

# A Scaling Analysis of a Friction Processes of Polyarylate

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**ABSTRACT:** The obtained data infer the applicability and usefulness of the scaling approach and fractal analysis for the description of friction and wearing processes of polymers. The scaling nature of the relationships used for the description of the above-mentioned processes is confirmed. Shown within the framework of the fractal analysis is the

interdependence between the structure of polymer and parameters involved in these relationships, which were considered previously as empirical. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2352–2355, 2004

**Key words:** polyether; yielding; glass transition

## INTRODUCTION

Ideas of scaling have received widespread acceptance in different areas of polymer physics.<sup>1</sup> Although the concepts of scaling (scale invariancy) for different researchers are highly diversified, in the present article the approach of de Gennes is used,<sup>1</sup> which considers that it is essential to abstract (as far as possible) from details of a considered system structure and to concentrate on simple universal features, specific for the broad class of systems. The scaling law always determines only some asymptotics, applicability of which, allowing for system specificity, should be analyzed for each concrete case. An example of the scaling characteristic (of a scaling index) is the fractal dimension, which, as shown for regular fractals, depends only on the object formation mechanism and determines a global structure of a system—distribution of mass depending on scale.

Simple examples of scaling relationships with reference to friction processes are<sup>2</sup>

$$A \sim P^n \quad (1)$$

and

$$F \sim P^n \quad (2)$$

where  $A$  is the real contact area of two bodies during friction,  $P$  is normal loading,  $F$  is the frictional force,  $n$

is the exponent varying from 2/3 (at elastic deformation) up to 1 (at plastic deformation).

The purpose of the present article was to confirm scaling of relationships (1) and (2), to clarify their physical sense, and to give treatment of parameters  $A$  and  $n$  within the framework of the fractal analysis.

## EXPERIMENTAL

Used for experiments was rigid-chain aromatic polyester, polyarylate (PAr), grade DV-102, synthesized by the method of emulsion polycondensation of diphenylolpropane with chloroanhydride of isophthalic and terephthalic acids taken in a ratio of 1 : 1. This PAr is an amorphous polymer with a density ( $\rho$ ) of 1240 kg/m<sup>3</sup> and a glass transition temperature ( $T_g$ ) of 468 K.<sup>3</sup>

The friction process was studied with the use of the disk machine of friction (pins are samples of material) according to a technique described in ref. 4. Used as a contrabody was the steel 45, quenched up to HRC 45–48 with surface roughness  $R_a = 0.32 \mu\text{m}$ . The experiments were carried out after final attrition of samples to a constant friction coefficient. Temperature in a zone of friction was measured by means of thermoelectric couples located at a distance of 0.2–0.5 mm from the friction surface.

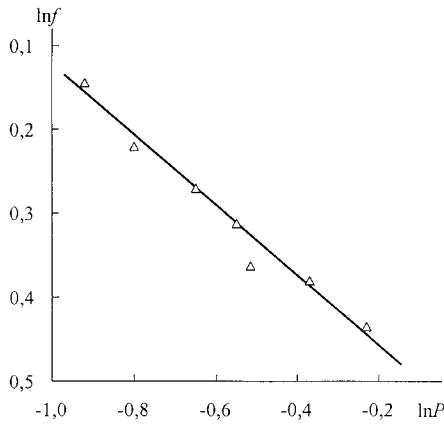
## RESULTS AND DISCUSSION

As is known,<sup>2</sup> the frictional force  $F$  can be determined as

$$F = fP \quad (3)$$

where  $f$  is the friction coefficient. In the present article, the kinetic friction coefficient will be utilized.

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**Figure 1** The dependence of a friction coefficient  $f$  on normal load  $P$  in double log-log coordinates for PAR.

The combination of relationships (2) and (3) gives the result

$$f \sim P^{n-1} \tag{4}$$

Presented in Figure 1 is a plot of function  $f(P)$  in double log-log coordinates, which allows us to determine exponent  $n$  from the slope of the linear plot: value.  $(n - 1) = -0.412$  and  $n = 0.588$ . The absolute value of exponent  $n$  is close to  $2/3$ , which assumes the mechanism of elastic deformation in friction zone for the considered case. Further, we can obtain analytical expression of  $f(P)$  for PAR of the kind

$$f \approx 0.60P^{-0.412} \tag{5}$$

which quantitatively well describes value  $f$  [the difference between experimental values of  $f$  and those calculated according to eq. (5) does not exceed 5%].

The real contact area  $A$  can be determined from<sup>2</sup>

$$A = \frac{P}{\sigma_Y} \tag{6}$$

where  $\sigma_Y$  is yield stress of polymer.

Substituting eq. (6) in relationship (1), we obtain

$$\sigma_Y \sim P^{1-n} \tag{7}$$

Shown in Figure 2 is the relation  $\sigma_Y(P)$  in double log-log coordinates, where the values  $\sigma_Y$  for PAR are adopted from ref. 5. As it is possible to see, the anticipated linear correlation allowing us to determine the value  $n$  from its slope is obtained. The values determined in this way are equal to  $(1 - n) = -0.52$  and  $n = 1.52$ . Apparently, in this case, exponent  $n$  is much greater than that estimated from the plot of Figure 1 and falls outside the limits, indicated in ref. 2.

Determination of real contact area is possible within the framework of the fractal analysis. As is known,<sup>6</sup> amorphous polymers are thermodynamically non-equilibrium solids having the fractal structure with dimension  $d_f$ . The real area of such body  $A_{fr}$  is determined by<sup>7</sup>

$$A_{fr} = L^{d_{sur}} r^{d-d_{sur}} \tag{8}$$

where  $L$  is the linear size of the surface,  $r$  is the scale of measurement,  $d_{sur}$  is the fractal dimension of surface ( $1 \leq d_{sur} < 2$ ), and  $d$  is the dimension of Euclidean space, in which fractal is considered. Apparently, in our case  $d = 2$  and for a Euclidean object (a smooth surface) at  $d_{sur} = d = 2$ , we obtain  $A_{fr} = L^2$ .

As is known, the upper linear limit of fractal behavior for polymers makes up  $\sim 100 \text{ \AA}^6$ , and the value  $r$  can be accepted to be equal to a characteristic size of the structure—the length of statistical segment  $l_{st}$ , defined as<sup>8</sup>.

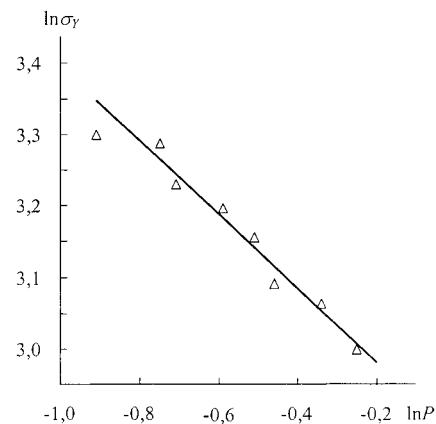
$$l_{st} = l_0 C_\infty \tag{9}$$

where  $l_0$  is the length of skeletal bond of the main chain, and  $C_\infty$  is the characteristic ratio, which is an indication of polymer chain statistical flexibility.<sup>9</sup> For PAR  $l_0 = 1.25 \text{ \AA}$ ,  $C_\infty = 2.4$ .<sup>9</sup>

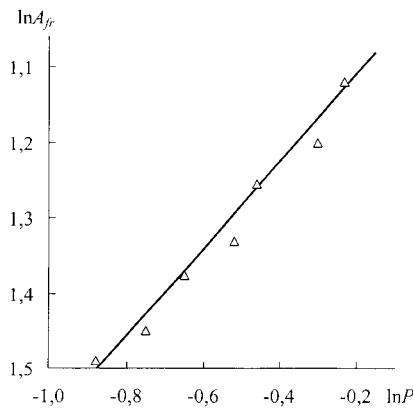
The value  $d_f$  can be determined according to the following technique. As is known,<sup>10</sup> the relative fraction of local order domains (clusters)  $\phi_{cl}$  can be determined from the following percolation relationship

$$\phi_{cl} \approx 0.33(T_g - T)^{0.55} \tag{10}$$

where  $T$  is the testing temperature, which in our case is equal to the temperature in friction zone, and is given for PAR in ref. 3.



**Figure 2** The dependence of yield stress  $\sigma_y$  on normal load  $P$  in double log-log coordinates for PAR.



**Figure 3** The dependence of a real contact area  $A_{fr}$ , calculated according to eq. (8), on normal load  $P$  in double log–log coordinates for PAr.

Further, it is possible to calculate the fractal dimension  $d_f$  of the structure of polymer structure according to<sup>10</sup>

$$d_f = d - \left( \frac{\phi_{cl}}{SC_\infty} \right)^{1/2} \quad (11)$$

where  $S$  is the cross-sectional area of a macromolecule, which is equal to  $30.7 \text{ \AA}^2$  (for PAr).<sup>11</sup>

By using eq. (11), we obtain in an interval  $P = 0.4\text{--}0.8$  MPa the following values  $d_f$ : 2.573–2.676. The values  $d_f$  and  $d_{sur}$  are connected to each other by the simple equation<sup>6</sup>

$$d_{sur} = d_f - 1 \quad (12)$$

Having calculated  $A_{fr}$  according to eq. (8) and having divided it by  $L^2$ , we shall obtain the relative real contact area. Shown in Figure 3 is the relation  $A_{fr}(P)$  in double log–log coordinates, which has turned out to be linear again. From the slope of this plot, exponent  $n$  was determined, that is, equal to 0.570, which well agrees with value  $n = 0.588$ , obtained from the plot of Figure 1. Thus, in offered treatment, the value  $A = A_{fr}$  is a structural characteristic, instead of being determined by random parameters (for example, by surface roughness). An increase of  $P$  results in a temperature growth in friction zone, a decrease of  $\phi_{cl}$ , an increase of  $d_f(d_{sur})$ , and a corresponding increase of  $A_{fr}$ . Within the framework of cluster model of polymers structure<sup>10</sup> for amorphous polymers, there are two structural components: clusters consisting of several closely packed collinear segments of different macromolecules, and loosely packed matrix, in which all fluctuation free volume of polymer concentrates. Apparently, a decrease of  $\phi_{cl}$  and a corresponding increase of the relative fraction of a more soft loosely packed

matrix with increasing  $P$  should result in growth of  $A$ . Analytical relation  $A_{fr}(P)$  for PAr can be expressed as

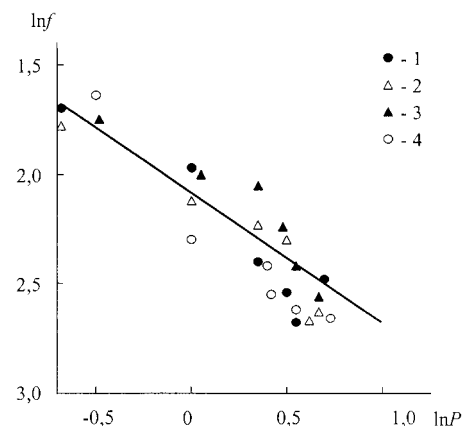
$$A_{fr} = 0.38P^{0.570} \quad (13)$$

Now we shall consider some fundamental physical aspects of the above scaling relationships. As was mentioned above, scaling determines some asymptotics, the applicability of which should be analyzed for each case. Allowing for this, we have shown in Figure 4 the relation  $f(P)$  in double log–log coordinates for carbon fiber reinforced plastic based on aromatic polyamide (Phenylone).<sup>12</sup> The linear correlation is again obtained; from the slope of which the following values are determined  $(n - 1) = -0.592$  and  $n = 0.408$ . These values are close enough to those obtained for PAr, despite the large difference between both materials and testing conditions (for carbon fiber reinforced plastic  $P = 0.6\text{--}2.0$  MPa<sup>12</sup>). The data of Figure 4 allow us to obtain the following empirical equation for estimation of  $f$  for carbon fiber reinforced plastic

$$f = 0.12P^{-0.592} \quad (14)$$

From comparison of eq. (5) and (14), it is easily to see that their general asymptotics are approximately identical, and the difference of materials is expressed by constant factors: 0.60 and 0.12, respectively.

As is shown above, during friction the mechanism of elastic deformation will be realized. As is known,<sup>13</sup> the quasi-brittle fracture of solids will be realized in an interval:  $2.50 \leq d_f \leq 2.67$ . From the above values  $d_f$  for PAr structure, it follows that they fall within the above-mentioned interval of quasi-brittle fracture, which determines the mechanism of elastic deformation.



**Figure 4** The dependence of friction coefficient  $f$  on a normal load  $P$  in double log–log coordinates for a carbon fiber reinforced plastic based on phenylone at sliding speeds: 1 (1), 1.5 (2), 2.0 (3), and 2.5 (4) m/s.

Exponent  $n = 0.588$  excellently agrees with a fractional part of fractal dimension of PAr structure  $d_f$ . Such an agreement is not accidental. As the fractal object (polymer surface) is subject to scuffing, such a process can be preserved by the way of a devil's staircase.<sup>14</sup> Its horizontal sections correspond to surface portions that are not subject to scuffing. Used for description of such processes are mathematical method of fractional derivation and integration.<sup>15</sup> As shown in ref. <sup>16</sup>, in this case, fractional exponent  $\nu$  indicates a fraction of system states kept for all time of evolution (in our case, of friction and wearing process). Then, adopted as  $\nu$  is the fractional part  $d_f$  or <sup>17</sup>

$$\nu = d_f - (d - 1) \quad (15)$$

As stated above, it is possible to assume that  $n \cong \nu$ . As an increase of  $d_f$  (and, therefore,  $\nu$ ) is accompanied by an increase of loosely packed matrix relative fraction, this circumstance assumes its invariance during friction and wearing. An assumption follows that the closely packed parts of polymer structure (clusters and crystallites) are subject to wearing, and the loosely packed matrix is only deformed. One of the reasons in favor of such an assumption is the data of ref. 18, where it is shown that semicrystalline Phenylone wears at a higher rate than amorphous Phenylone (wear rate is  $4.6 \times 10^{-9}$  and  $3.0 \times 10^{-9}$ , respectively), despite the fact that the first of these polymers has a higher hardness. Besides, some decreasing  $n$  for carbon fiber reinforced plastic based on Phenylone as contrasted to PAr can be explained by a decrease of  $d_f$  for carbon fiber reinforced plastic, which is due to its greater value  $\phi_{cl}$ .

## CONCLUSION

Thus, the obtained results assume the applicability and usefulness of the scaling approach and fractal

analysis for the description of friction and wearing processes of polymers. The scaling nature of the relationships (1) and (2) used for the description of the above-mentioned processes is confirmed. Shown within the framework of the fractal analysis is the interdependence between the structure of polymer and parameters  $A$  and  $n$  involved in relationships (1) and (2), which were considered as empirical ones previously.

## References

1. De Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, New York, 1979; p 348.
2. Bowers, R. C.; Zisman, W. A. *Engineering Design for Plastics*; Baer, E., Ed.; Reinhold Publishing: New York; 1965; pp 274–330.
3. Burya, A. I.; Chigvintseva, O. P.; Suchilina-Sokolenko, S. P. *Polyarylates: Synthesis, Properties, Composite Materials*; Nauka i osvita: Dnepropetrovsk, 2001; p 150.
4. Burya, A. I. *J Friction Wear* 1998, 5, 671–675.
5. Sanditov, D. S.; Kozlov, G. V.; Belousov, V. N.; Lipatov, Yu. S. *Polym J* 1992, 1 (3–4), 241–258.
6. Novikov, V. U.; Kozlov, G. V.; *Uspekhi Khimii* 2000; 69(6), 572–599.
7. Van Damme, H.; Levitz, P.; Bergaya, J. F.; Alcover, L.; Gatineau, L.; Fripiat, J. J. *J Chem Phys* 1986; 85(1), 616–625.
8. Wu, S. *J Polym Sci, Part B: Polym Phys* 1989; 27(4), 723–741.
9. Aharoni, S. M. *Macromolecules*. 1983; 16(9), 1722–1728.
10. Kozlov, G. V.; Novikov, V. U. *Uspekhi Fizich Nauk* 2001; 171(7), 717–764.
11. Aharoni, S. M. *Macromolecules* 1985; 18(12), 2624–2630.
12. Burya, A. I.; Levi, A. G.; Bedin, A. S.; Levit, R. M.; Raikin, V. G. *Trenie i iznos* 1984; 5 (5), 932–935.
13. Balankin, A. S. *Synergetics of Deformable Body*; MO SSSR: Moscow, 1991; p. 404.
14. Halsey, T. C.; Jensen, M. N.; Kadanoff, L. P.; Procaccia, I.; Shraiman, B. I. *Phys Rev A* 1986; 33(2), 1141–1151.
15. Bolotov, V. N.: *Pis'ma v ZhTF*. 1995; 21(10), 82–84.
16. Nigmatullin, R. R.: *Theoret. i Matemat. Fizika*. 1992; 90(3), 354–362.
17. Kozlov, G. V.; Shustov, G. B.; Zaikov, G. E.; *Chemistry and Biochemistry on the Leading Edge*; Zaikov, G., Ed.; Nova Science Publishers: New York, 2002; pp. 21–29.
18. Burya, A. I.; Prikhod'ko O. G.; Cholodilov, O. V.; Tref'yakov, O. A.: *Trenie i iznos* 1995, 16(3), 523–526.