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Surface and electrical properties of high density polyethylene + carbon black composites near the percolation threshold

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Abstract: We have studied friction, scratch resistance and electrical resistivity in high density polyethylene (HDPE) + carbon black (CB) composites in relation to electric resistivity percolation threshold. Below the threshold, CB addition lowers dynamic friction by providing a smaller surface area of contact of the composites with the pin surface; the effect is stronger at higher loads. Above the percolation concentration, an increase in friction is seen due to formation of CB agglomerates and thus an increase in the area of contact. The recovery depth in scratch testing behaves similarly as dynamic friction and for the same reasons, particularly so at high loads, with a minimum at the percolation threshold. Thus, at the threshold we have simultaneously superior scratch resistance, low dynamic friction and low electric resistivity.

Keywords: scratch resistance, dynamic friction, effective surface area, carbon black in polymers, electric conductivity threshold, polymer reinforcement.

Introduction

Polymer composites containing carbon black (CB) have numerous applications [1]. The presence of carbon in any form can modify electrical and other properties of polymers by several orders of magnitude [1 - 15]. The best way to explain the observed changes in electrical properties as a function of volume fraction of CB in polymer-based composites is the percolation theory [4]. One assumes that electrical conduction is carried via conductive pathways; the pathways are formed when the conductive particles achieve electrical contact at the percolation threshold. At the respective filler concentration, the formation of percolative carbon chains produces the change from a dielectric material to an electric conductor.

By embedding carbon inside the polymer matrix, mechanical and tribological properties are also usually modified. For polymeric materials in tribological applications, high wear resistance and low friction are often required simultaneously [16]. Several approaches are used to reinforce the polymers: fillers with micro and nanoparticles, reinforced fibers, binders or solid friction modifiers, or else irradiation [17]. For carbon-containing polymer composites most of the reports deal with mechanical, thermal or electrical behavior – although there are some publications on surface and tribological properties [12, 13, 18]. Also here the percolation threshold is important. Blends of irradiated and non irradiated CB + poly(vinylidene fluoride) + ultrahigh molecular weight polyethylene above the percolation threshold form a continuous surface CB phase [13]. The result is a lubricating effect and a consequent drop of friction – as well as the usual drop in electric resistivity at the threshold.

One cannot guarantee that improving electrical properties will automatically bring about an improvement in both mechanical and tribological properties - nor *vice versa*. In this situation we have decided to investigate a combination of electrical and tribological behavior of one more CB-containing polymer system. Since the results reported in [13] involve high density polyethylene (HDPE), we have studied HDPE + CB hybrids.

Results and discussion

Figure 1 shows the electric resistivity of the composites as a function of CB content for an extended range of CB wt. concentrations. Percolation threshold was numerical obtained using Origin 6 software. According to the percolation theory, for CB concentrations X higher than the percolative threshold X_c, we have used the equation [1, 2, 4]:

$$\rho(X) = \rho_0 (X - X_c)^{-\alpha} \qquad (1)$$

where ρ is the electric resistivity of the composite, ρ_0 is the resistivity of the main component (here our HDPE) while α = 1.7 [1,2,4]. We have used Eq. (1) to calculate the percolative threshold, with the result X_c = 13.95 % CB.

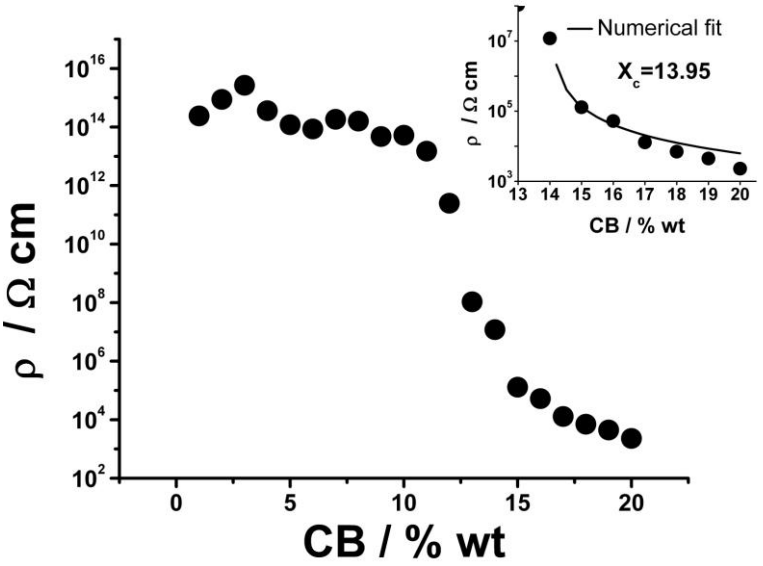

Fig. 1. Electrical resistivity of the composites as a function of CB concentration.

Figure 2 shows the residual (healing) depth R_h of the composites at several loads. We recall that this is the final or healing depth after viscoelastic recovery has taken place; the continuing change of the depth after the 'attack' by the indenter is the best seen in the computer simulation results [25, 26].

We see in Figure 2 that below 10 % of CB at all loads there is little reinforcement with respect to the pure polymer matrix - and only a weak dependence of R_h on the applied load. However, above 10 N we clearly observe improved scratch resistance (shallower R_h) - with a scratch depth minimum at the percolation threshold (13.95 % CB). Afterwards, a further increase in the CB concentration results first in deeper scratches; there is a minimum, often deeper than for the neat polymer.

Kopczynska and Ehrenstein [27] have stressed that properties of multiphase systems depend strongly on the interfaces. There is no chemical reaction between the polymer chains and CB particles; however, there are two competitive phenomena when the reinforcement acts against applied forces. First, there is polymer chain resistance to flow around the carbon black particles - responsible for the R_h decrease; the CB particles offer resistance to the chain movement - and thus also resistance to the indenter. The second effect is weakening of the matrix due to disruption of its structure (lower polymer matrix cohesion) caused by CB particles. At the percolation threshold the first effect of reinforcement is dominant; CB particles touch one another and form a network throughout the material. Above the threshold concentration CB particles begin to *agglomerate* - weakening the material against scratching due to more pronounced disruption of the polymer matrix structure.

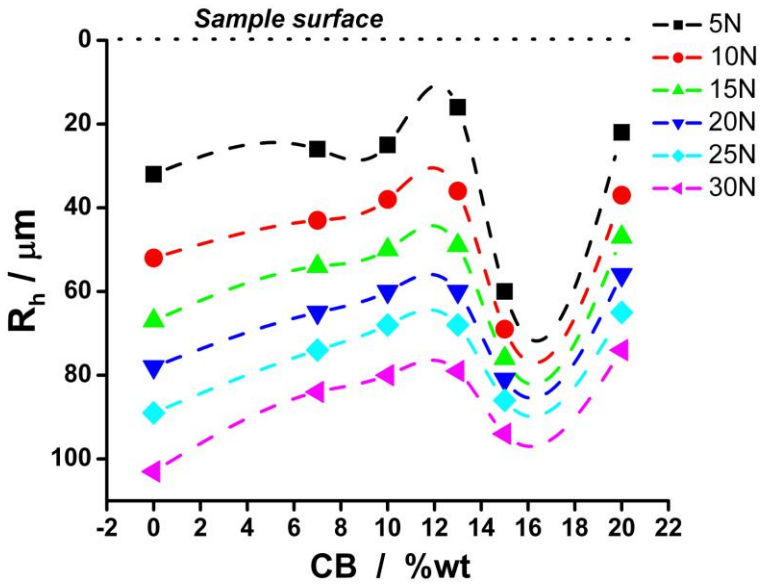

Fig. 2. Residual depth R_h at several normal loads.

Figure 3 shows the frictional behavior of the composites. As expected, the dynamic friction values depend on the normal force applied and on the CB concentration.

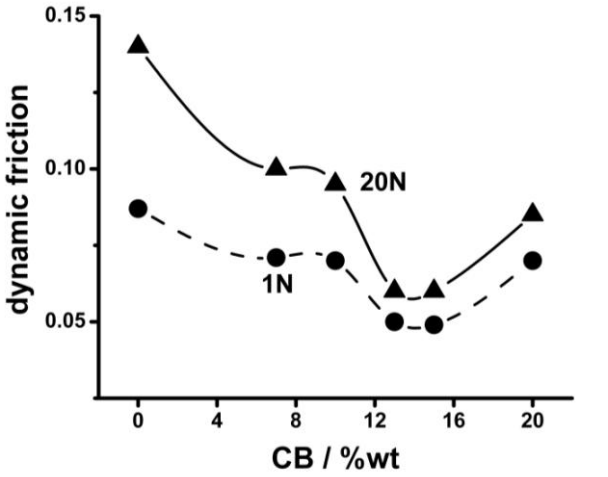

Fig. 3. Dynamic friction of the composites at 1.0 N and 20.0 N.

The effect of CB addition is analogous as for the scratch resistance: there is a decrease in friction as we keep on incorporating CB particles - down to the percolation threshold. Above the threshold, the friction begins to increase. We have seen a similar behavior in polymer + metal particles hybrids [28]. There is a minimum value of friction around the percolation concentration that represents a reduction of 43 % and 57 % for 1.0 N and 20.0 N, respectively. This can be explained in a similar way as for the scratch resistance. At low CB concentrations there is a reduction in the effective contact area of the composite surfaces with the pin. Since friction values are directly proportional to the effective contact area, we have lower friction. Moreover, since carbon black has lower friction than the polymer matrix with respect to the pin, a reduction in friction is expected as we incorporate more CB into the surface. Above the percolation concentration, the negative reinforcement effect discussed above produces a larger area of contact due the presence of CB particle agglomerates; an increase in friction is seen.

In recent work [29] we have studied tribological properties of nanocomposites of poly(methyl methacrylate) (PMMA) and montmorillonite (MMT) Brazilian clay. We have found a minimum of wear rate for 1 wt. % MMT. Up to that clay concentration a reinforcement of PMMA is seen. At higher clay concentrations, however, we have found an increase in wear rate caused by clay agglomeration – similarly as CB does in the system now under study. While putting additives into polymers to improve their properties is in general a worthwhile procedure [30], concentration of the additive has to be optimized carefully [31].

With respect to the load, a more pronounced effect on friction is seen at the higher load of 20.0 N. Necessarily at this load there is a closer contact between the areas of the composite surface and the pin surface. Achieving high scratch resistance and low friction simultaneously is difficult [16]. As already mentioned, we have demonstrated a connection between friction and electric resistivity for polymer blends [13]. We have now investigated a ‘triple’ connection between dynamic friction, scratch resistance and electric resistivity. For our HDPE + CB composites the CB concentration around the percolation threshold results simultaneously in superior scratch resistance at high loads, low friction and low electric resistivity.

Viscoelasticity is a property of all polymers and polymer-containing systems and serves for predictions of long term behavior from short term tests [32, 33].

Nanohybrids based on polymers such as of the polymer + metal powder type clearly show viscoelasticity – including healing in scratch testing [34]. Sometimes one does not pay sufficient attention to manifestations of viscoelastic behavior in other classes of materials. In fact, human teeth exhibit viscoelasticity [35]. Metals show viscoelastic behavior as well – a fact known for a long time [36] and confirmed also by recent dynamic mechanical analysis as well as scratch resistance determination results [37].

A survey of results

Tribological properties were correlated to electrical percolation concentration in HDPE + CB composites. At this concentration, calculated as 13.95% wt. CB from the data and Eq. (1), an improvement of the scratch resistance and a lowering of friction were found simultaneously with the drop in electric resistivity. This behavior has been explained in terms of electrical pathways in which CB particles are homogenously dispersed through all polymer matrix, producing the lowest contact surface (low friction) and the best viscoelastic reinforcement (the maximal healing or recovery). A further addition of carbon black results in agglomeration of the filler, adversely affecting scratch resistance as well as friction.

Experimental part

Sample preparation

We have used Yuzex 8800 HDPE from SK Corp., Seoul, Korea, and Vulcan XC72 carbon black donated by Cabot Corp., Boston, MA. The composites were made by mixing the two components in a mixer at 170°C and 75 rpm for 30 minutes. All samples were prepared by compression molding at 4000 psi and 170^0C for 15 minutes. For the friction and scratch tests, blocks of 2.0 x 2.0 x 0.5 cm were prepared while for the electric tests cylinders of 0.4 cm of radius and 0.5 cm height were used.

Electric resistivity determination

These were performed with a Keithley 6517A electrometer in the automatic resistance mode. Both sides of the cylindrical specimens were covered with silver paint.

Friction testing

A pin-on-disk Nanovea tribometer from Microphotonics was used as before [19, 20] at normal loads 1.0 N and 20.0 N and 200 rpm at 3000 cycles. The pin was made of silicon nitride with the radius = 3.0 mm. The reported friction values are those obtained once a steady state is reached.

Scratch resistance. A Micro Scratch Tester from CSM equipped with a diamond indenter of the Rockwell type was used [16, 21 - 24, 19, 20]. Scratch tests were performed in the constant load mode at several loads, and the recovery (healing) depth R_h reported. The instantaneous or penetration depth R_p was larger, as seen in experiments as well as in molecular dynamics computer simulations [25, 26]. Then viscoelastic healing took place and the bottom of the scratch groove went up (in

experiments inside 2 minutes). The scratch length and scratch velocity were 1.0 cm and 10.0 mm/min respectively.

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