

Acrylic Processing Aids: Key to the Future

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The development of new applications for PVC, such as foam and wood composites as well as the demand for higher productivity in these and other existing commercial applications, has dramatically highlighted the importance of processing aids as an integral part of most new and existing high productivity PVC formulations.

This paper reviews the important parameters of the transformation process and the role that process aids play in the optimization and enhancement of compound processability, end product properties and manufacturing efficiency.

- Introduction

In the 20th century, plastics have replaced metal, minerals or wood in various applications either to save natural resources or due to their advantages over these materials. PVC is one of these thermoplastic materials that have had tremendous growth, especially in building applications such as siding, windows and pipe. New applications such as foamed profiles and composites have boosted the growth of this mature product over the last 10 years.

PVC is a very special type of thermoplastic. This special character is in the fact that the thermal decomposition temperature is close to the processing temperature. The right choice of both additives and melt processing conditions is the key to improving processability and properties for the final application.

Processing behavior involves the gelation process of the polymer and the melt rheology of the polymer. Small quantities of processing aids can play a predominant role in improving both steps.

Most commercial processing aids are copolymers of methyl methacrylates and alkyl acrylates, with MMA as the major component. The molecular weight and the glass transition temperature control their efficiency. The effects of the processing aid can be summarized as follows:

- Acceleration of gelation
- Control of melt rheology
- Lubrication



- **Acceleration of gelation:**

In order to obtain a homogeneous melt, PVC particles should be broken down to their primary particles under heat and shear in the processing equipment. Without the addition of processing aids, PVC particles have a low coefficient of friction with the hot metal surface of the processing equipment ⁽¹⁾ and also with other particles ⁽²⁾. Hence long processing times at high temperatures would be required to achieve complete gelation. The addition of the processing aid increases particle to particle friction, combined with enhanced heat and shear transfer leading to a faster breakdown of the particles and a faster gelation.

The ability of processing aids to promote PVC gelation is greatly influenced by the processing aid's chemical composition and molecular weight. Lower Tg processing aids are more effective in reducing the gelation time or reducing the processing temperature.

Fast gelation is critical in obtaining a homogeneous melt and important in a number of manufacturing processes. Faster gelation enables lower residence time in the extruder or extrusion at lower temperatures. In some of today's high output extrusion applications, where die swell and higher gloss are not issues, higher Mw process aids are increasingly being used. Two of these applications are siding substrate and high-speed profile extrusion.

In the calendering process, complete gelation and homogeneous dispersion of the formulation ingredients are key factors in obtaining optimal transparency and reducing defects such as fish eyes in the product.

In the extrusion of foam profiles, gelation time needs to be properly adjusted in order to obtain the lowest density and best cell distribution. Fast gelation at lower temperatures prevents the gas produced from the decomposition of the blowing agent from escaping back up through the throat of the hopper ⁽³⁾. On the other hand if gelation happens too early, the dispersion of the gas from the blowing agent might not be completed before the rise in viscosity, and so the foaming process not optimized.

- **Control of melt rheology:**

The predominant effect of the processing aid is on rheological characteristics: homogeneity, strength and elasticity of the melt after gelation and during fabrication. Acrylic processing aids, due to their high compatibility with PVC and also their high molecular weight, entangle with the PVC chains leading to improved melt properties.

Depending on the processing technique and required properties, different PVC melts need to have different rheologies to match specific requirements.



In calendaring PVC sheet, the addition of the processing aid improves significantly the homogeneity of the bank, thus enhancing the quality of the surface and the edges of the sheet while decreasing flow marks and increasing gloss.

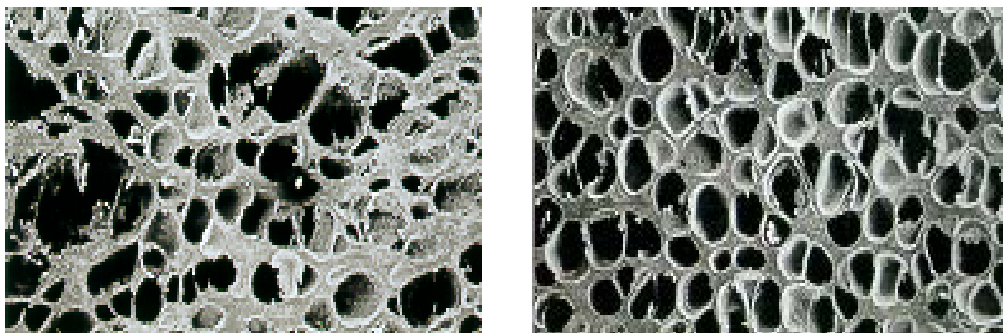
In injection molding, lower melt viscosity process aids improve productivity and visual aspects of the final product without affecting the physical properties due to low use levels. The use of a high melt viscosity process aid makes processing more difficult at lower temperatures and at higher production rates, because energy consumption is increased and good product quality is compromised. It is difficult to injection mold highly viscous materials with good mold definition without high processing temperatures that can cause polymer degradation. Also a strong weld line cannot be obtained without the use of processing aids.

In high output extrusion, the effect of the processing aid in optimizing the system cannot be neglected. The phenomenon of die swell in extrusion and its correlation with the Mw of the processing aid is well known. It can be assessed by using a laboratory extruder with a rod die, and comparing the diameter of the extrudate to the diameter of the die. If the extrusion line has high output, the melt will undergo high shear rates. As the profile is cooled and the shape is fixed within the calibrator, the polymer chains are frozen in their stretched configuration in the extrusion direction. If the profile undergoes a temperature increase after manufacturing, it will undergo reversion. This means the polymeric chains will return from a stretched configuration to the lower energy coil configuration. It has been proven that lower molecular weight process aids reduce reversion as well as having a lower die swell ⁽⁴⁾.

For applications such as blow molding, calendaring, thermoforming and foam extrusion, a high level of melt strength is required. Poor melt strength causes problems for blow molders and film blowers. The processing aid's ability to improve melt strength of PVC has been found to be proportional to the molecular weight of the processing aid.

To succeed in applications such as foam extrusion, the polymer should have high melt strength. With the help of a high molecular weight processing aid, the cell structure of extruded foam is more uniform with less cell collapse and the melt can withstand great extension before it breaks, so a lower foam density can be obtained.

Cell structure without process aid (left), 7 phr high Mw process aid (right)



Another critical value in the melt rheology of PVC is the critical stress value. If during processing, the shear stress applied on the melt exceeds this value, melt fracture occurs, resulting in rough surface and unsteady flow. This is reduced through the addition of lower molecular weight processing aids, and increasing the critical stress values through the entanglement of the polymer chains. This is a key element for high output extrusion and injection molding.

PVC has also been used as a polymer matrix for some wood-plastic composites. The processing of wood-filled PVC is rather challenging due to the following issues:

High temperature increase due to shear heating

High melt viscosities

Low melt strength leading to poor extrusion quality

Table I shows the effect of increasing the wood fiber level in a PVC formulation. The addition of a high molecular weight processing aid improves the processability of these materials and allows a higher loading of wood fiber. The suitable process aid should provide a high melt strength for improved surface and edge qualities while maintaining a low melt viscosity to reduce the torque and increase the output.

Figure I shows the effect of increasing the level of processing aid in a wood-filled compound. It can be seen that increasing the level of the processing aid leads to higher torque values and a higher level of heat generation. As wood is sensitive to degradation above 200 °C it is mandatory to keep shear heating at a minimum. Also, due to the low heat transfer coefficient of the wood, wood-filled compounds require longer cooling times.

The effect of increasing the level of processing aid on the extrusion of 40 % wood-filled PVC compound is reported in **Table II**. The output/torque ratio or the “process ease”⁽⁵⁾ is an indication of the efficiency of the extrusion process. Increasing the level of process aid has a negative effect on torque and output. While it may be necessary to increase the level of process aid in order to get the necessary extrusion properties, it is important to determine which process aid is optimum for the process. In the case of wood-filled PVC, high Mw process aids seem to be best suited for the application because of their fast gelation characteristics and the high melt strength that they impart to the compound. It is also important to know that not all high Mw process aids effect the compound in the same manner.

Figure II compares the torque and output/torque ratio of two commercial high molecular weight process aids. These results show that one of the processing aids (**Metablen P-530 commercialized by ATOFINA Chemicals**) provides a higher output/torque ratio than the second commercial product (PA-1) while maintaining extrusion quality. These differences can be traced to the difference in chemical/polymeric make up of the two products.

- **Lubrication:**

Through variation of chemical composition of the processing aid, the compatibility of the processing aid with the PVC can be controlled. Lower compatibility leads to a lubricating effect of the processing aid. The advantage of these materials is that contrary to classical lubricants, they have little or no effect on the gelation of PVC, they do not exude from the final product, but in the mean time they help metal release and reduce plate out at melt processing temperatures.

These types of process aids can be used as a solution in reducing the haze level of transparent calendered sheets. At a same level of metal release efficiency, lubricating processing aids have no negative effect on haze compared to external lubricants.

- **Conclusion:**

This paper reviews the role of the processing aids in the different aspects of manufacturing PVC products. Even though each effect is discussed separately, it is obvious that each processing aid has multifunctional roles in each formulation. The success of a manufacturing process is closely related to the appropriate choice of the type of processing aid used. As extrusion equipment and formulations are constantly being improved upon and output rates increased, it is necessary to keep in mind the effectiveness of process aids in helping the manufacturer achieve good processability and finished product properties.

Acknowledgements:

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References:

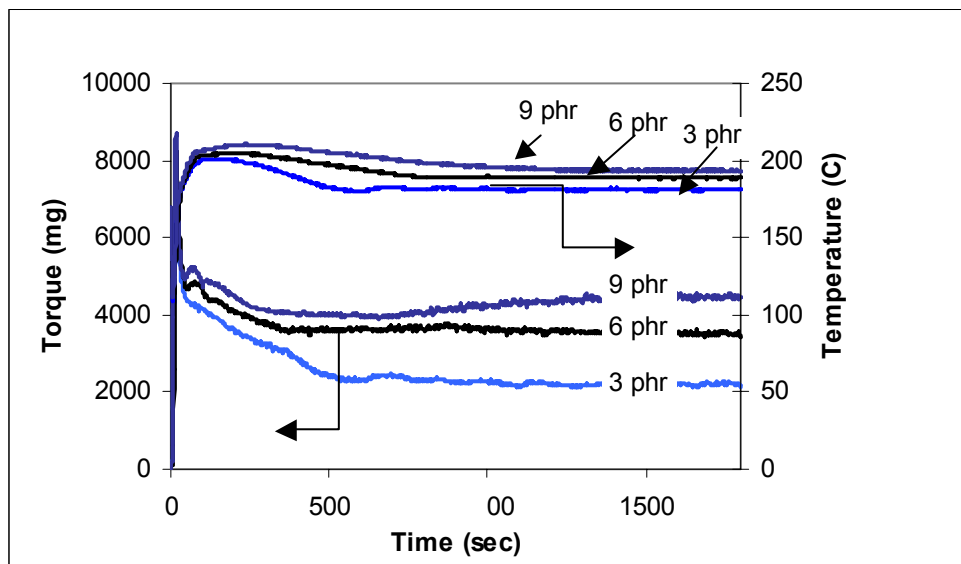
- (1) K. Bohme. *Angew Makromol Chem*, 47:243, 175
- (2) R. Gould, J. Player, *Kunststoffe*, 69, 562, 1979
- (3) Huls Aktiengesellschaft, August 1987, 2nd edition
- (4) J.P. Disson, *Vinyltech* 2000
- (5) J.B. Williams, *Antec* 2002

Table I - Effect of increasing wood content on torque rheometer and extruder results

Wood level (phr)	Torque @ 6 min (mg)	Temp (°C)	Extruder Out put (g/min)	Extruder Torque (mg)
0	2555	198	232	6683
10	2512	197	202	6093
30	2491	200	195	7085
50	2755	201	188	7593

Formulation: PVC/thermal stabilizer/CaSt/Lub/ PA/Impact modifier/CaCO₃/TiO₂/Wood flour 20 mesh: 100/0.7/1.2/1.3/1.4/5/5/10
 Torque Rheometer: 65 g, 190 °C and 75 RPM
 25 mm conical twin-screw extruder: 180/180/180/185 °C, 40 rpm

Figure I - Effect of increasing the level of high molecular weight processing aid on stock temperature and torque



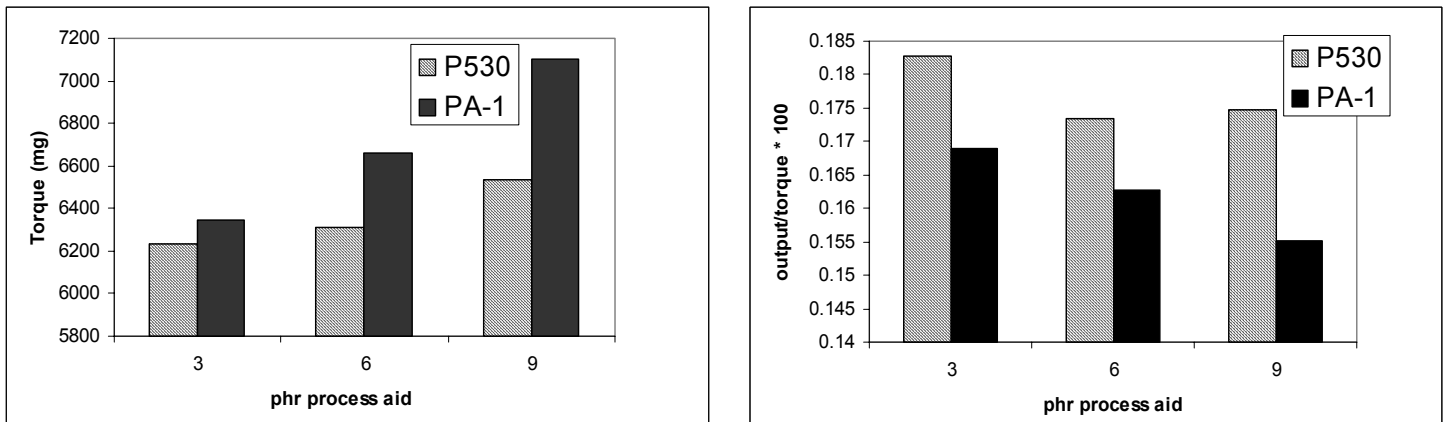
Formulation: PVC/thermal stabilizer/CaSt / Lub /process aid /Wood flour:
 100/1/1.2/1.4/5/5/80
 Torque Rheometer : 65 g , 170 °C and 75 RPM

Table II: Extrusion of PVC-wood fiber

	Process aid level		
	3 phr	6 phr	9 phr
Output (g)	11.4	10.9	11.4
Torque (mg)	6237	6312	6532
Output/Torque (*100)	0.182	0.173	0.174

25 mm conical twin-screw extruder: 175/180/180/180/185,30 rpm
 PVC/Tin stabilizer /Paraffin Wax/OPE/Calcium-
 Stearate/wood flour 40 mesh/process aid :100/1/1.1/0.2/1.2/80

Figure II: Effect of increasing the level of processing aid in wood-filled PVC



25 mm conical twin-screw extruder: 175/180/180/180/185,30 rpm
 PVC/Tin stabilizer /Paraffin Wax/OPE/Calcium-
 Stearate/wood flour 40 mesh/process aid :100/1/1.1/0.2/1.2/80