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RHEOLOGICAL CHARACTERIZATION OF EVAK COMPONENTS FOR HOT MELT ADHESIVES FORMULATION

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For formulation of hot melt adhesives, ethylene-vinyl acetate copolymers (EVAK) are most commonly used. In this paper, the results of measurements of mechanical and rheological properties of three EVAK components of various melt indexes are presented. These properties were studied under the steady shear and dynamic conditions using a DMA analyser and a Haake MARS rheometer. From the DMA experimental data, the glass transition temperatures of EVAK components were determined. On the rheometer MARS, the measurements of flow curves, primary normal stress differences, oscillatory and creep & recovery tests of melted samples were performed.

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Introduction

Adhesive bonding has gained more importance during the past decades, especially in high-tech applications. At the same time, adhesive joints often replace the classical joining procedures like welding or screwing [1,2].

An important group of adhesives are hot melt ones (hot melts) which are used in particular for speeding-up of production and for ecological reasons. They are employed in industrial applications (e.g., Refs [2-4]) as are, for example, construction, air craft and vehicles construction, product assembly, packaging, box and carton heat sealing, bookbinding, non-rigid bonding of fabrics, laminating processes, *etc*. Conventional nonreactive hot melt adhesives are available in an array of chemical types based on different polymers. The significant primary polymers used to formulate hot melt adhesives are ethylene — vinyl acetate copolymers (EVAK) [2]. For the optimal production technology of hot melt compositions and also for optimal processing of final hot melts, it is necessary to know the rheological behavior of molten materials in terms of production and application conditions (e.g., Ref. [5]).

In this contribution, the results are presented of measurements of the rheological behaviour of three EVAK components, designated as EVAK-25, EVAK-150, and EVAK-400, differing by their melt index. The steady shear and dynamic properties were measured using a Haake MARS rheometer and a DMA analyser.

Experimental

Materials

The polymeric components tested were prepared in Synpo a.s. for hot melt adhesive formulations. Their characteristics are given in Table I. The values of the glass transition temperature T_g were determined from DMA measurements (standard ČSN EN ISO 6721-7). The softening point was determined using a ring-and-ball method (standard ČSN EN 1427), the activation energy was evaluated from the dependence of the viscosity η_0 on the temperature, and the melt index was determined according to the standard ASTM D 1238.

Rheological Measurements

The rheological properties of the samples of polymeric EVAK components were examined using both a DMA analyser and a rotational rheometer (Haake MARS, Thermo Scientific). During DMA tests, the storage modulus G' and loss modulus G'' were measured in the dependence on the temperature at the frequency of 1 Hz.

The testing temperatures were in the range of –50-80 °C. On the rheometer MARS, the measurements of flow curves, primary normal stress differences, oscillatory, and creep & recovery tests of melted samples were carried out from the polymer melting point up to 180 ºC using parallel plate geometry. The gap and diameter of the plates were 1 mm and 35 mm, respectively.

For the determination of viscosity functions, the dependence of the shear stress vs. shear rate was measured. The measurements were performed in the control rate mode (CR mode) up-and-down in the shear rate interval from 0.01 to 100 s^{-1}. Simultaneously with the measurement of the flow curve, the primary normal stress difference N_1 was measured. For checking the limit of linear elasticity range, the stress amplitude sweeps were performed from 0.01 to 20 Pa at a fixed frequency of 1 Hz. Next, the frequency sweeps and creep & recovery tests were measured. The frequency sweeps were carried out from 0.01 to 100 Hz at the fixed stress of 0.1 Pa. The creep & recovery tests were performed at the fixed stress of 0.1 Pa, time of duration of the both creep and recovery phases was 120 s.

Results

The examples of the course of the dependences of the moduli G' and G'', and the loss tangent $\tan\delta = G''/G'$ on the temperature for components EVAK-25 and EVAK-400 are shown in Fig. 1. These dependences are in very good accordance with those measured by authors [6] for EVA-based hot-melt adhesives. It is evident that the measured material characteristics do not depend significantly on the melt index. The storage modulus curves for all EVAK components exhibit three obvious regions: glassy, transition and rubbery. From the *x*-coordinate of the point of the local maximum of the dependence of the loss tangent on the temperature, the glass transition temperatures, T_g, were determined. Their values are given in Table I.

For the evaluation of viscosity function courses, the experimental dependences of shear viscosity $\eta = \tau/\dot{\gamma}$ on the shear rate $\dot{\gamma}$ were plotted for all melts tested. The obtained viscosity functions are shown in Fig. 2. The melts have a constant viscosity at low shear rates; at the higher values ($\dot{\gamma}$ > 1-10 s^{-1}) they behave as shear thinning fluids. The hysteresis of viscosity function courses indicates a thixotropic behaviour of the melts. The melt viscosities, degree of shear thinning, and thixotropy decrease along with the increasing values of the melt index and temperature. The courses of the upper parts of viscosity functions were approximated by the three-parameter Carreau viscosity model

$$\eta = \eta_0\left[1 + (\lambda\dot{\gamma})^2\right]^{\frac{m-1}{2}} \quad (1)$$

Examples of values of the model parameters obtained at the temperature of 160 °C for the individual EVAK components are given in Table II.

Distinctive values of the primary normal stress differences, N_1, were recorded only in the case of the component EVAK-25.

In order to obtain more detailed information on the adhesive application behaviour, the frequency dependences of material functions for a small amplitude oscillatory shear flow (storage modulus G', loss modulus G'', complex viscosity η^*) were evaluated. Figure 3 shows the results of the oscillatory tests on the polymer melt EVAK-400 at the temperatures of 140 ºC and 180 ºC.

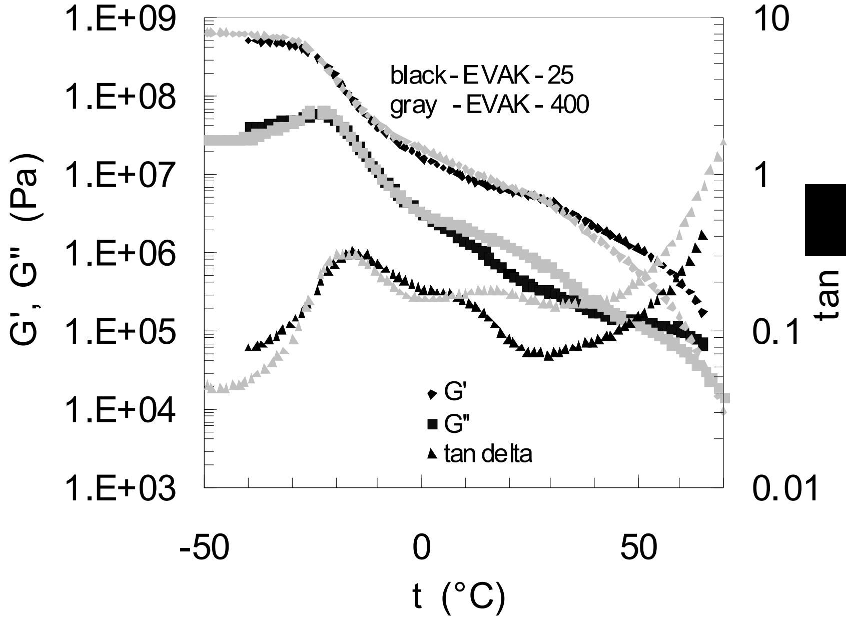


Fig. 1 Dependences of the moduli *G'* and *G''*, and the loss tangent tan δ on temperature measured at oscillation frequency of 1 Hz for polymer components EVAK-25 and EVAK-400

Table I Characteristics of polymer components tested

Polymer	Composition	Glass trans. temperatur e °C	Softening point °C	Activation energy of the flow J mol^{-1}	Melt index g/10 min
EVAK-25	Ethylene−vinyl-acetate copolymer	–15.8	118	61723	25
EVAK-150	Ethylene−vinyl-acetate copolymer	–15.4	89.5	40266	150
EVAK-400	Ethylene−vinyl-acetate copolymer	–18.1	85.7	46267	400

Table II Parameters of the Carreau viscosity model at 160°C

Polymer	η_0 Pa s	λ s	m
EVAK-25	1750	0.333	0.277
EVAK-150	167	0.038	0.020
EVAK-400	48.8	0.020	0.340

Table III Characteristics of the creep and recovery tests

Polymer	Temperature, °C	η_0, Pa s	γ_r	γ_r/γ_{max}, %
EVAK-25	160	1526	0.000354	6.2
	170	0.1441	0.000575	6.4
	180	0.08392	–0.00088	–5.9
EVAK–150	150	215.2	0.00196	3.8
	160	162.7	0	0
	170	112.4	0.00073	0.8
	180	82.8	0	0
EVAK–400	140	94.8	–0.002	–1.6
	150	67.9	0	0
	160	51.8	0.004	1.6
	170	36.3	– 0.002	–0.63
	180	27.0	–0.00368	–8.0

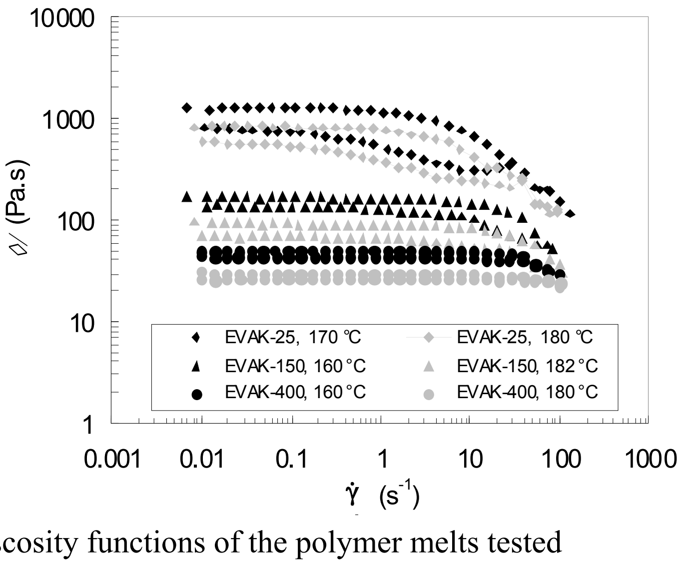
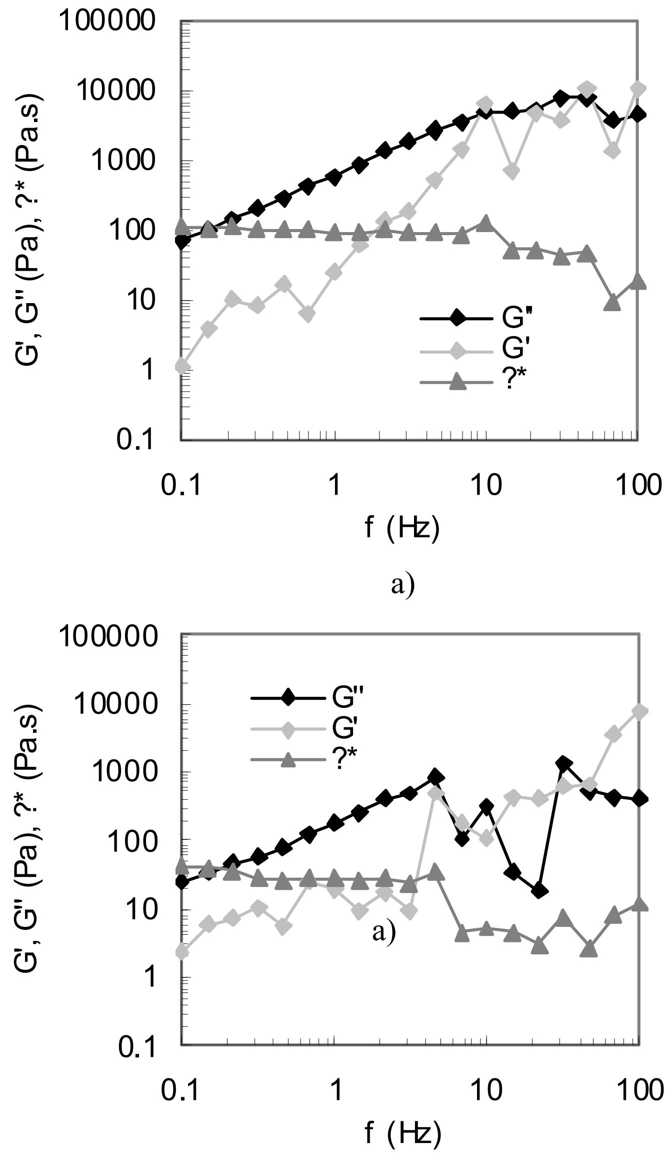


Fig. 2 Viscosity functions of the polymer melts tested



b)

Fig. 3 Frequency sweeps for polymer component EVAK-400 at the temperatures of 140 ºC (a) and 180 ºC (b)

Comparing the results of the dynamic tests, a qualitatively similar behaviour of all three polymer component melts was observed. The data displayed in Figs 3 show a clear dependence of the moduli G' and G'' on frequency. At the same time, the loss modulus prevails at low values of frequency. Along with the increasing frequency, the value of G' increases faster in comparison with that of G'' and, in the dependence on the polymer type, the cross-over of the both material functions occurs. The data scattering observed for f > 5-10 Hz is probably caused by instability of the torsional flow (e.g., Ref. [7]).

From the course of creep and recovery tests, the values of the zero shear rate viscosity η_0, maximum strain γ_{max}, reached at the end of the creep phase, and the recoverable strain γ_r, reached at the end of the recovery phase, were evaluated.

These values are summarized in Table III. The results obtained are in a good accordance with measurements of flow curves and dynamic tests. The values of η_0 correspond with the shear viscosity η_0 evaluated from the flow curve measurements (Table II); low values of the ratio γ_r/γ_{max} document that the polymer melts exhibit only insignificant degree of linear elasticity at the measurement conditions.

Conclusion

The mechanical and rheological properties of three EVAK polymer components for hot melt adhesives were measured under the steady shear and dynamic conditions using a DMA analyser and a Haake MARS rheometer.

In accordance with literature data, it was observed that the glass transition temperature evaluated from the DMA tests does not significantly depend on the melt index of the examined EVAK components.

All the melts tested behave as shear thinning and thixotropic fluids. It was found that the viscosity, degree of shear thinning, and thixotropy decrease with the increasing melt index and temperature. Distinctive values of the primary normal stress differences N_1 were recorded only in the case of the component EVAK-25.

From the oscillatory tests, the storage modulus G', loss modulus G'', and complex viscosity η^* were evaluated. At lower values of frequency, loss modulus prevails, which predicates that the wetting and adhesive flows can be sufficient to form a good contact with the substrate. Along with the increasing frequency, the value of G' increases faster in comparison with that of G'' and the shear resistance heightens.

The results of creep and recovery tests document that the polymer melts exhibit only insignificant degree of linear elasticity at the measurement conditions.

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Symbols

f frequency, Hz
G' storage modulus, Pa
G'' loss modulus, Pa
m Carreau model parameter

N_1 primary normal stress difference, Pa
n power law flow index
T_g glass transition temperature, °C
t time, s
γ strain
γ_r recoverable strain
λ time parameter of Carreau model, s
$\dot{\gamma}$ shear rate, s^{-1}
η viscosity, Pa s
η_0 zero shear rate viscosity, Carreau model parameter, Pa s
η^* magnitude of complex viskosity, Pa s

Subscripts

max maximum value

References

[1] Patrick R.L.: *Treatise on Adhesion and Adhesives*, Vol. 1-3, Marcel Dekker, N.Y., 1967.
[2] Pocius A.V.: *Adhesion and Adhesives Technology*, Hansher Publisher, New York, 1997.
[3] Lidická I., Balcar M.: XIV. International Conference Adhesives in Woodworking Industry, Vinné, Slovakia, 1999.
[4] Balcar M.: Print & Publishing, **34**/97, 58 (1997).
[5] Lee L. H. (ed.): *Adhesive Bonding,* Plenum Press, New York, 1990.
[6] Park Y.J., Joo H.S., Kim H.J., Lee Y.K.: Int. J. Adhes. Adhes. **26**, 571 (2006).
[7] Tanner R.I., Walters K.: *Rheology: An Historical Perspective*, Elsevier, Amsterdam, 1998.