, hydraulically-operated ejector ring on the moving die. This allows the molder to eject on the top surface of the jar and push the jar off the mold. This feature costs very little but allows him to mold jars with only 1/2° draft on each side. A small draft pays off in less wasted space when mounted in service. Hand-operated air valves on the molds for the insides of the jar and cover prevent a vacuum seal from hindering ejection from the mold. Air valves on the molds for the outsides help push the parts onto the moving sides as the molds open.

Cold slug wells are opposite the center gate in both cover and jar mold. This provides a trap for the first amount of cold plastic from the machine. The cover is center gated across the center post hole and machined out later. This gate arrangement insures uniform fill and minimizes stress concentration due to residual orientation. Effort was made to provide maximum cooling in all parts of the mold through special use of additional cold water passages. This is essential for
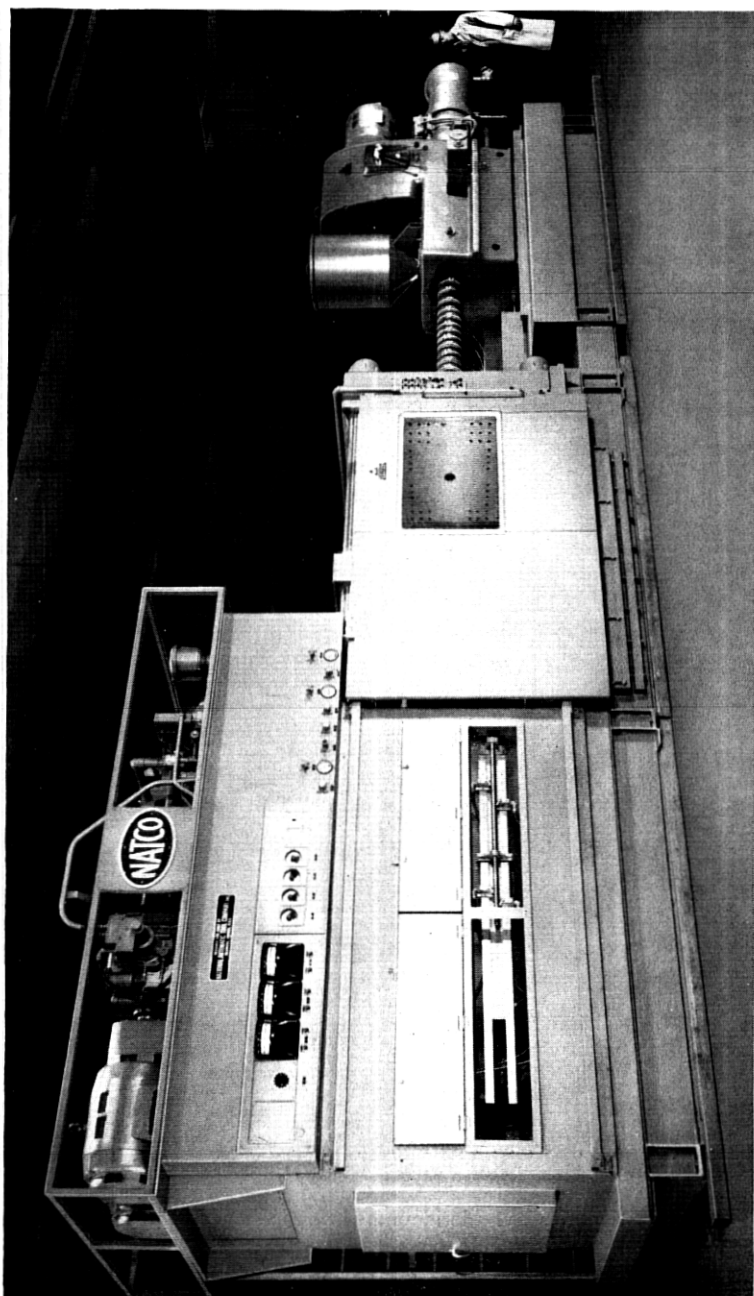
Fig. 12—Injection-molding machine.

Fig. 13—Injection-molded vinyl chloride-propylene copolymer battery jar and cover.

DIAPHRAGM CENTER GATE

LOCATION OF AIR VALVE

LARGE RADII

MINIMUM DRAFT INSIDE

5/6 INCH WALL THICKNESS

1/4 INCH WALL THICKNESS

1/2° DRAFT PER SIDE

EXTRA FINE SURFACE FINISH

CENTER GATE WITH COLD SLUG WELL AND LOCATING REGISTER
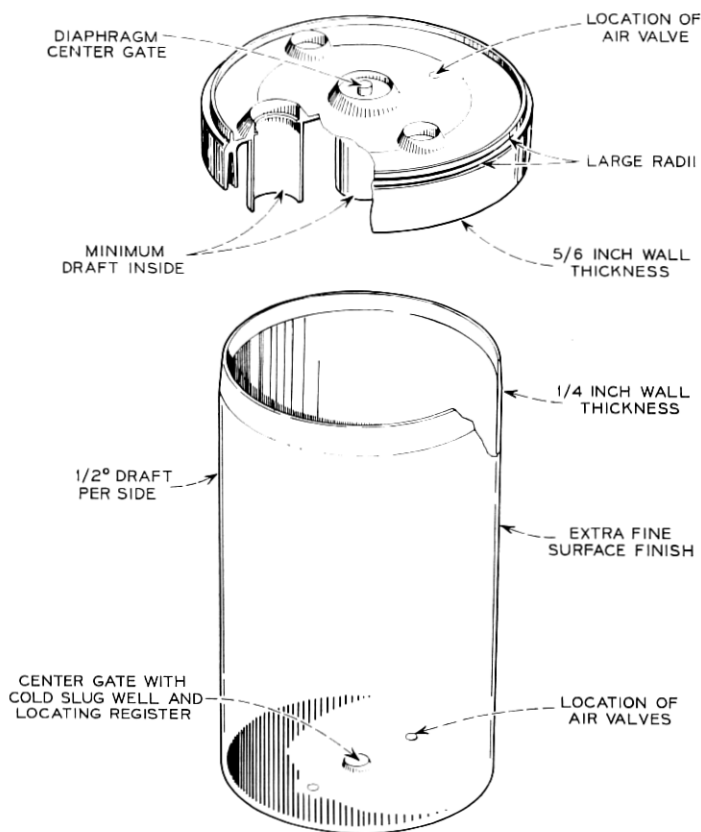
LOCATION OF AIR VALVES

Fig. 14—Illustration of battery jar and cover.

adequate cooling of large parts having uniformly thick sections of 1/4 inch or more. A mold finish of about two microinches was achieved by hand polishing following the final grinding. This extra fine finish was required for satisfactory transparency.

IV. SUMMARY

In conclusion, rigid polyvinyl chloride is a versatile design material exhibiting desirable mechanical properties, flame retardancy, and chemical resistance. Although not as easily processed as many plastics, it can be molded without difficulties using good molding practice. A detailed materials engineering development program has demon-

strated that properly compounded and stabilized PVC can be molded in conventional equipment under controlled manufacturing conditions using a properly designed mold to produce battery jars and covers of high reliability.

V. ACKNOWLEDGMENTS

REFERENCES

1. Fenimore, C. P., and Martin, F. J., "Candle-Type Test for Flammability of Polymers," Modern Plastics, 44, No. 2 (Nov. 1966), pp. 141, 142, 146, 148, 192.
2. Salovey, R., Luongo, J. P., and Yager, W. A., "On the Irradiation of Poly (Vinyl Chloride)," Macromolecules, 2, No. 2 (March-April 1969), pp. 198–200.
3. Cantow, M. J. R., Cline, C. W., Heiberger, C. A., Huibers, D. Th. A., and Phillips, R., "Vinyl Chloride/Propylene Copolymers," Modern Plastics, 46, No. 6 (June 1969), pp. 126, 127, 132, 136 and 138.
4. Bell System Manufacturing Standard 17000, Section 1171, "Torque Rheometer Test for Plastics," Method A.
5. Scalco, E., Huseby, T. W., and Blyler, L. L., "Some Viscoelastic Properties of ABS Polymer," J. Applied Polymer Sci., 12, No. 6 (June 1968), pp. 1343–1353.
6. Bergen, R. L., and Morris, H. L., "The Melt Rheology of ABS Polymers," Proceedings of the Fifth International Congress on Rheology, Vol. 4, Tokyo: University of Tokyo Press, 1969.
7. Malpass, V. E., "Flux and Melt Flow Behavior of Rigid ABS Modified PVC," SPE 27th Annual Technical Conference Preprints, 15 (1969), pp. 55–60.
8. Matsuo, M., Nozaki, C., and Jyo, Y., "Fine Structures and Physical Properties of Plastic/Rubber Two-Phase Polymer Systems," J. Electron Microscopy, 17, No. 1 (1968), pp. 7–15.
9. Kato, K., "Morphological Aspects of ABS (Acrylonitrile-Butadiene-Styrene) Plastics," Japan Plastics, 2, No. 2 (April 1968), pp. 6–17.
10. Ohtsuka, S., Watanabe, H., and Amagi, Y., "New PVC Impact Modifier," SPE 25th Annual Technical Conference Preprints, 12 (1967), pp. 707–716.
11. Malpass, V. E., "Prediction of Long-Term Acrylonitrile-Butadiene-Styrene Relaxation Behavior," J. Applied Polymer Sci., 12, No. 4 (April 1968), pp. 771–788.
12. Rusch, K. C., "The Relaxational Behavior of Heterogeneous Polymers," J. Macromol. Sci., Phys., B2, No. 3 (1968), pp. 419–445.