

EFFECTS OF BLENDING ACRYLIC POLYMERS ON THE PHYSICAL PROPERTIES AND PROCESSING BEHAVIOR OF POLY(VINYL CHLORIDE)

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Abstract - The effect of adding randomly copolymerized acrylic polymers on the processability of poly(vinyl chloride) is described, particularly in relation to the molecular structure of the copolymer. It has been found that acrylic copolymers enhance gelling and the Barus effect, thus greatly improving the processability of poly(vinyl chloride) during injection, expansion, and blow moldings as well as calendering. These improvements depend upon the molecular weight, glass transition temperature, type of comonomer and amount of incorporation of the copolymers. It has also been found that acrylic copolymers having grafted multilayer structure impart excellent processability and lubricant effectiveness to both rigid and flexible poly(vinyl chloride).

INTRODUCTION

Poly(vinyl chloride) is one of the relatively low-cost, high volume commodity resins which exhibits good mechanical properties and chemical resistance. The resin, however, shows inherently poor processability. In order to overcome this disadvantage, modifications in the resin systems by means of copolymerization or incorporation of additives have been studied extensively. The application of such modifications to commercial practice has contributed heavily to the expansion of the poly(vinyl chloride) market.

A wide variety of additives are currently in use, such as, plasticizers, heat stabilizers, reinforcing agents, lubricants, and processing aids. Processing aids are highly compatible with poly(vinyl chloride) and acrylic based polymers, which are represented by poly(methyl methacrylate) exhibiting molecular dispersibility, have been found to be highly effective(1). The nature of the behavior of such acrylic processing aids towards processability has not yet been fully elucidated.

This paper will describe the relationship between the molecular structure of random acrylic copolymers and the processing characteristics of poly(vinyl chloride). In addition, the characteristics and significance of a polymeric processing aid which consists of a grafted multilayer structure will be briefly mentioned.

GELLING BEHAVIOR

One of the basic behaviors of poly(vinyl chloride) during the extrusion process is the gelling behavior of the powder. The external aesthetic qualities and the physical properties as well as productivity are greatly influenced by this gelling behavior. In order to increase the rate of production, it is necessary not only to improve the flow characteristics of poly(vinyl chloride) but also to increase its gelling rate. Furthermore, it is important to achieve rapid and uniform gelling as well as uniform dispersion of the resin in order to impart good external surface quality and physical properties to the molded article.

The gelling rate of poly(vinyl chloride), in general, is dependent upon the following factors:

1. Form of poly(vinyl chloride) powder, which is determined by the method of production.
2. Degree of polymerization of the resin.
3. Plasticizers and formulating conditions.
4. Molding conditions.
5. Polymeric processing aids.

The addition of acrylic processing aids is particularly effective in varying the gelling behavior over a wide range, and also in increasing the gelling rate. Figure 1 shows the effect of the intrinsic viscosity of the acrylic processing aid on the gelling rates of both rigid and flexible poly(vinyl chloride) systems.

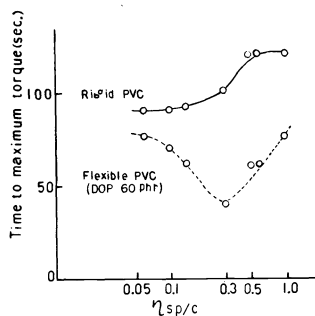


Fig. 1. Relation between the intrinsic viscosity of the acrylic polymer and the gelling rate. Acrylic polymer: 3 phr. Intrinsic viscosity: 0.1 g. polymer/100 ml. chloroform. (Labo-Plastomill)

In the rigid system, the gelling rate decreases as the intrinsic viscosity increases, while a maximum gelling rate appears in the flexible system, thus revealing the differences in behavior between the two systems.

In the rigid system, fusion of the secondary particles of poly(vinyl chloride) appears to be the governing factor. The melt characteristics of the acrylic processing aid plays an important role here. A polymer which melts readily and has a lower degree of polymerization will promote gelling. Conversely, in the flexible system, fusion of the secondary particles of poly(vinyl chloride) does not become a governing factor because of the co-existence of plasticizers, and the effective interaction of the shear force becomes important. The application of a high intrinsic viscosity acrylic processing aid, which serves to increase the viscosity of the system, will be very effective, but, if the intrinsic viscosity becomes excessively high, then the polymer will become difficult to melt and disperse. This is probably the reason that a maximum gelling rate at a certain intrinsic viscosity is observed.

A structural factor which is also believed to govern the gelling rate is the type and amount of comonomer which is combined to methyl methacrylate. Figure 2 shows the effect of butyl acrylate as a comonomer.

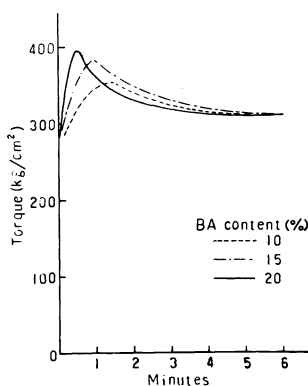


Fig. 2. Effect of butyl acrylate content of the acrylic polymer on the gelling behavior. Acrylic polymer: 3 phr.

The gelling rate increases as the amount of butyl acrylate is increased. One can also use the corresponding glass transition temperature of the copolymer to develop the same relationship.

Furthermore, the uniformity of gelling is an important consideration. This can be evaluated from the relative half-values of the peak torque obtained from a plastograph curve. It is

interesting to note that the uniformity of gelling increases as the intrinsic viscosity of the acrylic polymer increase as shown in Fig. 3.

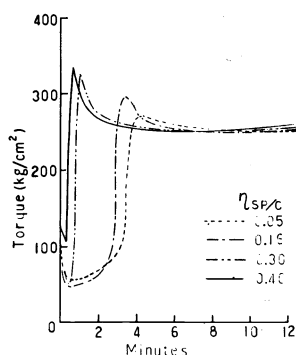


Fig. 3. Effect of the intrinsic viscosity of the acrylic polymer on gelling uniformity. Acrylic polymer: 3 phr. Dioctyl phthalate: 30 phr.

INJECTION MOLDING

Injection molding of high melt viscosity poly(vinyl chloride), which is susceptible to melt fracture, frequently produces molded articles with inferior external appearances due to so-called gate flash and jetting, and lower physical properties at the welds.

Gate flash is a phenomenon where portions exhibiting poor flow characteristics, such as, cold slag, initially form a skin layer over the surface of the mold cavity. This is then pushed forward by the resin flow which follows and enters into the cavity, thus causing the formation of rough surfaces. The flow front, where excessive flash is encountered, forms a very rough surface which is similar to deposition of microcrystals, while the transparent portion gives a smooth surface.

Jetting, on the other hand, corresponds to the most extreme case of gate flash. The cold slag does not expand after leaving the gate and protrudes into the mold. This is then encapsulated into the subsequent resin flow. While gate flash is characterized by a white mold-like radiating thin skin, jetting gives an undulating earthworm-like appearance.

In order to resolve jetting and flash problems, one tends to employ higher molding and cavity temperatures combined with lower injection speeds. There is, however, a limitation as to how far one can go to resolve such problems by relying upon processing conditions alone. The incorporation of acrylic processing aids is effective in varying flow characteristics and greatly improving the external aesthetics.

Table 1 shows the effect of the intrinsic viscosity of the acrylic polymer on gate flash.

TABLE 1. Effect of intrinsic viscosity on gate flash

Intrinsic viscosity	Gate Flash	
	Cylinder temperature 170°C	Cylinder temperature 180°C
Control	Poor	Poor
0.1	Poor	Poor
0.2	Poor	Fair
0.3	Good	Good
0.4	Excellent	Excellent
0.8	Excellent	Excellent

The table shows that gate flash decreases as the intrinsic viscosity increases, but the effect somewhat levels off at above 0.3 to 0.4. Figure 4 illustrates the filling process of poly(vinyl chloride) as it enters the cavity.

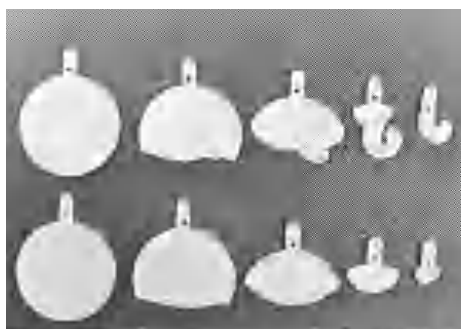


Fig. 4. Filling process of poly(vinyl chloride)

While a typical jetting phenomenon is encountered with a monocomponent poly(vinyl chloride) system, jetting does not occur in a system which employs an acrylic processing aid because the melt does not form a protuberance after it leaves the gate and fans out into the cavity.

The effect of the processing aid appears to be caused by the increased Barus effect and by the exotherm at the gate due to the viscosity buildup. The Barus effect is a phenomenon where the cross-sectional area of a polymer melt extruded from the nozzle becomes larger than that of the orifice. This is believed to be due to the elasticity of the polymer (2). Figure 5 illustrates the Barus effect as a function of the intrinsic viscosity of the acrylic polymer.

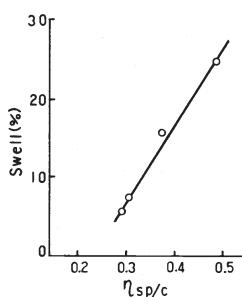


Fig. 5. Relation between the intrinsic viscosity of the acrylic polymer and swelling. Acrylic polymer: 4 phr.

This figure shows that the effect is enhanced as the intrinsic viscosity increases. The strong Barus effect which appears when high molecular weight acrylic polymers are added is probably due to the fact that poly(vinyl chloride) retains a higher elasticity at the given molding temperature.

In injection molding poly(vinyl chloride), weld lines are formed in certain shaped articles or when multiple point gates are employed. The physical properties of the molded parts generally decrease at the weld lines. When acrylic polymers are incorporated to such a system, appreciable improvements are noted in the breaking strength and breaking elongation at the weld. This is shown in Fig. 6. Promotion of gelling and complete kneading are considered to be the contributing factors in this case.

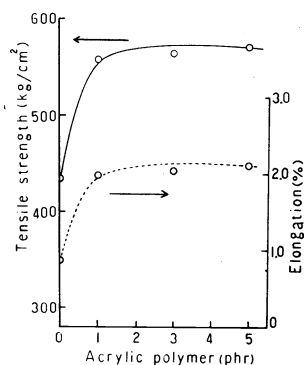


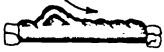







Fig. 6. Breaking strength and elongation at the weld as a function of the amount of acrylic polymer added. Intrinsic viscosity of the acrylic polymer: 0.4.

CALENDERING

Poor surface quality and gloss are sometimes encountered with poly(vinyl chloride) sheets and films during calendaring. This is due to the abnormality of the bank, that is, the generation of bank marks. It is for this reason that extreme importance is placed on the formation of a proper bank during the calendaring operation.

TABLE 2. Protuberant bank forming process

Classification	Two-roll testing machine	
	testing machine	Calender roll
Steady state		
Generation and disappearance of protuberance		
Thrusting out of protuberance		
Growth of protuberance		

The processes of forming protuberant banks with test rolls and calender rolls, respectively, are shown schematically in Table 2. In the former case, a bank protuberance forms between the end and the center of the roll. During the initial stage, the protuberance migrates towards the center and disappears. Then a new protuberance appears. This process is repeated until a protuberance is finally formed in the center. In the latter case, the bank is spindle-shaped in contrast to the cylindrical shape of the former, because the ends rotate faster than the center. This causes the internal exotherm at the ends to be greater than that at the center as shown in Table 3. and, therefore, lowers the apparent viscosity. With the elapse of time, the viscosity difference widens and a torsional force is exerted on the polymer, resulting in the formation of a bulge in the center which subsequently leads to the creation of bank marks.

One example of the relationship between the processing conditions and the occurrence of abnormal banks is illustrated in Fig. 7. If one maintains a constant charge and varies the sheet thickness from thick to thin, a rough bank (chicken tracks) will abruptly be transformed into a protuberant bank without forming a smooth bank when a monocomponent

TABLE 3. Change in bank temperature with time during calendering

Time (minutes)	State of rolling bank	Internal exotherm of bank (°C)		
		High Revolution	Low Revolution	ΔT
2	Stable	175	174	1
5	Stable	177	177	0
7	Stable	178	176	2
10	Unstable	179	176	3
13	Protuberant	186	177	9

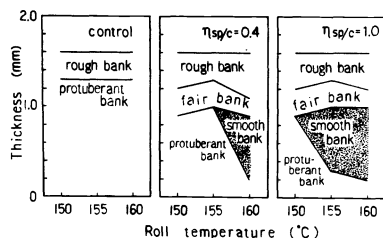


Fig. 7. Effect of the intrinsic viscosity of the acrylic polymer on processing range.

poly(vinyl chloride) system is employed. In contrast, if one employs a system to which acrylic polymers are incorporated, one will observe a transition from a rough bank to a fair bank and then to a smooth bank, thus enabling one to establish conditions for producing a smooth bank. The region of a smooth bank is broadened as the intrinsic viscosity and the amount of the acrylic processing aid is increased, thus proving the extensive effectiveness of the high molecular weight polymer.

Furthermore, one should pay attention to the generation of air marks and flow marks during the calendering process. Air marks are caused by air being sucked into the region of the rotating bank and can be correlated to the configurations of the bank as shown in Table 4. Flow marks are caused by the recovery of the free surface after the uneven skin of the bank

TABLE 4. Relation between bank configuration and air and flow marks

Classification	Side view	Top view	Air marks	Flow marks
Rough bank			Intense	Intense
Fair bank			Intermediate	Intermediate
Smooth bank			Slight	Slight
Protuberant bank			Intense	Intense

has been rolled. This can also be correlated to the abnormality of the bank. When a normal bank is formed with the aid of acrylic polymers, a smooth bank skin is obtained. This should in principle, reduce the formation of air and flow marks.

The addition of high molecular weight acrylic processing aids broadens the processing range for yielding smooth banks and, therefore, sheets having excellent external aesthetics with the least amount of air or flow marks. This is believed to be due to the presence of apparent cross-linking resulting from the high degree of entanglement of the long chain acrylic polymer with poly(vinyl chloride). This cross-linking interacts to impart rubber elasticity to the resin during processing, thus minimizing the surface area of the bank and forming a smooth spindle-shaped bank.

VACUUM FORMING

The ability to vacuum form sheet material is largely dependent upon the hot elongation behavior of a polymer. It is, therefore, desirable to formulate a system which exhibits high hot elongation and is the least sensible to heat. Hot elongation is increased significantly when acrylic polymers are added to poly(vinyl chloride). The higher the intrinsic viscosity of the polymer, the less dependent it becomes on the molding temperature, and the mixture exhibits high elongation at elevated temperatures as shown in Fig. 8. This signifies that acrylic polymers are effective in broadening the processing range,

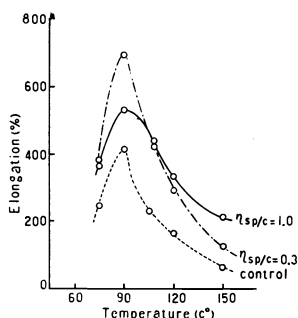


Fig. 8. Relation between intrinsic viscosity and hot elongation. Acrylic polymer: 7 phr.

and will enable one to produce deep formed articles with uniform wall thicknesses.

Recently, shorter molding cycles have become a focus of attention in order to increase the level of productivity. There is, therefore, a strong tendency to adopt higher and higher molding temperatures. This trend seems to indicate that people are paying more attention to the use of acrylic polymers, particularly, high molecular weight polymers. It appears that a cross-linking structure which is formed as a result of the high degree of entanglement between poly(vinyl chloride) and the high molecular weight acrylic polymers which are highly compatible with poly(vinyl chloride) contribute substantially to the effective behavior of such polymeric additives. In Fig. 9, the relaxation modulus is shown as a function of the intrinsic viscosity.

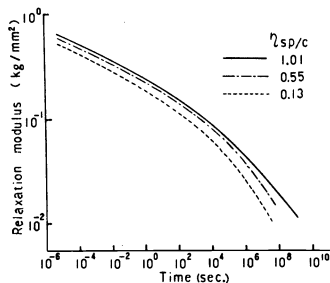


Fig. 9. Relation between intrinsic viscosity and relaxation modulus. Acrylic polymer: 4 phr.

BLOW MOLDING

In blow molding, it is desirable to select a molding range which enables one to mold at high temperatures and at high speeds without causing draw-down of the parison. It is of the utmost importance to prevent draw-down, and this can be achieved by incorporation of acrylic polymers.

Figure 10 shows the relationship between the intrinsic viscosity of the acrylic polymer and the length of the parison. It is apparent that the higher the intrinsic viscosity,

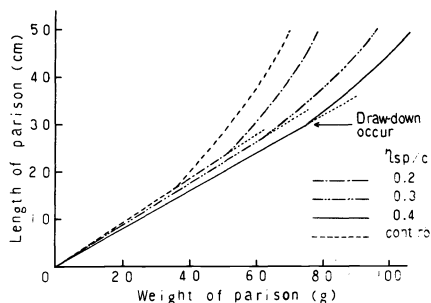


Fig. 10. Relation between intrinsic viscosity and parison length. Acrylic polymer: 3 phr.

the more appreciable becomes the effect on draw-down. This is due to the fact that the Barus effect is enhanced by the incorporation of the acrylic polymer to poly(vinyl chloride).

EXPANSION EXTRUSION

Expansion extrusion is one of the molding methods which has attracted attention from the standpoint of saving resources. The basic consideration in this fabrication process is to form a skin-core double layer structure with reduced specific gravity combined with good external characteristics and physical properties by effectively encapsulating the gas generated by the blowing agent. Such ideal structures cannot be obtained with a monocomponent poly(vinyl chloride) system. Only by incorporating acrylic processing aids is it possible to obtain poly(vinyl chloride) molded articles which have excellent external aesthetics and physical properties over a broad range of specific gravities from low to high foam.

Figure 11 shows the relationship between intrinsic viscosity and the specific gravity of foam. When the amount of blowing agent is low, the specific gravity decreases as the amount

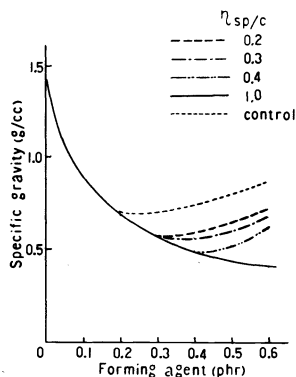


Fig. 11. Effect of intrinsic viscosity on foaming behavior. Acrylic polymer: 3 phr.

of blowing agent is increased. As the amount of blowing agent is increased, a monocomponent poly(vinyl chloride) system will produce extrudates with blowholes in the center, thus in-

creasing the specific gravity. On the other hand, with the incorporation of acrylic polymers, gas is utilized efficiently as the intrinsic viscosity is increased, and effective foaming is achieved as the specific gravity decreases with increased addition of the blowing agent.

In general, the surface appearance worsens as the amount of blowing agent is increased. This can be improved appreciably with the addition of acrylic polymers, and the effect becomes more pronounced as the intrinsic viscosity of the processing aid is increased.

It is of interest to note the relationship between the intrinsic viscosity and the physical properties of the foam. To illustrate this, the effect of intrinsic viscosity on flexural strength is given in Fig. 12.

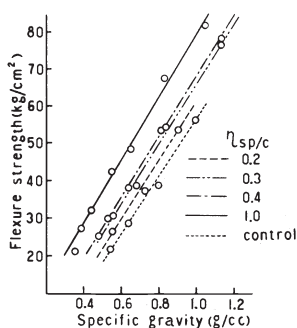


Fig. 12. Relation between intrinsic viscosity and flexural strength of the foam. Acrylic polymer: 3 phr.

This figure shows that the flexural strength is improved as the intrinsic viscosity is increased. Examples of foamed cellular structures are next given in Fig. 13. It is noted that the addition of high molecular weight acrylic processing aids will serve to yield

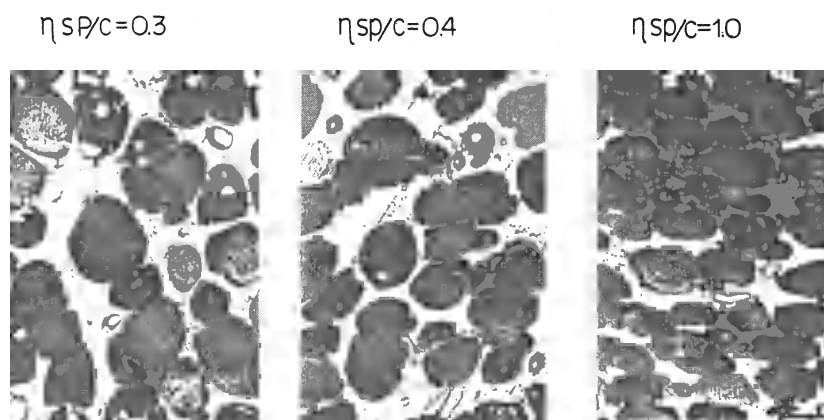


Fig. 13. Cross-sections of foams with acrylic processing aids of different intrinsic viscosities. Acrylic polymer: 3 phr. Blowing agent: 0.5 phr.

uniformly dispersed small diameter foamed micelles. This correlates to the excellent mechanical properties.

The reason that effective foaming is achieved and good external aesthetics and physical properties are obtained with incorporation of high molecular weight acrylic polymers is probably because uniform gelling occurs rapidly, the system exhibits high viscosity and elongation, the gas is effectively encapsulated, and the foamed micelles are uniformly dispersed.

MULTILAYER STRUCTURED POLYMERIC PROCESSING AIDS (3)

Random copolymers of acrylic polymers with methyl methacrylate as the main component impart

excellent processing characteristics to poly(vinyl chloride) as mentioned above. It is apparent from the molecular structure, however, that when the molecular weight is increased, the melt viscosity will also increase. Thus the applicability of this type of polymer to flexible poly(vinyl chloride) systems is generally unsuitable because one will encounter appreciable reduction in dispersibility and loss of clarity.

During the course of studies on processing aids based on a new concept, it was found that a grafted multilayer acrylic copolymer imparted excellent processability to poly(vinyl chloride). This polymer differs from conventional random copolymers in that different functionalities are imparted to the respective layers. It is, therefore, possible to design a polymeric processing aid which can be applied to both rigid and flexible poly(vinyl chloride) systems by combining to a high molecular weight polymer, a polymer having a relatively lower molecular weight and lower glass transition temperature. As shown in Table 5, the new grafted multilayer acrylic copolymer imparts excellent processability and external aesthetics in comparison to random copolymers.

TABLE 5. Relation between the structure of the acrylic polymer and the properties of the blend

	Random structure	Grafted multilayer structure
Gelling rate	Good	Excellent
Secondary processability	Good	Excellent
Clarity in flexible poly(vinyl chloride) systems	Poor	Excellent
Fish eye in flexible poly(vinyl chloride) systems	Poor	Excellent

MULTILAYER STRUCTURED POLYMERIC LUBRICANTS (3)

External lubricants, such as, waxes and metallic soaps, exhibit excellent lubricating properties. Because of their low molecular weights, they have inherent shortcomings, such as, difficulty in imparting clarity, lack of lubricant effectiveness over extended time periods, and tendency to bleed out. These problems are unavoidable as long as one designs polymer structures within the bounds of the conventional range of low molecular weights. In order to meet the needs for a polymeric lubricant, a grafted multilayer structured polymer similar to that proposed for a polymeric processing aid was studied and successfully developed. This new polymeric lubricant imparts good clarity and extended lubricant effectiveness. The structure basically consists of three layers as illustrated in Fig. 14. It is designed so that the layer flanked by the two outer layers carries out the function

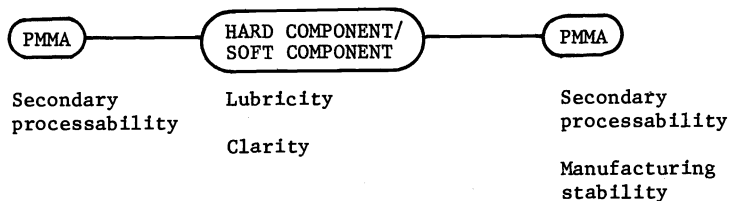


Fig. 14. Grafted multilayer structure (polymeric lubricant). PMMA: Poly-(methyl methacrylate)

of a lubricant while the outer layers aid in imparting secondary processability and other functions.

The kinetic viscoelastic behavior of a poly(vinyl chloride) formulation which employs this type of polymeric lubricant is shown in Fig. 15.

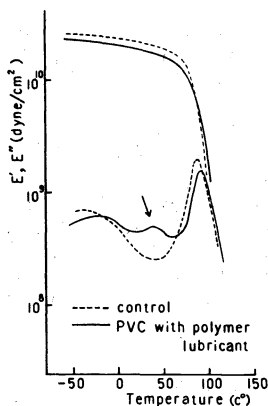


Fig. 15. Kinetic viscoelastic behavior of poly(vinyl chloride) with a polymeric lubricant. Polymeric lubricant: 10 phr.

The main feature of this type of lubricant is that each layer exists independently and lacks compatibility with poly(vinyl chloride). This is one of the conditions which is required for the polymer to exhibit external lubricant effectiveness, and is in sharp contrast to the polymeric processing aid which was described in the preceding section. It should be noted that the two outer layers are designed to have a structure which is highly compatible with poly(vinyl chloride). It is believed that the long term effectiveness of the lubricant is due to the fact that there is a balance between compatibility and non-compatibility which are respectively shared by different layers.

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