Mechanism of charge transport in castor oil-based polyurethane/carbon black composite (PU/CB)

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A B S T R A C T

In order to identify and quantify the conduction mechanisms involved in the transport process, castor oil based polyurethane/carbon black composite (PU/CB) was introduced in a statistical model that reproduced the ac conductivity of composite PU/CB measurements by the application of a transfer-matrix technique. The simulation is based on virtual composite sample generation represented by a two-dimensional model of a resistor–capacitor network. The network represents a microstructure that contains both insulating (polyurethane) and conductive regions (carbon black). Drude’s formula was applied in the conductance calculation between two neighboring sites in the CB particles or aggregates, and Miller–Abrahams formula in conductance between two neighboring sites of the polymeric matrix. The theoretical–experimental adjustment indicates that, at low frequencies (below $10^3 \text{Hz}$), the transport mechanism by charges hopping in the polymeric matrix is dominant. On the other hand, at high frequencies (above $10^3 \text{Hz}$) electron conduction in carbon black, given by Drude’s formula, is dominant. The ac conductivity in the polymeric matrix is determined by the competition of two processes, one connected to hopping between the nearest sites with large energy difference or to hopping between the sites beyond the nearest neighbors with small energy difference.

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1. Introduction

In polymeric composites with low content of conducting filler, the mean distance between particles or clusters is sufficiently large and the conductivity is restricted by the presence of the insulating matrix. However, around the critical concentration, a small increase in the concentration of the conducting phase content increases the conductivity by several orders of magnitude and above the critical concentration; in general, this brings only a small further increase in the conductivity. This critical concentration is known as the percolation threshold [1]. In classical percolation theory, a continuous network of the conducting phase must be present in composite through the connection between adjacent conducting particles and typical power-law dependence of the electrical conductivity $\sigma$ on the volume percentage of the conducting phase $\phi$:

$$\sigma \propto |\phi - \phi_c|^t$$  \hspace{1cm} (1)

where $\phi_c$ is the critical volume at which the composite changes from the insulate state almost to the conducting state and $t$ is the conductivity critical exponent. Thus, an abrupt change occurs in the electrical conductivity of composites near $\phi_c$, especially when there is a larger difference between the electrical conductivity of the different components of the composites. The conductivity given by Eq. (1) strongly depends on the microstructure of the composite, and the critical exponent $t$ is considered universal, depending only on the spatial dimension of the composites [11].

The mechanisms of charge transport in polymeric composite are to a large extent governed by the amount of the dispersed phase and the characteristics of its distribution in the polymeric matrix [2]. In polymeric composites, both the filler/filler interaction and the filler/polymer-matrix interaction play an important role in the mechanisms of charge transport in the percolation threshold [3,4]. The mechanisms of charge transport that involve an intricate network of insulating and conducting phases are determined by two mechanisms [5,6]; a percolation model for hopping conduction in a continuous conducting network [7,8,9] and the tunneling effect between isolated conducting particles [10,11].

For the case where the particles do not physically touch each other, the conductance must be attributed to the existence of inter-particle tunneling. The resulting tunneling conductance decays exponentially with the inter-particle distance, which is on the order of a fraction to a few nanometers depending on the material properties [12].

The percolation threshold is determined by the amount of particles necessary for that network to form. In particular, above the threshold of percolation, a continuous conductive network is formed...
by physical contact between the particles. On the other hand, below
the threshold of percolation, in contrast with the expectation from
percolation theory, a considerable finite conductivity is observed
where a continuous network is absent. This conductivity has been
attributed to inter-particle tunneling [13, 14]. However, the tunneling-
percolation mechanism of conduction in a disordered conducting
composite incorporates the coexistence of a lattice of sites together
with a sub-network of tunneling between particles [15, 16, 17].

The electrical properties of composite materials consisting of a dis-
ersion of carbon black particles in an insulating polymeric matrix
have been the subject of numerous works, due to possible applica-
tions in electronic devices. They are used as antistatic materials, elec-
 tromagnetic radiation shielding, and electronic nose and chemical
capacitors [18, 19, 20]. The conductivity of these composites de-
composes on the size of the particles and the aggregates and how these
are dispersed in the polymeric matrix. In general, small particles uni-
formly dispersed into the matrix lead to a lower percolation threshold
[21]. These polymeric composites can be fabricated with controlled
levels of electrical conductivity while maintaining the desired me-
canical properties of the polymeric matrix, due to the low percola-
tion threshold and to the continuous increase in the conductivity for
volume fractions above the threshold.

The percolation threshold depends on both the structure of the
carbon black and the composite processing conditions. Forces and in-
teractions at the molecular scale have been taken into account in
order to accurately describe the behavior of small particles within a
matrix. Carbon black particles can have charges induced during the
mixing process. These particles with surface charge interact among
themselves and with the polymer matrix. London–Van der Waals
forces promote flocculation of the carbon black particles, while Cou-
lomb forces lead to a stabilization of the dispersion in composite
composites [22]. Schueller et al. [23] used these concepts to explain the formation of a conductive network at low filler in the percolation threshold for
carbon black in an epoxy.

Several conduction mechanisms are involved in the charge trans-
port process of these composite materials, such as percolation,
tunneling, and hopping conduction. Percolation theory explains the
formation and structure of three-dimensional conducting networks
when the conductive filler is added to the polymer matrix. On in-
creasing the amount of the conducting filler in the polymer matrix,
the resistivity of the composite decreases and the composite un-
dergoes an insulator-to-conductor transition at a certain critical con-
tent of the filler. The variable range hopping model [24] has been used
to describe the temperature dependence of conductivity, and takes
into account the contribution due to tunneling and hopping mecha-
nisms. In the hopping mechanism, the charge carriers gain energy
through random thermal fluctuations and the escape of its localized
states and are recaptured by another localized state. The tunneling
conduction takes place between two conducting particles when elec-
trons passing through a thin barrier potential, driven by voltage po-
tential or thermal activation.

In the present study, a statistical model of resistor–capacitor net-
works was developed to simulate virtual samples of castor oil based
polyurethane/carbon black composite, and to reproduce the real and
imaginary components of its ac conductivity by the application of a
transfer-matrix technique [25]. The statistical model takes into ac-
count the electron hopping and tunneling processes through the dis-
persed carbon black aggregates in a castor oil based polyurethane
matrix. The system is theoretically described by a percolation model,
where the basic ingredients responsible for the conductivity are
incorporated. It takes into account the large dispersivity of the
polymeric material as well as charge transport processes in the car-
bon black and the interfacial processes between conducting islands
and the insulating matrix. The model calculates the complex conduc-
tivity of these structures by a transfer-matrix technique. The conduc-
tance between two neighboring sites of the carbon black particles
was determined by Drude’s model [26], and the conductance be-
tween sites of the insulating polymer was obtained by the Miller–
Abrahams model [27, 28]. The behavior of the complex conductivity
in the disordered structure of the polymeric matrix is explained in
terms of the random free energy barrier model (RFEB), proposed by
J.C. Dyre to explain conduction in disordered media [29]. He used
the continuous-time random walk and effective medium approxima-
tion to solve the model and to derive a simple expression for complex
conductivity as a function of the frequency.

2. Theory and statistical model

2.1. Determination of electrical conductivity

Derrida et al. [25] introduce a transfer-matrix formulation to com-
pute the conductance of random resistor networks. It is similar to the
transfer-matrix method of statistical mechanics, but involves non-
linear matrix recursion relations. The calculation of the conductance
per unit length of networks consists of very long strips with resistors
placed at random on a square lattice. The results obtained for varying
strip widths are analyzed in terms of a finite-size scaling hypothesis.
The authors study the case where the resistors are either cut with
probability $(1 − p)$ or present with probability $p$.

If one adds a horizontal resistor $R$ on a site $\alpha$ of the network, then
the matrix $A_{\alpha \alpha}$ becomes a new matrix $A_{\alpha \alpha}'$, according to Eq. (2):

$$A_{\alpha \alpha}' = A_{\alpha \alpha} - \frac{RA_{\alpha \alpha}A_{\alpha \alpha}}{1 + RA_{\alpha \alpha}}$$  (2)

where $R$ is the resistance of the resistor.

The effect of the vertical bonds is given by Eq. (3):

$$A_{\alpha m}' = A_{\alpha m} + \frac{1}{R} \left( \delta_{\alpha m} - \delta_{\alpha m}' \right) \left( \delta_{m \alpha} - \delta_{m \alpha}' \right)$$  (3)

where $\delta_{m \alpha}$ is Kronecker’s symbol ($\delta_{m \alpha} = 1$ if $m = \alpha$ and $\delta_{m \alpha} = 0$ oth-

wise). The complex conductivity $\sigma$ of a strip of length $L$ is given by:

$$\sigma = \lim_{L \to \infty} A_{11}/L$$  (4)

where $A_{11}$ is an element at the first row and column of the matrix for
$L = \infty$.

We extend this transfer-matrix technique to calculate ac conduc-
tivity of a resistor–capacitor network, introducing the impedance $Z$

in place of the resistance $R$. Impedance that represents the difficulty
of a charge carrier jump from one site to another (potential barrier)
depends on the structure and characteristics of the material. For
PU/CB films, we use the Drude model to represent the impedence of
CB and the Miller–Abrahams model to represent the impedence of
PU.

The Drude model was developed in the 1900s by Paul Drude. This
model is usually applied to materials in which the charge carriers
have delocalized wave functions. This means that the charge carriers
can move more or less freely through the material, as in a metal.
When the Drude theory is applied to semiconductors, the mass
should be replaced by the effective mass of the charge carriers [30].

In our statistical model, each bond of carbon black aggregates or
particles is represented by a resistor $R_{WB}$ whose Drude impedance $Z_{D}$

is given by Drude’s formula [31], as shown in Eq. (5):

$$Z_{D} = A \left( \frac{1 - i \omega \tau_{CB}}{\epsilon_{CB}} \right)$$  (5)

where $A$ is a constant that depends on the effective mass and charge
of the charge carrier and of the optically active free carrier’s density,
$\omega$ is the angular frequency of the electric field, and $\tau_{CB}$ is the waiting
time. In this case, the Drude impedance is equal to resistance $R_{CB}$.
The Miller–Abrahams model consists of reducing the incoherent hopping transitions in a disordered lattice to a random resistor network [32,33]. This network is used to calculate the hopping conductivity in semiconductor materials in the presence of a weak external field. The hopping process theory of amorphous semiconductors is just applied to the nearest neighbor, in which carriers have to hop from one localized state to another following the Miller–Abrahams hopping rate \( v_{mn} \) given in Eq. (6):

\[
v_{mn} = v_o \exp \left( \frac{2r_{mn}}{a} \right) \exp \left( \frac{E_{mn}}{kT} \right)
\]

where \( v_{mn} \) is the hopping rate between sites \( m \) and \( n \) with energy mismatch \( E_{mn} \), the distance hopping between two sites \( r_{mn} \), and the localization length \( a \).

The first exponential in Eq. (6) describes the electronic wave function overlap that favors tunneling or short hops, and the second one describes the Boltzmann factor given by the energy difference between the initial and final states of the hopping process that is compared with the thermal activation energy \( kT \).

In a resistor–capacitor network, the complex impedance \( Z_{MA} \) (Miller–Abrahams impedance) between two sites \((m, n)\) of a polyurethane matrix, represented by a RC circuit in parallel, is obtained by:

\[
Z_{hs} = \frac{R_{mn}}{1 + (\omega R_{mn} C_{mn})^2}
\]

where \( R_{mn} \) is the resistance and \( C_{mn} \) the capacitance between sites \( m \) and \( n \) [34]. The resistances describe the difficulty with which a unit charge is transported from site \( m \) to site \( n \), while the capacitances reveal how much charge can be generated in sites \( m \) and \( n \) due to application of an electric field unit. Both resistance and capacitance are given as:

\[
R_{mn} = \frac{kT}{e^2 v_{ph}} \exp \left( \frac{E_{mn} + eF r_{mn}}{kT} + \frac{2r_{mn}}{a} \right) F(\omega)
\]

\[
C_{mn} = B \frac{e^2}{kT} \exp \left( -\frac{E_{mn}}{kT} \right)
\]

where \( e \) is the electronic charge, \( v_{ph} \) is the phonon frequency, \( k \) is the Boltzmann constant, \( T \) is the temperature in Kelvin, \( E \) is the root mean square value of the electric field, and \( B \) is a constant. \( F(\omega) \) is a function that represents the behavior of resistance \( R_{mn} \) with frequency, given by:

\[
F(\omega) = \frac{1}{(1 + \omega / \omega_c)}
\]

where \( \omega_c \) is the critical frequency [35]. In our model the function \( F(\omega) \) was incorporated in the \( R_{mn} \) equation obtained by Miller and Abrahams. Since \( R_{mn} \) represents the variable range hopping processes in the polymeric matrix, its dependence on the frequency is explained in terms of this energy barrier distribution. A given waiting time, \( \tau \), is associated with an energy barrier. In the low-frequency region, the electron motion is hampered mainly by the high-energy barriers that represent hopping obstacles. On the other hand, for frequency greater that waiting time, the electronic carriers become localized in small regions of low-energy barriers, thus increasing the carrier’s mobility [36].

2.2. Statistical model

In this work a statistical model of a resistor–capacitor network was developed to study its electrical transport properties, taking into account the geometrical structure composite and the calculation of ac conductivity. Castor oil based polyurethane elastomers (PU) usually show a two-phase structure in which hard segment-enriched domains are dispersed in a matrix of soft segments, as shown in Fig. 1. The hard segment domains are composed mainly of diisocyanate and the chain extender, while the soft segment matrix is composed of a sequence of macroglycol groups. For this reason, polyurethanes are often referred to as segmented block copolymers [37,38].

Carbon black particles and aggregates are distributed in the polymeric matrix. A single carbon black particle is spherical or nearly spherical, with its diameter between tens and hundreds of nanometers. In general, an aggregate of low structure carbon black is composed of 30–100 particles and 100–300 particles to that of the high structure one [39].

The statistical model computes the conductance per unit length of networks consisting of very long two-dimensional strips built by juxtaposing \( N \) square cells. Each cell consists of sequences of resistors serially (polymeric chains) arranged randomly, and of resistors connected to the nearest neighbors of the central site (particles and aggregates), also distributed randomly in the cell.

Initially the structure of the PU/CB composite is simulated by distribution of carbon black particles in a square cell. The particle size is determined by the choice of diameter, given by the bond number. After that, a site is randomly selected and this is connected to the nearest neighbors by resistors with impedance \( Z_{bp} \), inside a previously determined region, thus forming the conducting particles. The formation of particles occurs until a predefined bonds density is reached.

After that, the molecular chains are built to generate the polymeric matrix. Before this some rectangular regions of the cell are randomly chosen to reserve the growth of the hard polyurethane segments, in both a vertical and a horizontal direction. Initially an empty lattice site \( m \) of the cell is randomly chosen and connected with an empty site \( n \), the nearest neighbor of the site \( m \), also randomly chosen, and an RC circuit of impedance \( Z_{MA} \) is attributed to the bond connecting these two sites. The process is repeated until the chosen polymer size is reached. After the chain has reached the selected size, a search in all of its sites is performed looking for a pair of nearest neighbor sites not connected by a resistor that may or may not belong to the same chain. If such a pair is found, then these sites are connected, with probability \( p \), by a RC circuit. This RC circuit is a parallel association where \( C \) is the capacitance and \( R \) is the interchain resistance. The idea is to incorporate induced charges and hopping or tunneling mechanisms. Repeating the procedure described above, new polymer chains are built inside the cell until a determinate concentration \( k \) of the occupied lattice bonds is reached.

The structure of the PU/CB composite was constructed by filling the bonds of a square cell by resistor \( R_{mn} \) between two sites of

**Fig. 1.** Hard and soft segment domains of the polyurethane.
conducting particles and the RC circuit, in parallel association between two sites of the polymeric matrix. The carbon black particles are represented by a dark line and the polyurethane hard and soft segments are represented by a gray line. An example of a cell formed by 80×80 sites for PU/CB (90/10) is shown in Fig. 2. A sample of composite thin film can be represented by a long strip formed by juxtaposing N square cells with L×L sites.

Values of impedance $Z_{0}$ and $Z_{MA}$ from all bonds of the cell are used to calculate the conductivity. After that a new cell is built beside the first cell. Of course, care should be taken when passing from one cell to another: horizontal and vertical bonds on the boundary must be stored in order to correctly construct the next cell. This process is repeated until an infinitely long strip has been generated.

3. Experimental

Samples of PU/CB were prepared by casting method [40] to have 1–10% carbon black by weight of the film. Ac conductivity in the PU/CB films was measured by an impedance analyzer by Hewlett Packard (HP Model 4192A), in the frequency range from $10^{2}$ to $10^{6}$ Hz, and dc conductivity was obtained by using the two- and four-probe method. The equipment uncertainty of the impedance measurement was smaller than 1%. However, there was a 5% error bar due to the uncertainty of the film thickness and of the exact area of the top electrode, which was patterned by shadow mask.

4. Results

Generally, composites formed by a polymeric matrix and randomly dispersed conducting particles are electrical insulating material due to their low concentration of free charge carriers. Thus, under the influence of an electric field, their electrical behavior is essentially associated with the relaxation phenomena that occur through the space charge migration and dipolar orientation effects.

It is well known that, for carbon black-polymer composites, the conductivity dependence on the additive concentration exhibits a percolation threshold. The result of the measurement of the conductivity as a function of the carbon black concentration in mixtures with castor oil based polyurethane is shown in Fig. 3. At the percolation threshold of about 3.0 wt.%, the conductivity of the composite increased by 10 orders of magnitude. It is noted that the conductivity has a substantial increase between 6 and 8 wt.% of about two orders of magnitude.

In polymeric composites filled with low content carbon black particles, the mean distance between particles or clusters is sufficiently large and the conductivity is restricted by the presence of the polyurethane matrix. However, by increasing the conducting phase content at the percolation threshold, a physical path is formed between electrodes and an increase in conductivity is observed (see Fig. 4).

In ac, conductivity should take into account that the existence of the interfacial polarization mechanism that is the result of the non-homogeneous system, like the trapping of free charges at the carbon black–polyurethane matrix interface, forms large dipoles. The mechanism of conduction for these composites can be understood by the hopping transport model in the polyurethane matrix, by the theory of bands in carbon black, and by tunneling between carbon black particles or clusters.

The real and imaginary components of ac conductivity measurement are faithfully reproduced by our model. The results of the simulation are presented in Fig. 5. The free charge response of carbon black was modeled using the Drude model, while the motion of charge carriers in the polymer matrix was modeled by the Miller–Abrahams model.

The composite PU/CB structure was built by simulation of 500 square cells with 30×30 sites each. The $Z_{0}$ impedance was obtained by fixing the A parameter equal to $7.1 \times 10^{-2}$ Ωs, $6.7 \times 10^{-3}$ Ωs and $2.0 \times 10^{-10}$ Ωs and the median value of waiting time $\tau_{\text{CM}}$ equal to 9.0 ms, 9.5 ms, and 0.25 ns for samples with ratios of 99/01, 95/05, and 90/10, respectively. A variation around both of these values of 10% did not influence the fittings to frequency below $10^{3}$ Hz. The $Z_{MA}$ impedance was determined from resistance $R_{\text{MA}}$ and capacitance $C_{\text{MA}}$ between sites $m$ and $n$, for 303 K. In the simulation, the $\beta$ parameter was equal to $3.6 \times 10^{9} \text{ QS}$, $3.8 \times 10^{10} \text{ QS}$, and $3.5 \times 10^{11} \text{ QS}$, and the critical frequency $\omega_{c}$ was equal to 3700 Hz, 600 Hz, and 20 Hz for samples with ratios of 99/01, 95/05, and 90/10, respectively. The adjusted value of the phonon frequency and the value of the localization length were fixed at $\nu_{\text{ph}} = 1.0 \times 10^{13}$ Hz and at $\sigma = 30.0$ nm, respectively. However, a variation around both of these values of 10% did not influence the fittings to frequency above $10^{7}$ Hz.

Drude’s formula parameters used to fit the statistical model to the experimental data have showed greater sensitivity in frequencies above $10^{5}$ Hz, whereas the Miller–Abrahams formula parameters, in frequencies below $10^{5}$ Hz. In this way, the transport mechanism hopping in the polymeric matrix is dominant at low frequencies, on the
other hand, at high frequencies; the electronic conduction in carbon black is dominant.

Extrapolating the dependence of $R$ and $C$ with $f$ for low frequencies, unattainable in our equipment, as shown in Figs. 6 and 7, our simulations anticipate the real and imaginary component of the resistivity (Fig. 5). The resistance and capacitance between the sites $m$ and $n$, given by Eqs. (8) and (9), are presented in Figs. 6 and 7 as a function of frequency.

The frequency dependence of the resistance is explained in terms of the energy barrier distribution, and the frequency dependence of the capacitance in terms of induced charge by alternating electric field applied.

The values of energy mismatch $\varepsilon_{mn}$ and the hopping distance $r_{mn}$ as a function of frequency were obtained by fitting the theoretical data to the experimental values, as shown in Table 1.

The estimated relative error of mismatch energy is $\pm 0.01$ meV from the adjustment used. The hopping distance uncertainty is estimated to be $\pm 0.1$ nm.

5. Discussion

In a highly disordered bulk structure, charge transfer processes of electronic carriers can be represented by a distribution of energy barriers $W$ of the hopping process. A given waiting time $\tau$ is associated with an energy barrier $W$ by $\tau \sim e^{W/kT}$. In the low-frequency region, where $f \gtrsim \tau^{-1}$, electron motion is hampered mainly by the high-energy barriers, which represent obstacles between sites. On the other hand, for high-frequency $f \gtrsim \tau^{-1}$, the electronic carriers become localized in small regions of low-energy barriers and are therefore more mobile.

As shown in Table 1, the energy $\varepsilon_{mn}$ increases with frequency for all samples, while the hopping distance $r_{mn}$ decreases with frequency in the polymeric matrix. These results show that there is competition between $\varepsilon_{mn}$ and $r_{mn}$, as emphasized by Mott [41].

In the regime of low frequencies, the charge carrier located at the site $m$ jumps preferably to site $n$, farther if this site has an energy level close to the energy level of the site $m$, as the potential energy barrier diagram illustrates in Fig. 8.

In the high frequencies, the charge carrier located on site $m$ jumps preferably to site $n$ closest with a higher energy level (or lower) than
the energy level of site $m$, as in the potential energy diagram shown in Fig. 9.

In the amorphous region of the polymer matrix, many localized states exist in the forbidden band, and the carrier mobility in those materials is considered to be strongly energy dependent. In the deep localized state where overlap of the electronic wave function between neighboring localized states is small, the transport process of carriers, in the localized states, occurs predominantly by phonon-assisted hopping. According to Mott, the hopping conduction process is determined by optimizing the competition between the overlap term $\exp(-r_{mn}/a)$, which favors short hops of charge carriers, and the activation energy $\exp(\varepsilon_{mn}/kT)$, which favors long hops [42,43]. The results obtained by using the statistical model, as shown in Table 1, indicate that conductivity in a polymeric matrix is governed by Mott’s variable-range hopping (VRH) law.

The increase of the contents of carbon black in the composite causes a decrease the local electric field in the polymer matrix. The amount of charge stored in the capacitor decreases due to the increase in electrical conductivity. Thus, the hopping distance of charge carriers decreases and the energy mismatch increases with content of carbon black.

### 6. Conclusion

In conclusion, we introduced a two-dimensional statistical model that was developed based on a resistor–capacitor networks that reproduce the morphological structure and calculate the alternating conductivity of a castor oil based polyurethane/carbon black composite (PU/CB). Simulations based on a transfer-matrix technique and performed at the critical percolation threshold reproduce the measured alternating conductivity in these films in a large range of frequencies. The charge transport properties can be studied by modeling the system with carbon black nanoparticles and carbon black aggregates randomly distributed in an insulated matrix. Before the physical contacts between particles have been achieved, the system becomes conductive due to the tunneling effect between particles that decrease the percolation threshold.

### Table 1

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>Mismatch energy $\varepsilon_{mn}$ (meV)</th>
<th>Hopping distance $r_{mn}$ (nm)</th>
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<tr>
<td></td>
<td>(± 0.01 meV)</td>
<td>(± 0.1 nm)</td>
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<tr>
<td>PU/CB (99/01)</td>
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<td>5.39</td>
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