Production of Viscosity Improvers for PVC

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Summary: Some oil-based samples having oxygen, ester, amide, acid and/or hydroxyl structure were prepared for using as lubricants in PVC extrusion. After characterization studies, all samples were tested in PVC formulation using Brabender W50 EHT Lab-Station mixer and extruder. The results were compared with that of a commercial product. From the mixer results, it can be noted that energy consumption was lowered for samples containing acid and amide structures. Surface roughness and opacity of the products were improved when the extruder screw speed was increased from 20 rpm to 60 rpm.

Keywords: additives; lubricants; mixer; PVC

Introduction

In recent years production and consumption of plastics has increased rapidly in Turkey. In 2003, plastic consumption has reached to 6.6 billion tones per year. Additive consumption has also increased rapidly in this period.

PVC is largely used for industrial applications.[1] The rheology of PVC melts is very complex. It exhibits not only liquid flow, but also particle flow at elevated temperatures, i.e. the structures of the polymer particles are still retained in the melt. At about 110°C PVC starts to melt and turns to globules. At 190°C PVC nodules are formed. This phenomenon is called PVC fusion. This behavior can be explained by DSC curve of PVC (Figure 1). During the processing, either molecular friction between small particles, or macro-friction between bulk polymer and metal surface of the processing machine, are caused energy consumption and rough surface. For this purpose, PVC needs lubricants.[2]

 DOI: 10.1002/masy.200551021

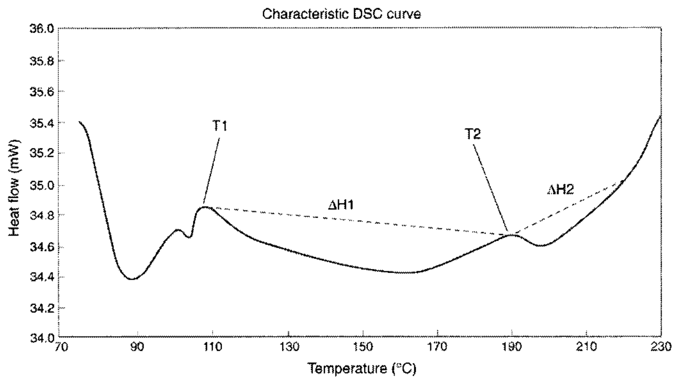


Figure 1. DSC curve for PVC.[2]

Since PVC exhibits pseudo-plastic flow behavior, it is necessary to increase shear stress for lower viscosity. On the other hand, high stress causes rough surfaces. For this reason, processing conditions should be optimized, and some additives, such as lubricants, should be used.[2,3]

As an exception of polyolefin waxes, a lubricant generally has a polar group and non-polar residue. The chemical structure is an important effect of the lubricant during processing. With degreasing polarity, solubility in the highly polar PVC degreases.[3,4] Virtually insoluble lubricants are referred to as external. They form lubricating films between the PVC and metal surface of processing machine. On the other hand internal lubricants are soluble in PVC and they decrease the friction between chains of polymer in PVC melt. A lubricant should not change mechanical property of end product. It should decrease energy consumption and delay thermal degradation of PVC.[3,5]

Characterization of the lubricants is becoming increasingly important for processors. Some of the methods commonly used are determination of drop point, pour point and chemical characterizations such as acid and iodine value, viscosity, density etc. [4] For assessment of lubricant effect, they are carried out by measuring property changes in polymers. For this purpose a mixer and/or an extruder are used.

In this study, eight samples were prepared from triglyceride oil. After characterization, they were tested in PVC formulation as lubricant. The results were compared with those of the samples with Finalux G-101 and without lubricant.

Experimental

Oil-based oligomers and polymers were tested as lubricants. For structural characterization of samples FTIR Spectrophotometer Mattson 1000 was used. Their molecular weights were determined by using HPLC Agilent 1100 Series System.

In order to understand the effect of sample structure on bulk polymer during the process, Brabender W50 EHT Lab-Station mixer and extruder were used. PVC samples were prepared according to following formulation.

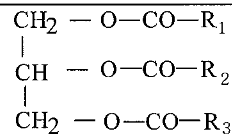
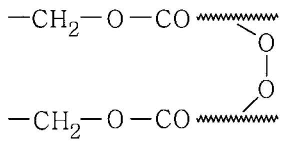
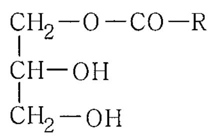
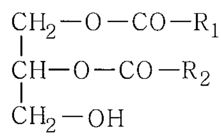
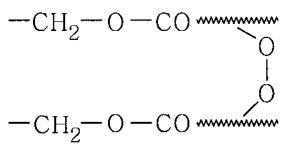
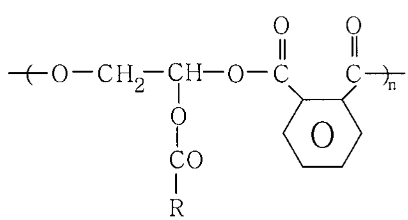
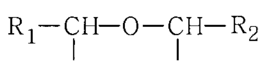
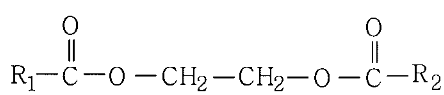
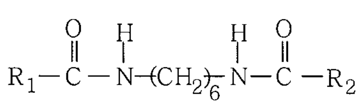
Ingredient	Part by weight
PVC	100
Lubricant	0.8
Ca/Zn Stabilizer	2.5
Calcite	3.0

Heating zones on extruder are measured 180, 175, 170 °C and head of die with 180°C. During the extrusion various mixing speeds between 20-60 rpm were applied. Finalux G-101 (Fine Organics) was used as comparative sample.

Results

For lubrication purposes, eight samples were prepared from triglyceride oils. The chemical structures of the samples are shown in Table 1. LUB-OAY, LUB-OKG and LUB-OAYYA were prepared from LUB-AY, LUB-KG and LUB-AYYA, respectively, by oxidation reaction. LUB-KG was obtained from the reaction of LUB-AY and glycerin. LUB-AR is the ester product synthesized with the reaction between phtalic anhydride with LUB-KG. From the reaction of ethylene glycol with LUB-AYYA, LUB-AE was prepared. For obtaining LUB-AA, hexamethylendiamine (HMDA) was reacted with LUB-AYYA.

Table 1. Structures of samples.

Code	Structure
LUB-AY	
LUB-OAY	
LUB-KG	A mixture of:  and 
LUB-OKG	
LUB-AR	
LUB-AYYA	$R-COOH$
LUB-OAYYA	
LUB-AE	
LUB-AA	

Acid, iodine, saponification and peroxide values, refractive index, density, molecular weight and polydispersity of samples were given in Table 2.

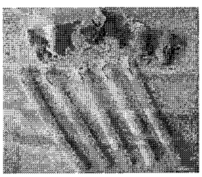
Table 2. Some properties of samples.

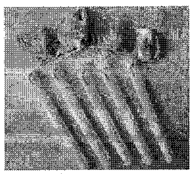
Sample	Acid Value (mg.KOH /g)	Iodine Value (gJ_2./100 g)	Sponification Value (mg.KOH /g)	Peroxide Value (mg.KOH/1000g)	Refractive Index (25°C)	Density (g/cm^3, 25°C)	Molecular Weight (M_w, g/mol)	Polidispersity (M_w/M_n)
LUB-AY	1.4	115.9	199.6	8.1	1.4711	0.918	1528.3	1.01
LUB-OAY	1.7	108.9	239.4	303.8	1.4731	0.931	1993.0	1.23
LUB-KG	1.1	108.3	186.6	27.3	1.4708	0.941	1078.2	1.13
LUB-OKG	1.7	101.2	187.3	181.2	1.4722	0.942	1204.5	1.18
LUB-AR	18.2	91.6	261.4	18.2	1.4862	0.985	2076.5	1.28
LUB-AYYA	196.0	128.0	206.0	10.3	1.4618	0.898	416.0	1.02
LUB-OAYYA	180.2	112.4	210.4	11.9	1.4655	0.916	679.4	1.30
LUB-AE	34.4	115.8	192.1	43.9	1.4680	0.912	958.1	1.27
LUB-AA	10.3	111.2	6.8	0	---	solid	1203.6	1.25
Finalux G-101	max.3	65-80	---	----	---	---	---	---

Lubricants can be classified into two groups, internal and external lubricants according to their lubricating effect. For the determination of the type of a lubricant, fusion time is an important parameter that can be obtained from the mixer. As it can be seen from the Table 3, since LUB-AA has less fusion time, it is more internal lubricant and the others especially LUB-AR and LUB-AYYA are more external lubricants. The specific energy defined as energy consumption per sample weight for extrusion process, also decreased with addition of LUB-AYYA and LUB-AR.

Table 3. Brabender mixer results.

Sample	Fusion			Decomposition				Energy Con. [kNm/g]
	Time (s)	Torque (Nm)	Temp. (°C)	Time (s)	Torque (Nm)	Temp. (°C)	Torque (Nm)	
LUB-AE	61.8	32.7	89	4.80	25.9	206	47.1	0.84
LUB-AR	79.8	32.1	192	4.83	25.4	206	44.8	0.80
LUB-OAY	66.0	32.1	190	4.83	25.4	206	46.2	0.83
LUB-OKG	67.8	33.7	190	4.83	25.8	206	47.5	0.85
LUB-KG	58.2	33.7	189	4.83	26.0	206	48.5	0.87
LUB-AYYA	94.2	27.7	192	4.83	26.1	204	41.9	0.75
LUB-OAYYA	67.8	32.5	191	4.87	26.1	206	49.2	0.88
LUB-AA	49.8	34.2	189	4.83	25.9	206	49.8	0.89
Non-LUB	58.2	35.7	190	4.83	27.0	207	50.7	0.91
Finalux G-101	58.2	34.1	189	4.83	25.6	206	48.6	0.87


LUB-AE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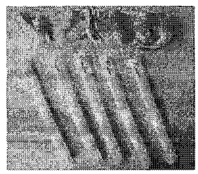
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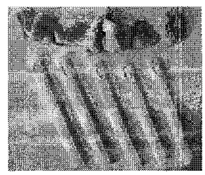
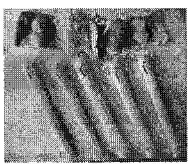

LUB-OKG


LUB-KG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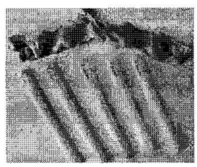
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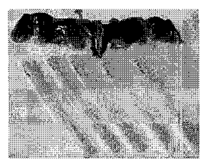
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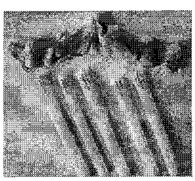
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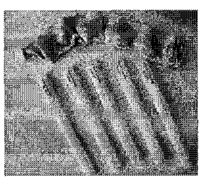
Finalux-G 101

Figure 2. PVC pipe profiles.

The surface roughness and colors of PVC produced for clean pipe got better when the screw speed of the extruder increased from 20 rpm to 60 rpm. In Figure 2, pipe profiles are shown for each process with and without lubricant. It is possible to produce pipe without using lubricant, because some plasticizers have lubricating effect during process. However, the energy consumption is very high for the process without lubricant as compared to those of the processes with LUB-AYYA and LUB-AR (Table 3). Additionally, pipes with LUB-AA burned during mixing and they had the worst color and surface property (Figure 2).

Conclusion

In this study, various oil-based samples were tested as PVC lubricant. As a result of the study, the energy consumption decreased for PVC profile using LUB-AYYA and LUB-AR. The best surface properties and colors were obtained at 50 and 60 rpm of extruder screw speed.

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