

Melt Rheology Parameters of Ethylene–Vinyl Acetate Copolymer Modified with 3-(Tetrabromopentadecyl) 2,4,6-Tribromo Phenol

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SYNOPSIS

Processability characteristics of ethylene–vinyl acetate (EVA) copolymer formulations modified with a flame-retardant 3-(tetrabromopentadecyl) 2,4,6-tribromo phenol (TBPTP) have been studied on a Brabender Plasticorder at various shear rates and temperatures. The plasticizing effect of TBPTP on EVA has been confirmed by the increase in flow behavior index and decreases in melt viscosity, melt elasticity, and activation energy of melt flow. The improvement in processability of the TBPTP-modified EVA over the unmodified sample was reflected in a reduction in power consumption during mixing of the former. The study was undertaken because of the potential of TBPTP-modified EVA for application in flame retardant low smoke (FRLS) cable sheathings. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

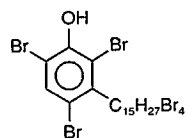
The ethylene–vinyl acetate (EVA) copolymer and its blends with other polymers modified with suitable flame-retardant additives find extensive use in applications such as cable sheathings, insulations, etc.^{1–3} However, the processability of such formulations may be of concern, especially when they contain a large proportion of inorganic fillers. Recently, derivatives of cardanol-containing phosphorus and bromine have been found to be ideal flame retardants for a variety of polymers.^{4–7} Among these flame retardants, 3-(tetrabromopentadecyl) 2,4,6-tribromo phenol (TBPTP) (see Scheme 1) has been found to be promising as a flame retardant for polyethylene (PE) and EVA formulations for cable sheathings and insulations.^{7,8} Addition of TBPTP has been found to improve the processability of PE without deleterious effects on the mechanical properties.⁸

It has been shown that the consistency and processability of plastics on production machines can be predicted satisfactorily from the results of studies

on smaller batches on a Brabender Plasticorder.^{9–11} Goodrich and Porter have shown that the Brabender torque rheometer data can be converted to fundamental rheological units.¹² Blyler and Daane converted the torque data from Plasticorder to fundamental flow curves.¹³ Lee and Purdon showed that the flow behavior index obtained on a Brabender Plasticorder was the same as that obtained from a capillary rheometer.¹⁴ The flow behavior index may be obtained from a log-log plot of Brabender torque against rotor speed.¹⁵ A reduction in the bandwidth of the Brabender torque profile has been shown to be an indication of a reduction in melt elasticity.¹⁶

Previous studies in this laboratory have led to the development of TBPTP-modified EVA formulations for cable sheathings and insulations having very good flame retardancy, low smoke density ratings, and good electrical and mechanical properties.^{8,17,18} However, since the manufacturing of products like cable sheathings involves operations such as mixing and extrusion under high shear rates and temperatures, it is essential to have an idea of the melt flow characteristics and melt elasticity of the formulations under these conditions. The shear rate range of a typical Brabender Plasticorder falls well within that of larger mixers. Hence, the processability characteristics of un-

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Scheme 1.

modified and TBPTP-modified EVA and their filled formulations were studied on a Brabender Plasticorder at various rotor speeds and temperatures, and the results are reported in this paper.

EXPERIMENTAL

Materials

The EVA copolymer of PILENE EVA-2018 grade was supplied by M/s Indian Petrochemicals Corporation Ltd., Baroda. TBPTP (Scheme 1) having a bromine content of 63% and LOI 53 was prepared according to the patented process.¹⁸

Alumina trihydrate (ATH) of APYRAL grade was obtained from M/s Bayer India Ltd. Other chemicals were of the laboratory reagent grade.

Methods

Blends of EVA, TBPTP, and other additives were prepared (as per the formulations given in Table I) on a Brabender Plasticorder (Model PLE-651) fitted with a roller mixing measuring head at 100°C under a rotor speed of 30 rpm. The torque profiles of 40 g each of the samples were measured at 80, 100, 120, and 160°C at pre-set rotor speeds of 30, 60, and 90 rpm. Parameters such as melt viscosity index, flow behavior index, activation energy of melt flow, and power consumption for mixing were calculated from the steady value of torque at the tenth minute using the relations, as mentioned earlier.⁷

RESULTS AND DISCUSSION

Unfilled Samples

Melt-Viscosity and Power Consumption for Mixing

Melt viscosity is a parameter of prime importance in the processing of polymers. The dependence of melt viscosity on shear rate and temperature are factors of major significance with respect to processing operations, such as extrusion.¹⁹ Melt viscosity influences the pressure build up in the barrel

of an extruder and its output and is inversely dependent on the concentration of plasticizer in the polymer system.²⁰

Modification of EVA with 10% TBPTP resulted in a reduction in the melt viscosity (compared to the unmodified sample) with an increase in shear rates and temperatures. The melt viscosity index calculated from the stable Brabender torque values at rotor speed ranging from 30 to 90 rpm and temperature ranging from 80 to 160°C for the unmodified and TBPTP-modified EVA samples are given in Table II. The results show a pronounced decrease in the melt viscosity for the TBPTP-modified sample, especially at lower shear rates and temperatures.

The effect of certain special purpose multifunctional additives, such as flame retardants, on the melt rheology of polymers is well known. It has been reported that flame retardants that are liquid at the processing temperature (e.g., dibromo propyl phosphate) usually act as lubricants and decrease the viscosity of melts.²¹ Since TBPTP is in a viscous liquid stage at room temperature and at elevated temperatures, it is expected that its lubricating effect and, specifically, the plasticizing effect of the C₁₅ side chain on EVA are responsible for the observed reduction in melt viscosity. It has been shown in an earlier work that the presence of the aliphatic moiety of the flame retardant enhances processability and improves miscibility and compatibility with polyolefins, such as polyethylene,²² and the presence of the ethylene segments in EVA possibly might assure greater compatibility. The melt viscosity of a polymer at any specified temperature is often considered to be a measure of the mobility of the polymeric chains relative to each other and is controlled by the flexibility of the chains.²³ It is probable that the plasticizing effect of TBPTP on EVA improves the flexibility of the latter, leading to a lowering of the melt viscosity.

The lower melt viscosities of the TBPTP-modified EVA at the various temperatures and shear rates

Table I Formulations

Ingredients	Sample Codes			
	UG	MG	UF	MF
EVA	100	100	100	100
TBPTP	—	10	—	30
ATH	—	—	60	60
Sb ₂ O ₃	—	—	10	10
MoO ₃	—	—	6	6
Fe ₂ O ₃	—	—	1	1

Table II Melt Viscosity Index and Power Consumption of Unfilled EVA Before and After Modification with TBPTP

Parameter	Temp (°C)	Sample Code: UG			Sample Code: MG		
		Rotor Speed (rpm)					
		30	60	90	30	60	90
Melt viscosity index (m · g/rpm)	80	53	27	18	49	25	16
	120	37	20	14	32	17	12
	160	24	14	10	20	13	10
Power consumption (W)	80	49	101	151	46	93	132
	120	34	74	115	30	64	99
	160	22	50	83	19	47	80

in turn lead to a reduction in the power consumption for mixing compared to the unmodified sample as shown in Table II. The lower power consumption for mixing the TBPTP-modified EVA, especially at lower temperatures and higher shear rates, may be helpful in enhancing the productivity in processing operations, such as mixing and extrusion.

The Brabender torque profiles showed a reduction in the melt elasticity of EVA on modification with TBPTP, as evidenced by the decrease in bandwidth with an increase in rotor speed and temperature. Smooth and uniform torque profiles with reduced bandwidth generally imply an improvement in processability,¹⁶ typical of polymer melts having a high degree of plasticity. Polymer melts having a narrow molecular weight distribution are reported to show a great dependence of viscosity on temperature and low melt elasticity, which can lead to less warping in injection moldings.¹⁵

Melt-Flow Characteristics: Flow Behavior Index and Activation Energy of Melt-Flow

Flow behavior index (pseudoplasticity index, n) and activation energy of melt flow at constant shear rate (E) are two parameters of significance with respect to polymer melt flow.^{15,24} An increase in the value of the former and a decrease in the value of the latter under an increase in temperature and shear rate, respectively, may be considered ideal for processing operations involving melt flow.

Table III shows the flow behavior index, n , and activation energy of melt flow, E , of the raw polymer before and after mixing with 10% TBPTP. The results show a higher rate of increase in flow behavior index with temperature (over the range 80–160°C)

for the TBPTP-modified sample, with the higher values indicating a near Newtonian behavior.^{15,23}

The activation energy of melt flow at constant shear rate (E) of the samples were determined from the viscosity-temperature dependence following the Arrhenius relationship,¹⁵ namely, $\eta = Ae^{(E/RT)}$, where η is the viscosity index, R is the gas constant, and T is the temperature in absolute scale. The results given in Table III show comparatively lower activation energy of melt flow for the TBPTP-modified sample at the different rotor speeds. Also, the higher rate of decrease in activation energy for the TBPTP-modified EVA, with the increase in rotor speed, indicates its higher shear sensitivity for melt flow. The increase in flow behavior index and decrease in activation energy of melt flow with the increase in temperature and shear rate, respectively, are typical of conventional pseudoplastic polymer melts.^{15,25}

Table III Melt Flow Characteristics of Unfilled EVA Before and After Modification with TBPTP

Parameter	Sample Code	Temperature (°C)		
		80	120	160
Flow behavior index (n)	UG	0.02	0.10	0.20
	MG	0.03	0.10	0.32
		Rotor Speed (rpm)		
		30	60	90
Activation energy of melt flow (E) (kCal/mol)	UG	3.43	3.16	2.51
	MG	3.34	2.46	1.85

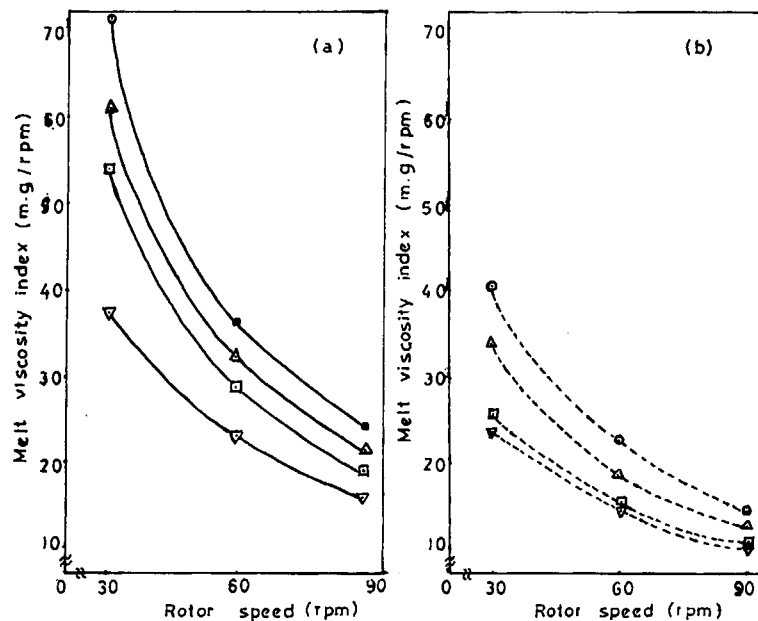


Figure 1 Plots of torque to speed ratio versus rotor speed: (a) UF; (b) MF. Symbols are as follows: \circ , 80°C; Δ , 100°C; \square , 120°C; ∇ , 160°C.

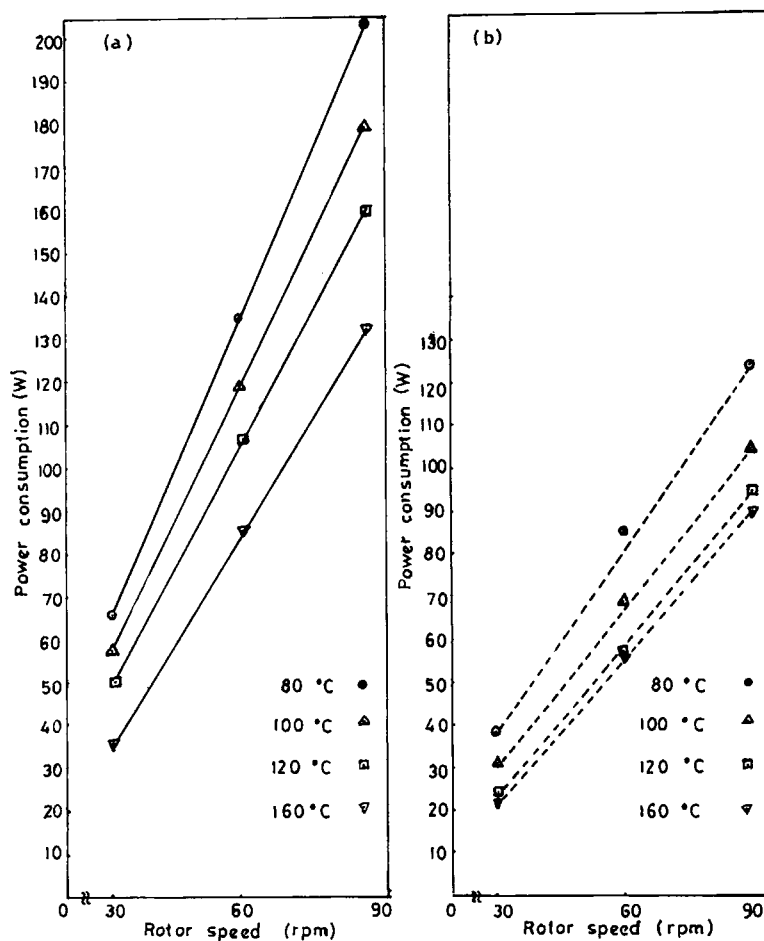


Figure 2 Power consumption during mixing: (a) UF; (b) MF.

Table IV Melt Flow Characteristics of ATH-filled EVA Before and After Modification with TBPTP

Parameter	Sample Code	Temperature (°C)			
		80	100	120	160
Flow behavior index (<i>n</i>)	UF	0.02	0.06	0.06	0.23
	MF	0.09	0.13	0.28	0.32
		Rotor Speed (rpm)			
		30	60	90	
Activation energy of melt flow (<i>E</i>) (kCal/mol)	UF	2.5	1.8	1.7	
	MF	2	1.5	1.2	

Activation energy of melt flow is often considered to be an indicator of the mobility of macromolecules in polymer melts.²⁶ The lower values of activation energy of TBPTP-modified EVA probably indicates a higher degree of segmental mobility of EVA in the presence of TBPTP as against that of the unmodified sample. This is understood from the structure

of TBPTP, which, with its a long aliphatic moiety at the meta position, possibly penetrates the polyethylene segments of EVA, permitting improved segmental motion of molecules. Similar effects have been observed when TBPTP was blended with polyethylene alone in a previous study.⁷ These results, particularly the decreases in melt viscosity, melt elasticity, and activation energy of melt flow and the increase in flow behavior index of EVA in presence of TBPTP indicate the plasticizing effect of the latter on the former.

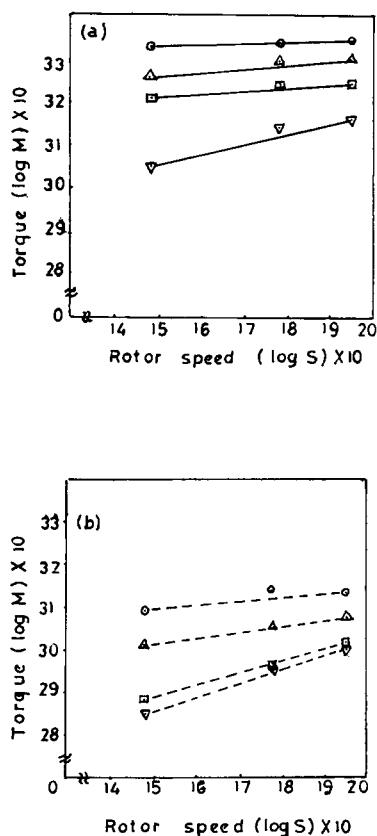


Figure 3 Flow curves: (a) UF; (b) MF. Symbols are as follows: ○, 80°C; △, 100°C; □, 120°C; ▽, 160°C.

ATH-filled Formulations

TBPTP-modified EVA formulations containing ATH as a filler and other additives have been found to meet the specifications laid down for flame-retardant low-smoke (FRLS) cable sheathings^{8,18} (A typical formulation has been found to give a value of LOI 30, % transmission of smoke < 20, acid gas emission < 2, and other properties within specifications). However, to ensure good processability of the formulations, it is essential to carry out the melt rheology studies at a range of temperatures and shear rates. Hence, the melt viscosity and melt flow characteristics of typical ATH-filled EVA formulations, as given in Table I, were determined, the results of which are given below.

Melt-Viscosity and Power Consumption for Mixing

Figure 1 (a) and (b) show the plots of the melt viscosity index versus the rotor speed of the filled formulations. The melt viscosity of the formulation modified with 30% TBPTP was found to be considerably lower than that of the unmodified sample at

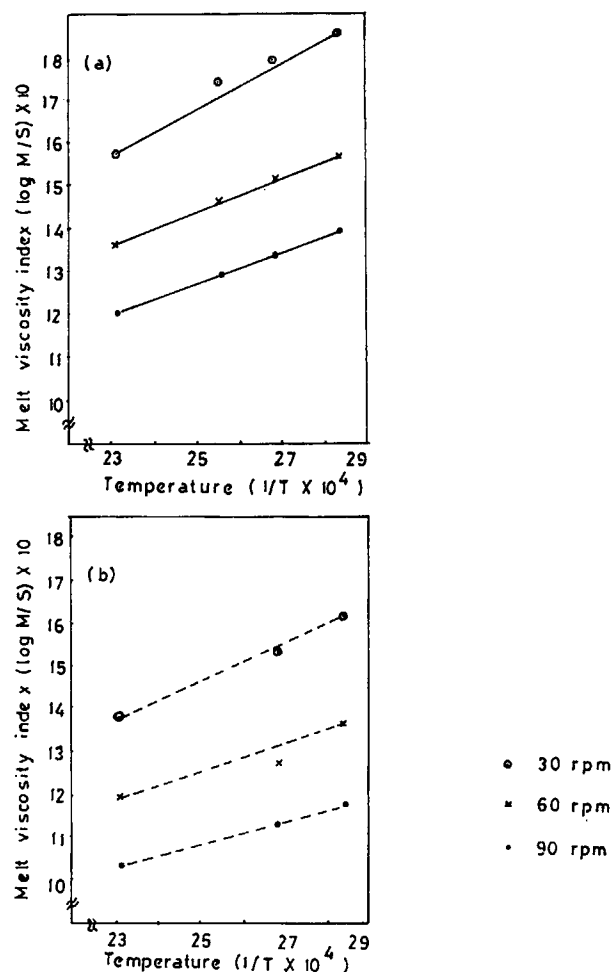


Figure 4 Arrhenius plots: (a) UF; (b) MF. Symbols are as follows: ○, 30 rpm; ×, 60 rpm; ●, 90 rpm.

the various test temperatures. Also, it decreased to a lower value with the increase in rotor speed. The lower melt viscosity of the TBPTP-modified formulation, in turn, facilitated easy mixing of the formulation with reduced energy consumption. This is clear from Figure 2, which shows the power consumption plots of the filled formulations at various rotor speeds and temperatures. The energy requirement for mixing the TBPTP-modified formulation was considerably lower than that for the unmodified formulation, particularly at the lower temperatures. The reduction in melt elasticity of the TBPTP-modified EVA formulation containing ATH at higher temperatures and rotor speeds was shown by the reduction in bandwidth and uniformity of the Brabender torque profiles. This indicated the superior processability of the ATH-filled EVA formulation containing TBPTP, compared to that of the unmodified one. The TBPTP-modified formulation gave extrudates having good surface finish

and smoothness as flame-retardant cable sheathings,¹⁸ thereby substantiating the above observation.

Flow Behavior Index and Activation Energy of Melt-Flow

The flow curves of the filled formulations before and after modification with TBPTP for temperatures ranging from 80 to 160°C are given Figure 3 (a & b). The values of the flow behavior index (n), calculated from the slope of these plots, are given in Table IV. The increase in the flow behavior index on modification with TBPTP and with the increase in temperature is quite prominent.

The Arrhenius plots of melt viscosity index versus temperature of the samples at the rotor speeds of 30, 60, and 90 rpm are given in Figure 4 (a) and (b). The values of activation energy at constant shear rates calculated from the slope of these plots are given in Table IV. The lower activation energy for the TBPTP-modified formulation at the different rotor speeds clearly indicates its ease of melt flow compared to that of the unmodified sample.

These results lend evidence to the plasticizing effect of TBPTP on EVA in the ATH-filled formulation also, as observed in the case of the unfilled sample.

The higher flow behavior index (especially at the lower temperatures) and the lower activation energy of melt flow of the TBPTP-modified formulation may be considered advantageous in processing operations, such as extrusion, where enhanced productivity is one of the essential requirements. In such cases, the need for a low melt temperature is especially relevant for EVA copolymers with higher vinyl acetate content, which have higher tendency to degrade at elevated temperatures.²⁷ The present study shows that the TBPTP-modified EVA formulation can be processed easily at a low temperature (80°C) with reduced energy requirement. Thus, TBPTP, with its excellent flame retardancy and low smoke emissions when blended with EVA, can be considered a suitable additive for composition for applications such as flame-retardant cable sheathings or insulations.

CONCLUSIONS

1. TBPTP improves the processability of unfilled and ATH-filled EVA formulations by acting as a plasticizer, as indicated by the in-

crease in flow behavior index and the decrease in melt viscosity, melt elasticity, and activation energy of melt flow.

2. The improved processability of TBPTP-modified EVA over the unmodified sample (in unfilled and filled formulations) is reflected by the reduced energy requirement for mixing at various shear rates and temperatures.

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