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Linear Flexible-Chain Polymer Electrification Conditions and Pattern at $T > T_G$

V. E. Dreval, V. P. Protasov and G. V. Vinogradov

Institute of Petrochemical Synthesis, USSR Academy of Sciences, SU-117912, GSP-1, Moscow, V-71, USSR

SUMMARY

A study has been made concerning the static electrification of such linear flexible-chain polymers as polybutadiene, polyisoprene, and fluorine rubber with wide and narrow molecular-weight distributions at $T > T_g$. It has been found that static electrification occurs as a result of a relaxation transition of polymers from the fluid to high-elastic state, accompanied by breakdown of the specimens and their detachment from the walls confining the flow, which leads to slippage of the polymers. This phenomenon is explained in terms of the activation theory of polymer friction. The dependence of static electrification on temperature, molecular weight, and molecular-weight distribution is determined by the effect of these parameters on the relaxation characteristics of a polymer, and, more particularly, its segmental mobility.

INTRODUCTION

The process of static electrification of natural rubber has been known for more than a century ever since it started to be processed on roll mills. The static electrification of polymer materials has been extensively investigated. A wealth of experimental data and facts have been summarized and systematized in some monographs (LOEB 1958, SAZHIN at al. 1970, SAZHIN 1977, OHARA 1979, VASILENOK 1981) treating the nature of the process and its dependence on various factors from different points of view. However, no one has been able so far to establish a relationship between the static electrification process, straining conditions, and such important parameters of polymers as the initial viscosity, dissipation loss modulus, and others.

As was observed by VINOGRADOV (1971), the static electrification of polymers in the fluid state is initiated by the "spurt" that is by jumpwise increase of flow rate (VINOGRADOV 1973) while in another work (OHARA 1979) it was found that the mobility of the macromolecular segments involved in friction contributes to the static electrification process.

EXPERIMENTAL

In the present work, the static electrification of polymers was studied using an experimental setup built around a constant-pressure capillary viscometer CPCV (VINOGRADOV AND PROZOROVSKAYA 1964). The polymer jet emerging from a capillary passed along the longitudinal axis of a measuring capacitor comprising two coaxially arranged and mutually insulated cylinders. The internal cylinder was connected to an electrometric voltmeter, whereas the external one and the rest of setup components, including the metal capillary, were grounded. Cylindrical steel capillaries were used in the experiments, and duct surface was polished. Taking into account the electrostatic interaction between individual parts of the experimental setup it was possible to evaluate the surface electric charge density (σ) on the polymer starting from the value of the potential induced at the internal cylinder of the capacitor by the polymer jet (the latter being as long as the capacitor) and the mass of the jet. Since the static electrification took place in the capillary, the effect of the ambient air humidity on static electrification was eliminated. The coefficient of variation of σ was about ± 12% at a 95% reliability of the results.

The experiments were carried out on 1,4-polybutadienes (PB) obtained by anionic polymerization with narrow and wide molecular weight distributions (MWD), as well as on 1,4-polyisoprene (PI) and fluorine rubber SKF-32.

RESULTS AND DISCUSSION

The results obtained when the polymers were squeezed through steel capillaries indicated that no electric charges are present on the jet surface in the case of laminar flow of the polymer. As soon as the critical shear stress was attained, a spurt occurs (VINOGRADOV 1973) and a smooth portion of the emerging polymer jet, equal in size to the capillary, was obtained. The smooth portion was immediately followed by an irregular jet, marking the onset of supercritical polymer flow. The spurt is due to an isothermal transition of the flowing polymer to the high-elastic (rubbery) state in which the flow inside the jet ceases, and the polymer starts slipping over the duct walls. On the surface of the smooth portion of all examined polymers a negative charge was observed, which agrees well with Deryagin's theory (DERYAGIN at al. 1973) and corroborates the fact that we are dealing with the spurt of the polymer adhering to the duct walls.

Concerning the jet portion following the smooth one, the conditions of its contact with the capillary are radically different from those observed in the case of the smooth portion. The supercritical flow (when the polymer flow rate through the duct exceeds the critical one during the spurt) is characterized by external friction of the polymer. In this case, the jet surface may carry a negative (fluorine rubber SKF-32) as well as positive (PB, PI) charge, depending on the electrophilic properties of the polymer. It was also observed that electric current flows through the insulated capillary with PB. Thus, PB gives up electrons to the metal capillary whilst itself becoming positively charged. The nature of the positive charge on PB and PI remains unknown.

Let us now quantify the static electrification process involving PB with a molecular weight $M_w = 2.6 \cdot 10^5$ at a capillary diameter of 1 mm and a temperature of 20°C. The quantitative data are represented in Figs. 1 and 2. Considering first the effect of the capillary length on the static electrification process (Fig.1) it can be seen that the charge density on the polymer surface increases with the capillary length (i.e. path of friction).

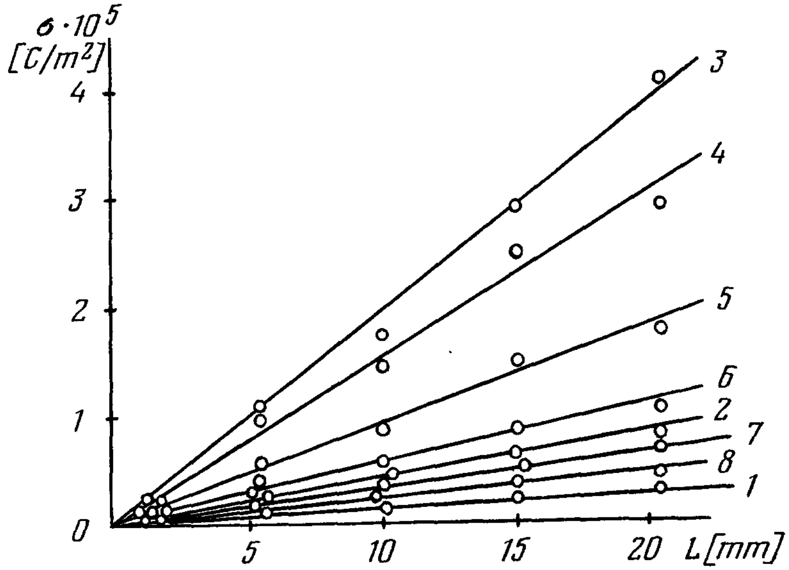

Fig.1. Surface charge density (σ) versus capillary length (L) at 20°C for PB with narrow MWD and $M_w = 2.6 \cdot 10^5$ at different slippage speeds (log V, m/s): -2.2 (1);-2.1(2); -2.0(3);-1.8(4);-1.6(5);-1.4(6);-1.2(7);-1.0(8).

As can be inferred from extrapolation of σ to zero length of the capillary, the static electrification of polymers begins at the capillary entrance. It should be pointed out that the surface charge density at predetermined slippage speeds and at a constant capillary length is independent of the capillary diameter, which suggests that the static electrification of polymers in capillaries is a surface phenomenon.

The relationship between static electrification and polymer slippage speed (Fig.2a) shows a maximum on the $\sigma = f(V)$ curve. Since static electrification is observed during supercritical polymer flow when external friction along the duct wall occurs, it is worthwhile to review also the data concerning the friction of cured rubbers against smooth metal surfaces. Fig.2b shows the force of friction versus slippage speed, according to LUDEMA and TABOR (1966).

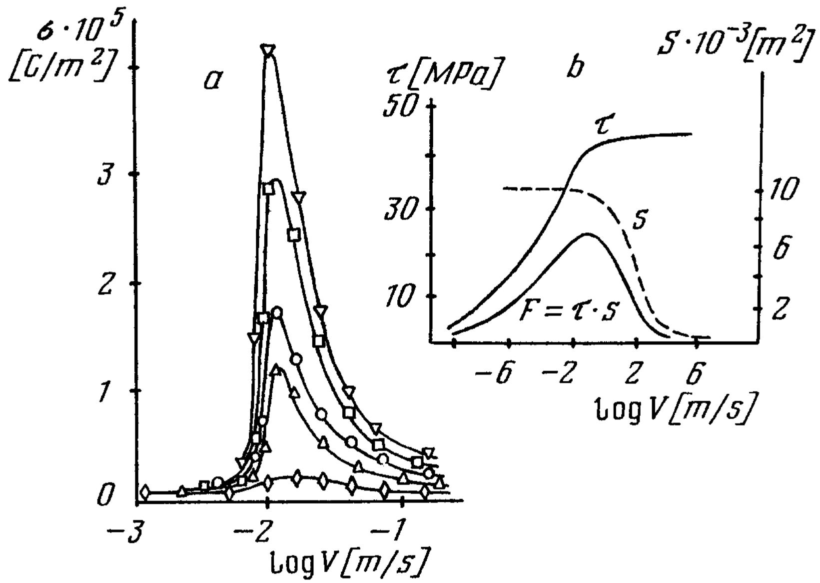

Fig.2 (a) Surface charge density versus slippage speed at 20°C for PB with narrow MWD and $M_w = 2.6 \cdot 10^5$ at different capillary lengths (L,mm): ◇-1.2; △-5.4; o -9.9; □ -15.0; ▽-20.4. (b) Force of friction versus slippage speed for cured rubber. τ - shear stress; S - actual contact area.

Comparing the above data, it becomes evident that the static electrification process is determined by external friction and can be qualitatively represented by the same relations as external friction insofar as the effect of the relaxation characteristics of polymers on these processes, more particularly their segmental mobility, is concerned. Indeed, the decrease in the force of friction and static electrification, starting from a certain value of the slippage speed, is due to the shorter time of contact between the polymer chain segments and the metal surface, which is equivalent to a reduction in the actual contact area (LUDEMA AND TABOR 1966).

It is also evident that the dependence of static electrification on the slippage speed is more pronounced than the dependence of the force of friction on the latter. According to BARTENEV and LAVRENTYEV (1972), the nonuniformity of the cured rubber network and the pronounced effect of the macromolecular chain ends not tied into the network (this effect becomes still more pronounced with decreasing molecular weight of the polymer and widening MWD of the latter) make the friction of the cured rubbers against metal less dependent on the slippage speed than that of a polymer with a uniform network. The data concerning the effect of the polymer molecular weight and MWD on static electrification (Fig.3) corroborate the viewpoint expressed by the authors of the above-cited work.

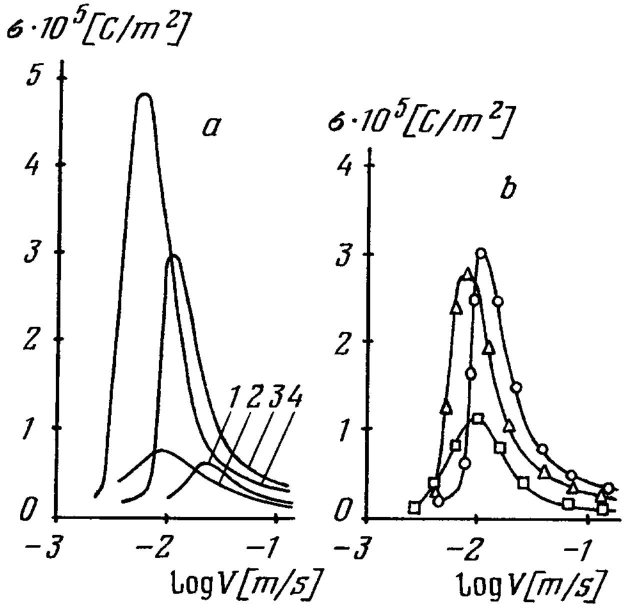

Fig.3 Surface charge density versus slippage speed at 20°C and capillary length L = 15.0 mm for PB: (a) with narrow MWD and M_w: 1-1.10·10^5; 2-2.0·10^5; 3-2.6·10^5; 4-3.2·10^5. (b) with M_w = 2.6·10^5 and M_w/M_n = 1.15 (o); M_w = 2.7·10^5 and M_w/M_n = 1.44 (△); M_w = 2.6·105 and M_w/M_n = 2.73 (□).

Static electrification becomes more pronounced with increasing molecular weight of the polymer. The basic differences in the high-elastic state of polymers with different molecular weights are determined by the values of the dissipation loss modulus. The minimal dissipation loss corresponds to the most perfect polymer chain entanglement network, when the amount of the energy irrevocably dissipated throughout the polymer is minimal, hence the amount of static electricity is maximal.

A rise in temperature shifts the $\sigma = f(V)$ curve toward greater slippage speed values. In this case, the shape and magnitude of the curve remain unaffected, whilst the amount of shift is numerically equivalent to the change in the initial polymer viscosity with increasing temperature. The generalized curve showing the relationship between static electrification and the slippage speed at 20°C is represented in Fig.4.

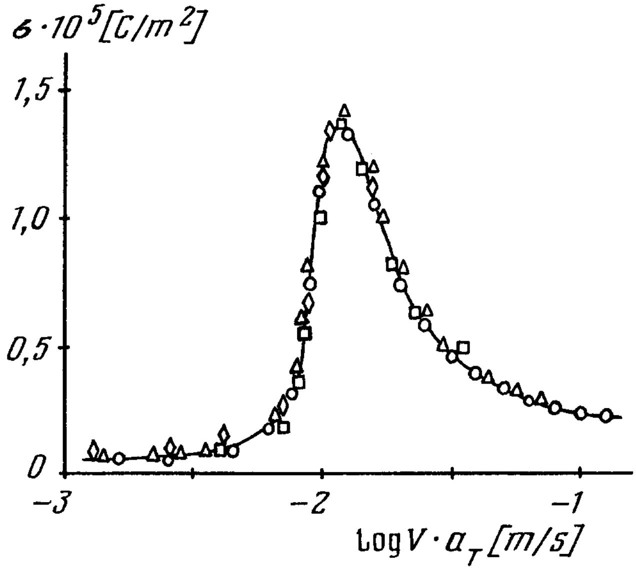

Fig.4 Generalized curve showing surface charge density versus slippage speed for PB with narrow MWD and $M_w = 2.6 \cdot 10^5$ reduced to 20°C. Capillary length: 5.4 mm. Temperatures, °C: o – 20; △ – 40; □ – 60; ◇ – 80.

The activation energy of the static electrification process was found equal to 33 kJ/mole, which approaches that of viscous flow in the case of PB (31 to 33 kJ/mole). This is another proof that static electrification is determined by the mobility of polymer chain segments and suggests a close relationship between this process and friction.

CONCLUSIONS

The herein established relationship between static electrification and such basic polymer parameters as molecular weight, MWD and initial viscosity permits selecting such condition under which the static electrification may be minimal and produce no adverse effect on processing.

REFERENCES

BARTENEV G.M. and LAVRENTYEV V.V.: Friction and Wear of Polymers, Leningrad: Khimiya 1972 (In Russian).

DERYAGIN B.V., KROTOVA N.A. and SMILGA V.P.: The Adhesion of Solids, Moscow: Nauka 1973 (in Russian).

LOEB L.B.: Static Electrification, Berlin: Springer 1958.

LUDEMA K.C. and TABOR D.: Wear No.2, 329 (1966).

OHARA K.: Electrostatics 1979, Invit. and Contrib. Pap., 5th Conf. Electrostat. Phenom., Oxford, 1979, Bristol-London, 257, (1979).

SAZHIN B.I., LOBANOV A.M., EIDELNANT M.P., KOIKOV S.N., ROMANOVSKAYA O.S.: Electrical Properties of Polymers, Leningrad: Khimiya 1970 (in Russian).

SAZHIN B.I. (editor): Static Electricity in the Chemical Industry, 2nd edition, Leningrad: Khimiya 1977 (in Russian).

VASILENOK Yu.I.: Prevention of Static Electrification of Polymers, Leningrad: Khimiya 1981 (in Russian).

VINOGRADOV G.V. and PROZOROVSKAYA N.V.: Plasticheskie massy, No.5, 50 (1964).

VINOGRADOV G.V.: Pure and Appl.Chem., 26, 423 (1971).

VINOGRADOV G.V.: Rheol. Acta, 12, 157 (1973).

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