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**VISCOSITY OF HOT-MELT ADHESIVES BASED
ON ETHYLENE VINYL ACETATE COPOLYMERS**

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In this paper, the results of measurements are presented concerning the shear viscosities in the dependence on temperature of five hot melts adhesives based on polyvinyl acetate – polyethylene copolymers EVAK. Using the viscosity data measured, the accuracy of three blending models, reported in the literature for multicomponent blends, was tested for viscosity predicting. It has been found that no model was capable to estimate satisfactorily the adhesive melt viscosity in the whole interval of the temperature examined. To achieve a higher accuracy of viscosity estimation, it is necessary to incorporate into models a corrective function of temperature.

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Introduction

Adhesive bonding has gained more importance during the past decades; especially, in high-tech applications. An important group of adhesives are the hot melts (HMA) that are employed in a variety of industrial applications. Hot melts are formed from the melt, gaining strength upon solidification and crystallisation. Conventional hot melt adhesives are available in an array of chemical types based on different polymers. The significant primary polymers used to formulate the hot melt adhesives are polyvinyl acetate – polyethylene copolymers (EVAK). Generally, these polymers do not exhibit desired performance and that is why they are combined with tackifying resins, waxes, antioxidants, and other additives. The polymer contributes to the strength and toughness, while the tackifier enhances wetting and tack. The wax lowers the melt viscosity, whereas the antioxidant reduces thermal degradation during the processing (see, e.g., Ref. [1]).

For optimum formulation of hot melt compositions and effective processing of final hot melts as well, it is important to know their rheological behaviour. One of the basic rheological properties is the viscosity which significantly affects the performance of a hot melt adhesive. In processing, the melt viscosity must be fairly low at the temperature applied in order to allow good substrate wetting. On the other hand, it should not be too low to avoid running the molten adhesive off the substrate.

In this contribution, the suitability of three mixing rules reported in the literature for prediction of viscosities of multicomponent liquid blends were tested for five hot melt adhesives based on polyvinyl acetate – polyethylene copolymers EVAK-25 and EVAK-400. The adhesives, which are designated as HM-VO-4, HM-L-05-1, HM-L-05-2, HM-L-05-3, and HM-L-05-7, differ each other in the content of tackifying resins HRR-2 and ARR-9. The accuracy of the mixing rules examined was evaluated according to the agreement attained between the predicted viscosities and those being determined experimentally.

Experimental

Materials

The polymeric compositions HM-VO-4, HM-L-05-1, HM-L-05-2, HM-L-05-3, and HM-L-05-7 were prepared in Synpo a.s. Their composition and other features are given in Table I; the characteristics of the individual components of HM adhesives are given in Table II. The glass transition temperature, T_g , was evaluated from dynamic mechanical analysis (DMA) measurements [2], the softening point, T_s , then determined using a ring-and-ball method and the melt index according to the corresponding norms (ČSN EN 1427 and ASTM D 1238, respectively).

Table I Characteristics of polymer compositions tested

Designation	T_s °C	T_g °C	Basic polymer		Tackifier		Wax	
			EVAK-25	EVAK-400	HRR-2	ARR-9	V-5	
			%, wt.		Hydrogenation %	%, wt.	%, wt.	%, wt.
HM-VO-4	99	-7.3	15	15	70	53	0	17
HM-L-05-1	98	-	15	15	90	47	6	17
HM-L-05-2	100	-8.2	15	15	90	42	11	17
HM-L-05-3	100	-	15	15	90	37	16	17
HM-L-05-7	96	-9.7	15	15	90	46	7	17

Table II Characteristics of HMA components

Designation	Composition	Glass transition temp., T_g , °C	Softening point T_s , °C	Melt index $g (10 \text{ min})^{-1}$
EVAK-25	Polyethylene- vinylacetate copolymer	-15.8	119	25
EVAK-400	Polyethylene- vinylacetate copolymer	-18.1	85.7	400
HRR-2	Non-polar partly hydrogenated hydrocarbon resin	-	99	-
ARR-9	Hydrocarbon resins based on α - methylstyrene	-	100	-
V-5	Non-polar Fischer Tropsch wax	62.7	105	-

Rheological Measurements

The flow curves of melts of polymeric HM compositions and their components were measured in the dependence on temperature by employing the rotational rheometer (Haake MARS). The measurements were carried out in the temperature range of 120-180 °C using parallel plate geometry. The gap and diameter of the plates were 1 mm and 35 mm, respectively. For the determination of viscosity function $\eta = \eta(\dot{\gamma})$, the dependence of the shear stress τ vs. shear rate $\dot{\gamma}$ was measured (CR mode, up- and down-) in the shear rate interval from 0.1 to 200 s^{-1} [2,3].

Results and Discussion

Experimental Viscosity Data

Based on the flow curve measurements, the experimental dependences of shear viscosity $\eta = \tau / \dot{\gamma}$ on the shear rate $\dot{\gamma}$ were plotted for all the melts examined. It has been found that the course of viscosity functions is almost identical for all compositions. An example of viscosity functions obtained for HM-L-05-2 composition is shown in Fig. 1. The melts are slightly shear thinning and thixotropic fluids. Their viscosities, the degree of shear thinning, and thixotropy decrease all with the increasing temperature. Due to the content of the wax, the viscosity of the HM compositions is significantly lower than that of the basic EVAK components. The values of the viscosity η_0 measured at the shear rate $\dot{\gamma} = 0.1 \text{ s}^{-1}$ are given for HM compositions in Table III. It is evident that the different content of tackifying resins in the compositions practically does not affect the viscosity of melts.

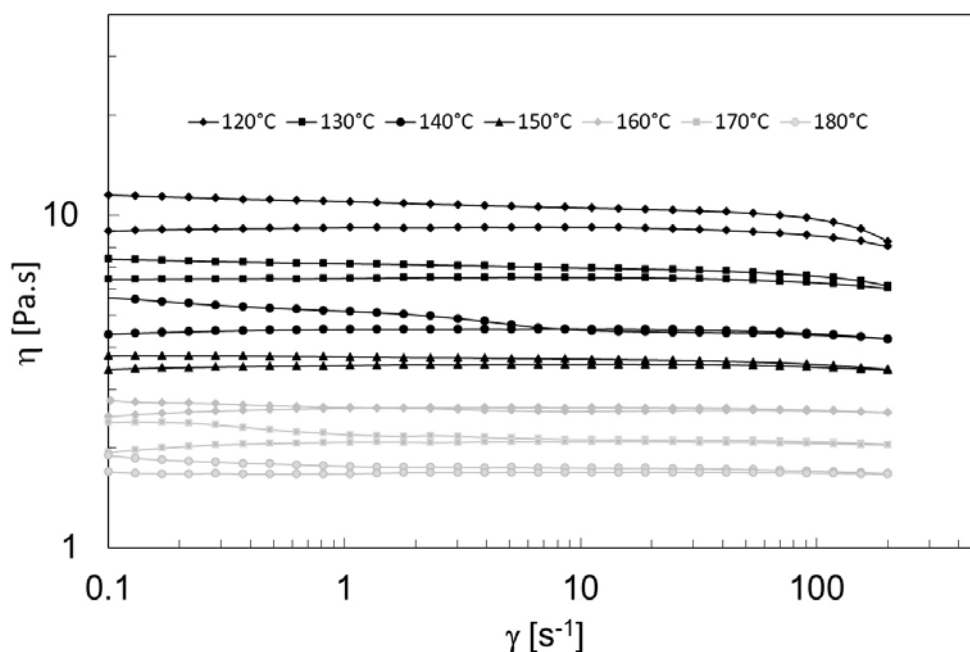


Fig. 1 Viscosity functions of HM-L-05-2 composition at various temperatures

Making use of the linear regression of dependences of quantity $\ln \eta_0$ on $1/T_a$, and based on the Arrhenius type equation

$$\eta = Ae^{\frac{E_a}{RT_a}} \quad (1)$$

the viscosity activation energy E_a was evaluated for the individual composition melts. An example of such dependence is for the composition HM-L-05-2 shown in Fig. 2. The resulting values E_a are summarized in Table III.

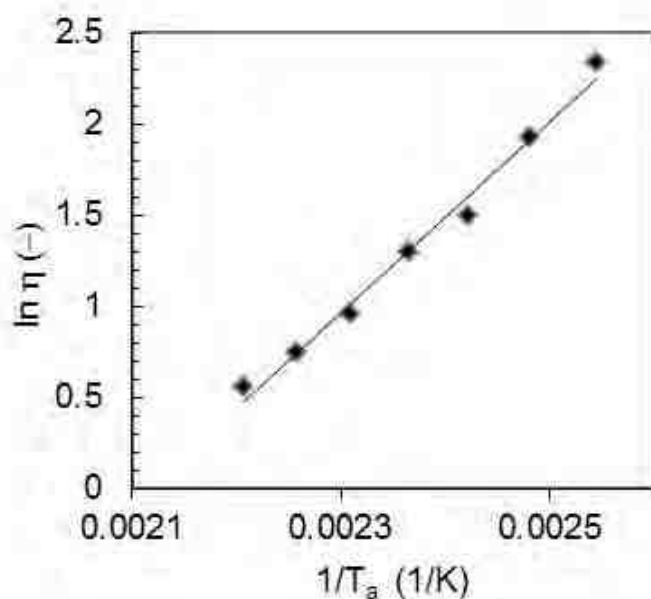


Fig. 2 Dependence of $\ln \eta$ on $1/T_a$ for composition HM-L-05-2

Table III Viscosity η_0 of HM compositions tested

T °C	η_0 , Pa s				
	HM-VO-4	HM-L-05-1	HM-L-05-2	HM-L-05-3	HM-L-05-7
120	9.77	10.6	10.3	11.2	10.3
130	6.55	6.64	6.83	7.43	6.82
140	4.63	4.53	4.47	4.97	4.00
150	3.32	3.23	3.67	3.62	3.30
160	2.44	2.39	2.59	2.62	2.09
170	1.81	1.93	2.11	2.05	1.94
180	1.43	1.47	1.74	1.53	1.47
E_a , J mol ⁻¹	47 570	47 985	43 716	48 711	47 877

Viscosity Prediction

Even though the rheological behaviour of polymer compositions is complex in nature, we have tried to predict their viscosity, supposing that there is a Newtonian behaviour ($\eta = \eta_0$) and by using relatively simple blending models. A number of

mixing models have been proposed in the literature (see, e.g., Ref. [4]) for the viscosity prediction of liquid blends. The respective models for polymer blends are unfortunately predominantly limited to the two-component blends (see Ref. [4]). A simple model suitable for multi-component mixtures is the log additive model defined as

$$\ln \eta_B = \sum_i x_i \eta_i \quad (2)$$

where x_i is the mass fraction and η_i the viscosity of the components. This model has been often employed for the prediction of viscosities of homologous polymer blends [6]. However, in blend systems, there are serious deviations from the log additive model. Utracki [6] classified such non-ideal blends as negative, positive, or mixed, according to whether or not the blend viscosity is lesser than that calculated from Eq.(2). In this case, the log additive model is supplemented by a viscosity excess function [7] so that one has

$$\ln \eta_B = \sum_i x_i \eta_i \pm (\ln \eta)_{exc} \quad (3)$$

Other models proposed for the viscosity prediction of multicomponent blends are those being based on the calculation of the viscosity blending index VBI_i of each component. The Refutas method [4] employs the following relations

$$VB_i = 10.975 + 14.535 \ln \ln (v_i + 0.8) \quad (4)$$

$$VBI_B = \sum_i x_i VBI_i \quad (5)$$

and the resulting viscosity of the blend is given as

$$v_i = \exp \left[\exp \left(\frac{VBI_B - 10.975}{14.534} \right) \right] - 0.8 \quad (6)$$

Here v_i is the kinematic viscosity of each component in cSt. In the Chevron modification of the Refutas method [4] the VBI indexes are given can be formulated as

$$VBI_i = \frac{\ln v_i}{\ln 1000 v_i} \quad (7)$$

and

$$VBI_B = \sum_i VBI_i y_i \quad (8)$$

where y_i is the volume fraction of each component. Then, one can write

$$v_B = \exp\left(\frac{\ln 1000 V B I_B}{1 - V B I_B}\right) \quad (9)$$

The above-mentioned blending models were tested for the prediction of the viscosity η_0 of HM compositions from the data given in Tables I and IV. In the respective calculations, the value of melt density $\rho = 950 \text{ kg m}^{-3}$ was used for all components. The results of the prediction of composition viscosities according to Eq. (3) are summarised in Table V, according to Eq. (6) in Table VI, and according to Eq. (9) in Table VII in the left columns.

Table IV Viscosity of the additional components and polymer compositions

T °C	η_0 , Pa s				
	EVAK-25	EVAK-400	HRR-2	ARR-9	V-5
120	10 225*	190*	120	53.2	0.0131
140	4 950*	95.5*	11.2	8.20	0.0086
160	1 750	48.8	1.45	0.87	0.0065
180	811	29.6	0.25	0.379	0.0050

* values calculated using Eq. (1)

By comparing the viscosity data calculated with the experimental values (see Table III), it is evident that their agreement is only qualitative and the magnitude of deviations between experimental and calculated viscosity data depends on the temperature of the melted composition.

In the case of the log additive model, these deviations are negative in a temperature interval from 120 to 160 °C and their magnitude is decreasing. The value of the mean relative deviation

$$\delta_m = \frac{1}{5} \sum_{i=1}^5 \frac{\eta_{\text{exp},i} - \eta_{\text{cal},i}}{\eta_{\text{exp},i}} \times 100 \quad (10)$$

at 160 °C is -12% and at 180 °C the deviation, δ_m , is already positive, achieving the value of $+39 \%$.

The Refutas and Chevrons models yield almost the same results of the viscosity prediction. The deviations, δ_m , at 120 °C are negative and their values are about -33% . From 140 °C to 180 °C the deviations, δ_m , are positive and their

Table V Viscosity calculated according to the log additive blending model

T °C	η_0 , Pa s					
	HM-VO-4		HM-L-05-1		HM-L-05-2	
	(2)	(11)	(2)	(11)	(2)	(11)
120	53.1	10.9	50.6	10.4	48.6	10.0
140	11.4	4.87	11.2	4.78	11.0	4.70
160	2.83	2.39	2.74	2.32	2.67	2.26
180	0.885	1.41	0.953	1.52	0.926	1.47

T °C	η_0 , Pa s			
	HM-L-05-3		HM-L-05-7	
	(2)	(11)	(2)	(11)
120	46.6	9.60	50.1	10.3
140	10.8	4.63	11.1	4.76
160	2.61	2.21	2.73	2.31
180	0.946	1.50	0.911	1.45

magnitudes are increasing from 25 % to 39 %.

Better agreement between experimental and calculated viscosity data can be achieved after correction of calculated blend viscosities $\eta_{B,cal}$ by an experimental function of temperature. Then,

$$\eta_B = \eta_{B,cal} f(T) \quad (11)$$

The corrective functions were sought in the form of a polynomial of degree two by minimisation of deviations of experimental and calculated viscosities. Using this approach, the respective functions $f(T)$ are as follows

$$\text{log additive model} \quad \ln f(T) = 6.313 \times 10^{-5} T^2 + 5.301 \times 10^{-2} T - 7.032 \quad (12)$$

$$\text{Refutas model} \quad f(T) = 1.045 \times 10^{-3} T^2 - 2.456 \times 10^{-1} T + 15.24 \quad (13)$$

$$\text{Chevron modification} \quad f(T) = 9.40 \times 10^{-4} T^2 - 2.223 \times 10^{-1} T + 13.95 \quad (14)$$

The results of viscosity calculated according to the corresponding corrected models (11) are also given in Tables V-VII. In all these cases, the magnitude of the relative deviation, δ_m , between all experimental and the calculated viscosities is about 8 %.

Table VI Viscosity calculated according to Refutas blending model

T °C	η_0 , Pa s					
	HM-VO-4		HM-L-05-1		HM-L-05-2	
	(6)	(11)	(6)	(11)	(6)	(11)
120	14.6	11.8	14.1	11.3	13.6	10.9
140	3.46	4.60	3.40	4.49	3.35	4.43
160	0.956	2.55	0.929	2.48	0.906	2.42
180	0.305	1.48	0.313	1.52	0.320	1.56

T °C	η_0 , Pa s			
	HM-L-05-3		HM-L-05-7	
	(6)	(11)	(6)	(11)
120	13.1	10.5	14.0	11.2
140	3.31	4.37	3.39	4.48
160	0.884	2.36	0.924	2.47
180	0.326	1.59	0.314	1.53

Table VII Viscosity calculated according to Chevron blending model

T °C	η_0 , Pa s					
	HM-VO-4		HM-L-05-1		HM-L-05-2	
	(9)	(11)	(9)	(11)	(9)	(11)
120	14.0	11.5	13.4	11.1	13.0	10.7
140	3.57	4.53	3.51	4.46	3.46	4.40
160	1.04	2.55	0.996	2.46	0.982	2.40
180	0.334	1.50	0.343	1.52	0.358	1.55

T °C	η_0 , Pa s			
	HM-L-05-3		HM-L-05-7	
	(9)	(11)	(9)	(11)
120	12.6	10.4	13.3	11.7
140	3.41	4.34	3.50	4.45
160	0.948	2.34	1.00	2.46
180	0.361	0.56	0.348	1.54

Conclusion

The shear viscosities of five HM hot melt adhesives were measured in the dependence on the temperature using a Haake MARS rheometer. It has been ascertained that all the melts tested behave as slightly shear thinning and thixotropic fluids. Their viscosities, degree of shear thinning, and thixotropy decrease with the increasing temperature. Due to the wax content, the viscosity of the HM compositions is significantly lower than that of the basic EVAK components.

The accuracy of log additive, Refutas, and Chevron blending models has been examined for the prediction of viscosity of HM adhesives tested. Comparing the calculated viscosity data with the experimental ones, it has been found that agreement is only qualitative. The magnitude of deviations between the experimental and calculated viscosities depend on the temperature. At the same time, the Refutas and Chevron models have yielded almost the same results of the viscosity prediction. Finally, by minimising the deviations between experimental and calculated data, the temperature corrections of blending models have been evaluated for a more precise viscosity prediction.

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Symbols

A	pre-exponential factor, Pa s
E_a	viscosity activation energy, J mol ⁻¹
R	universal gas constant, J mol ⁻¹ K ⁻¹
T	temperature, °C
T_a	absolute temperature, °K
T_g	glass transition temperature, °C
T_S	softening point, °C
t	time, s
x_i	mass fraction
y_i	volume fraction
$\dot{\gamma}$	shear rate, s ⁻¹
δ_m	mean relative deviation, Eq. (10), %
η	shear viscosity, Pa s
η_0	zero shear rate viscosity, Pa s

ν kinematic viscosity, cSt
 τ shear stress, Pa

Subscripts

B related to blend
cal calculated value
exp experimental value
i related to component
max maximum value

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