

# Destruction of ultrahigh conductivity of oxidized polypropylene by critical current

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The passage of a current is observed to sharply reduce the electrical resistance of conducting channels in oxidized polypropylene. The resistance falls to a value lower than can be measured. As the current is increased further, the superconducting state is destroyed at a critical value  $j_c \geq 10^8$  A/cm<sup>2</sup>. Lower limits are estimated for the local conductivity,  $\sigma \geq 10^{11}$  S/cm, and the critical temperature,  $T_c > 700$  K.

The superconductivity at  $\sim 300$  K of oxidized polypropylene, which was suggested in Refs. 1 and 2 and also in some subsequent studies,<sup>3,4</sup> is a consequence of one-dimensional channels.<sup>1,4</sup> Previous attempts to measure the conductivity  $\sigma$  and superconductivity critical parameters  $j_c$  and  $T_c$  of these channels have not been successful. This letter reports some experiments carried out to evaluate these properties. The test samples were polypropylene films with a thickness  $h \approx 30$   $\mu\text{m}$  synthesized on copper by the technique of Refs. 1 and 2. As a result of this synthesis, conducting channels appeared in the polypropylene, distributed in a statistical way over the volume of this polymer.<sup>3</sup> The apparatus of Ref. 5 made it possible to position the tip of a copper microprobe of diameter  $D \approx 10$   $\mu\text{m}$  by means of a micromanipulator at an arbitrary point on the surface of the polypropylene. This procedure and all the subsequent measurements were carried out during continuous observation through a microscope,

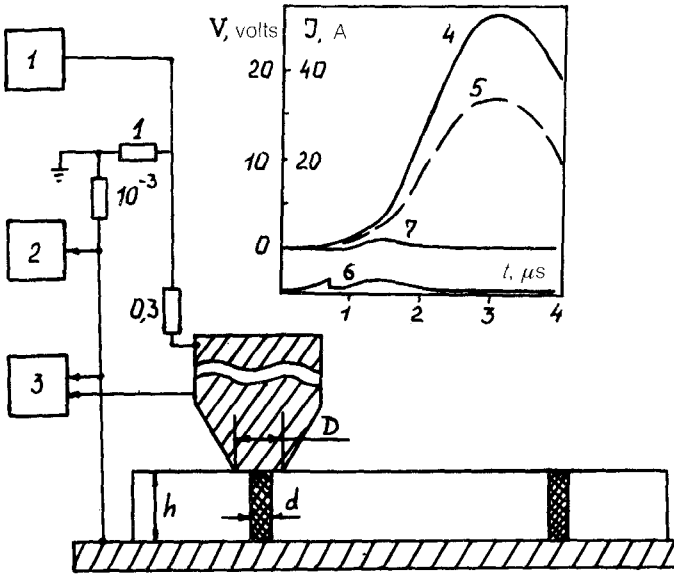


FIG. 1. Layout for measuring the critical current in the superconducting channels of polypropylene (the cross-hatching) by means of copper electrodes (the oblique hatching). 1—Source of the sum of the constant and pulsed voltages (a current up to 300 A in a 0.3 —  $\Omega$  load); 2—Shch 301/3 microvoltmeter for measuring the dc conductivity; 3—S8-14 storage oscilloscope. The resistances are given in ohms. The inset shows oscilloscope traces of the pulses for  $J(t) < J_c$ . 4) Output voltage from the source; 5) current through a channel; 6) voltage at the probe-polypropylene contact in the case of single pulses; 7) the same, for a pulse repetition frequency of 25 Hz. Curve 6 begins at a zero voltage; it has been shifted downward for clarity.

so we could be certain that the polypropylene layer *was* never punctured and that the probe was never short-circuited to the substrate. If insulating properties were exhibited at a given point on the polypropylene, the probe was moved to a different point. This procedure was continued until we were able to position the probe at a conducting channel running all the way through the film. At this time, a weak current,  $\sim 10$  mA, began to flow through the circuit and made it possible to measure the dc resistance of the sample,  $R \sim 1 \Omega$ , in the circuit in Fig. 1. The fluctuations in this resistance, which are characteristic of polypropylene,<sup>3,6</sup> were further evidence that the probe was not short-circuited to the substrate.

Once we found a conducting channel, we began to measure  $j_c$ . Previous attempts to find a dc value of this critical current<sup>2</sup> failed because of a heating of the probe at the point where it contacted the polypropylene. The heating occurred because the current density in the metal was at a maximum at this point. It was found possible to reduce this heating by passing short current pulses, formed by a voltage source and a ballast resistance of 0.3  $\Omega$  (Fig. 1), through the channel. Some special experiments (which will be reported separately) showed that, despite the high electrical conductivity of the channel, its thermal conductivity was as low as that of the polymer ( $\chi_{pp} = 10^{-3}$  cm<sup>2</sup>/s). At this value of  $\chi$ , and with the heat evolution confined to a short pulse of length  $\theta \approx 10^{-6}$  s, the heat front could propagate no more than 0.3  $\mu$ m

along the channel, i.e., a distance much shorter than the channel itself. There was essentially no heat transfer between the polypropylene channel and the probe during the pulse. Consequently, the heat which could in principle have evolved in the volume of the channel during the pulse was not drawn away from the channel through the metal probe, while the heat evolved in the contact region of the probe could be drawn off only through the probe itself. It thus became possible to experimentally determine the maximum temperature of the contact and of the thin polypropylene layer adjacent to it:

$$T_{\text{cont}} \approx T_0 + (T_m - T_0) (J_0/J_m)^2, \quad (1)$$

where  $T_0$  is room temperature,  $T_m = 1356$  K is the melting point of copper,  $J_0$  is the height of the bell-shaped current pulse  $J(t)$  (Fig. 1), and  $J_m = 120$  A is that height of this pulse at which a probe which penetrated through the polypropylene layer to the point that it made contact with the substrate and became welded to the latter.

Measurements were carried out both at a high repetition frequency of the current pulses,  $f = 25$  Hz, with slowly increasing pulse height ( $dj_0/dt = 50\text{--}100$  A/min), and in single pulses ( $f \leq 0.02$  Hz,  $\Delta J_0 \leq 2$  A). A dual-trace storage oscilloscope detected the voltage at the point at which the probe made contact with the polypropylene,  $U_1(t)$ , and also a voltage [ $U_2(t)$ ] with the shape of  $J(t)$ , measured across a resistance of  $10^{-3} \Omega$ . The voltage between the microprobe and the substrate which is shown in Figs. 1 and 2 corresponds to the difference between  $U_1(t)$  and  $U_2(t)$ .

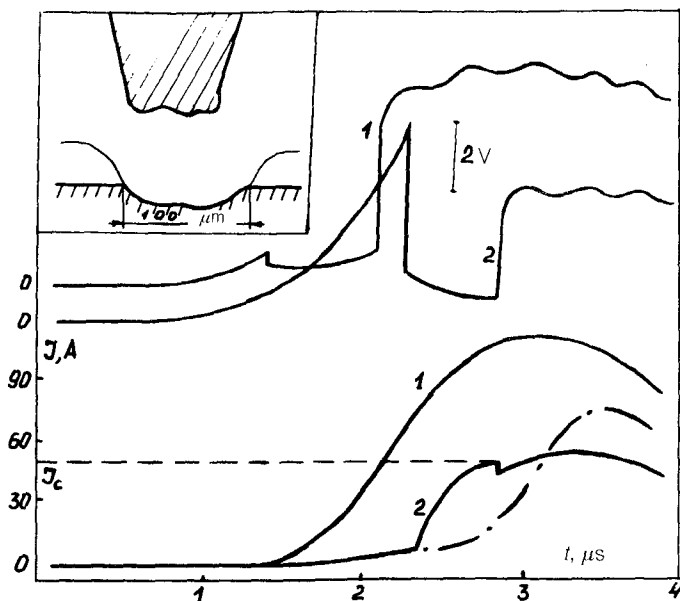


FIG. 2. Oscilloscope traces of the current (bottom) and the voltage (top) on the microprobe during the destruction of superconductivity by single pulses. 1—Current height  $J_0 \gg J_c$ ; 2— $J_0$  just above  $J_c$  [the dot-dashed line shows the temperature evolution  $T(t)$  at the point of contact for this pulse, for  $J_0$  just below  $J_c$ ]. The inset shows the typical shape of the sample and the electrodes after the very first pulse with  $J_0 > J_c$ .

When the probe was positioned at an insulating point of the polypropylene, we measured  $J(t) = 0$  until breakdown occurred, at a pulsed voltage of 230–240 V. At conducting points, in contrast, the resistance  $R$  depended on the current, falling sharply from  $\sim 1 \Omega$  to  $\leq 2 \times 10^{-3} \Omega$  as  $J(t)$  was increased to 1–2 A. The low value of  $R$  persisted for  $\sim 1$  min after the pulse, so there were no sharp changes in the voltage at  $f = 25$  Hz and  $J(t) < J_c$  (Fig. 1). (For a probe-substrate contact, there were no such sharp changes at any values of  $f$  and  $J_0$ .) Evidence that there was no significant heat evolution in the polymer came from the circumstance that the appearance of the polypropylene under the probe remained unchanged even at  $f = 25$  Hz and at all  $J(t) < J_c$ .

At any  $f$ , however, the very first pulse at which  $J(t) = J_c$  was reached (the average value was  $J_c = 63$  A, with a scatter of  $\pm 17$  over the various samples) caused a bright flash under the probe. A crater formed in the polypropylene, and the probe and substrate fused together (see the inset in Fig. 2). It was found that the increment in current height required to cause this destruction was no greater than  $\Delta J_0 = 0.04$  A  $\sim 10^{-13} J_c$  (at  $f = 25$  Hz and  $dJ_0/dt = 50$  A/min). Analysis of the traces in Fig. 2 shows that even at the front ( $\tau_f \leq 5 \times 10^{-8}$  s) of the jump in the resistance of the polymer,  $R_{pp}$ , the amount of energy evolved in the channel volume  $v$  was sufficient to heat the polymer in this volume to the extent that it underwent complete thermal decomposition and gasification. Accordingly, immediately after  $\tau_f$  a high-temperature arc occurs, as can be seen from the high-frequency oscillations and the low value of the voltage across the discharge gap ( $U_1 - U_2 = 4\text{--}6$  V).

The jump in  $R$  at  $J = J_c$  is caused by specifically the critical current, not the temperature, since even at very small values of  $\Delta J_0$  the effect is always observed in the region of the increase of  $J(t)$ , while the temperature maximum corresponds to the region of the current decay (Fig. 2). Furthermore, the value of  $J_c$  is not affected by a replacement of the copper probe by a tungsten one, which heats up to a greater extent ( $\chi_w < \chi_{Cu}$  and  $\sigma_w < \sigma_{Cu}$ ). Since the presumed superconductivity of the channel is not destroyed by a heating of the polypropylene near the contact with the copper at currents just below  $J_c$ , we can estimate a lower limit on  $T_c$  from (1) for values  $J_c = 70\text{--}80$  A:  $T_c > T_{cont} \gtrsim 700$  K. A lower boundary on the critical current density can be estimated from the area ( $\approx 70 \mu\text{m}^2$ ) of the contact of the polypropylene with the probe:  $j_c \geq 10^8$  A/cm<sup>2</sup>.

In order to refine the value of  $j_c$ , we must refer  $J_c$  to the cross section of the channel, not that of the probe. The results (which will be published in a detailed paper) lead to an estimate  $d \leq 0.7 \mu\text{m}$ . Approximately the same estimate,  $d < 2 \mu\text{m}$ , is found independently from the data in Fig. 2, when we calculate the polypropylene volume which is completely destroyed in the channel over the time  $\tau_f$  (the energy expended on the destruction is  $E \sim 5 \times 10^4$  J/cm<sup>3</sup>):

$$d = 2\sqrt{v/\pi nh} < \sqrt{2 (U_1 - U_2) J_c \tau_f / \pi h E} \quad (2)$$

In light of the value  $d \sim 1 \mu\text{m}$ , the estimate  $j_c \sim 5 \times 10^9$  A/cm<sup>2</sup> appears more accurate.

Let us assume that the channel conductivity  $\sigma$  is nonzero, and let us estimate it. In this case, each current pulse will lead to heat evolution in a channel of diameter

$d \sim 1 \mu\text{m}$ . Essentially all this heat will remain in the channel volume  $v$ , since the low value of  $\chi$  of the channel would prevent a heat transfer to either the insulating polypropylene matrix or the conducting electrodes, as was mentioned above. On the other hand, at a current height near  $J_c$  the heating in the channel should not exceed  $\Delta T \ll 10^3$  K, since otherwise the polymer would decompose completely in 1–10 s at  $f = 25$  Hz, and this is not what happens experimentally. We can thus write the following expressions for the intrinsic resistance of the channel,  $R_{pp}$ , and the corresponding value of  $\sigma$ :

$$R_{pp} \leq \frac{\pi c h d^2}{4 \theta J_c^2} \Delta T \quad \sigma \geq \frac{16 \theta J_c^2}{\pi^2 c d^4 \Delta T}, \quad (3)$$

where  $c \approx 1 \text{ J}/(\text{K} \cdot \text{cm}^3)$  is the specific heat of polypropylene. At the parameter values given above, we find from (3) the very low value  $R_{pp} \leq 5 \times 10^{-6} \Omega$ . This result explains why only the resistance of the conducting contacts was detected in Refs. 1–6. On the other hand, the estimate  $\sigma \leq 10^{11} \text{ S/cm}$ , which follows from (3), is higher than the conductivity of the best metals by more than five orders of magnitude.

Since these results show that the mechanism for the conductivity of the polypropylene channels differs from that in normal metals, future experiments should be aimed at deciding among three possibilities: (1) an ultrahigh conductivity with a nonzero  $\sigma$ ; (2) an ideal conductor with  $\sigma = \infty$ ; (3) a superconductor. In our opinion, regardless of how this question is eventually decided, we must be dealing with some completely new mechanism, which introduces several extremely unexpected features in the phenomenon, e.g., the abrupt decrease in the resistance upon an increase in the current. Working from estimate (3), we might suggest that the resistance  $\sim 1 \Omega$  corresponding to the low currents is a consequence of the small area in which the channel makes contact with the probe and that as the current is increased, this area increases abruptly as a result of an ability of the channel to move within the highly elastic polymer matrix. As a result, the contact resistance is reduced.

Since a physical mechanism for such a high conductivity is not known at this point, choosing among the three possibilities just listed will probably be a far from simple task. Existing results, e.g., the abrupt destruction of the ultrahigh conductivity of polypropylene by a critical current and the anomalously strong diamagnetism, which can be destroyed by a magnetic field,<sup>1,2,6</sup> favor a true superconductivity for polypropylene, by virtue of the analogy with known superconductors. On the other hand, neither the magnitude of this diamagnetism, which could be caused only by currents in rings of macroscopic size, nor the channel conductivity  $\sigma > 10^{21} \text{ S/cm}$  which we estimate from the decay time of the diamagnetism in a nondestructive magnetic field,  $\tau > 10^3$  s, contradicts the two other possibilities. Unfortunately, it would apparently be impossible to observe the Meissner effect in the case of polypropylene, even in the case of a true superconductivity, because of the estimate  $T_c > 700 \text{ K}$  which we found above: At such a temperature the polymer would decompose completely in a fraction of a second. This circumstance means that it will be necessary to seek some other criteria for distinguishing between a superconductor and an ideal conductor.

<sup>1</sup>L. N. Grigorov and S. G. Smirnova, Deposited article No. 2381-V 88, All-Union Institute of Scientific and Technological Information, 23 March 1988.

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<sup>3</sup>S. G. Smirnova *et al.*, *Vysokomolek. soed.*, **31(B)**, 667 (1989).

<sup>4</sup>V. M. Arkhangorodskii *et al.*, *Dokl. Akad. Nauk SSSR* **309**, 624 (1989) [*Sov. Phys. Dokl.* **34**, 407 (1989)].

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<sup>6</sup>S. G. Smirnova, *Candidate's Dissertation*, MFTI, Moscow, 1989.

Translated by Dave Parsons