

Effects of carbon black on tribology of blends of poly(vinylidene fluoride) with irradiated and non-irradiated ultrahigh molecular weight polyethylene

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Abstract

Friction and wear resistance are two vital tribological properties of polymer-based materials but optimization of both is rarely attempted. We have investigated blends of 70 wt% poly(vinylidene fluoride) (PVDF) + 30% ultra high molecular weight polyethylene, the latter either un-irradiated or else γ -irradiated. Each sample contained varying amounts of carbon black (CB) and also had a varied degree of crosslinking and irradiation dose. We have determined static and dynamic friction, scratch resistance, and sliding wear in multiple scratching tests. Effects of the irradiation dose and CB concentration have been quantified. The electric conductivity threshold is reflected in a drop of static friction; formation of a continuous phase of the lubricant affects tribology as well as electrical properties—both for irradiated and for un-irradiated samples. The scratch resistance as represented by the residual (healing) depth is affected by crosslinking, by the stage at which irradiation is applied (before or after blending) and by CB addition. Crosslinking by moderate amounts of irradiation provides shallower residual depths while higher doses cause adverse results. Similarly, the CB lubricant can either improve or worsen the scratch resistance. A combination of both approaches produces either better or else worse results than crosslinking alone. Lower friction seems accompanied by higher scratch resistance. A combination of a specific irradiation dose and an optimized CB concentration lowers the sliding wear significantly. Strain hardening in sliding wear determination takes place for all materials studied, irrespective of the extent or radiation-induced crosslinking and of the presence and concentration of carbon black.

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1. Introduction

As discussed by Garbassi and Occhiello [1], the

application of polymer-based materials (PBMs) in an increasing number of fields requires also a better understanding and a better control of their surface properties. As also noted by these authors, there are at least two complicating factors. The first is dependence of surface behavior not only on temperature but also on time—in contrast to metal or ceramic surfaces. The second factor according to Garbassi and Occhiello constitute ‘the restrictions and constraints that the three-dimensional macromolecular chains have to satisfy for accommodating at and near the surface layer’.

Another complication arises in moving components and structures used in industry (as well as in everyday life) which require periodical replacement because of wear. The problem has been eloquently discussed in a book by

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Rabinowicz [2]. Wear is defined as the unwanted loss of solid material from solid surfaces due to mechanical interaction [2,3]. Metal components undergo replacement also for another reason, namely corrosion. A way out is the substitution of a metal part by one made from a different material. Given the brittleness and rigidity of ceramics, PBMs are used more and more to replace metal components. This, however, brings about a new problem: polymer surfaces are softer and undergo wear more easily than metal surfaces.

The situation characterized above behoves us to develop new PBMs with improved wear resistance as compared to ordinary plastics. Generally, wear is attributed to either high friction or else to low scratch resistance. It is still often believed that one can provide either low friction or high scratch resistance but not both. Actually, we have shown for a commercial epoxy that addition of a fluoropolymer results in lowering friction [4] and also increasing scratch resistance [5]; both these kinds of properties are also related to the surface tension [6]. Given the results achieved by blending with a fluoropolymer, we have also followed a route of fluorination; for fluorinated poly(methyl methacrylate) (PMMA) a lowering of dynamic friction in comparison to the usual PMMA has been achieved [7]. A still different option consists in using external lubricants. The Cartagena group has demonstrated that monomer liquid crystals (MLCs) lower the pin-on-disk wear of aluminum disks vs. steel balls [8]. We have used the same MLCs as in [8] and achieved lowering of static and dynamic friction of polystyrene (PS) and styrene/acrylonitrile (SAN) against stainless steel or polytetrafluoroethylene (PTFE) [9]. The MLCs also increase the sliding wear resistance of PS, SAN and Polyamide 6 [9].

We report in this paper another approach to lower friction and improve scratch resistance of selected PBMs—but this time by addition of carbon black (CB). The present work is based on earlier results by two of us [10] on blends of 70 wt% poly(vinylidene fluoride) (PVDF) + either 30% of ultra high molecular weight polyethylene (UHMWPE), or 30% of crosslinked UHMW polyethylene obtained by application of γ radiation (XL-UHMWPE). In all cases varying low amounts of CB were added. PVDF is a flexible polymer; addition of CB has been found to increase stiffness and also to increase the electric conductivity above a certain CB concentration threshold [10].

A continuous phase of UHMWPE or XL-UHMWPE exists within the PVDF matrix. Both types of polyethylene are joined at their boundaries, forming a cluster embracing the PVDF matrix; this implies a co-continuous morphology, although in some locations PVDF actually occurs as a dispersed phase inside small UHMWPE or XL-UHMWPE regions [10]. Carbon black is attracted to the PE phase rather than the PVDF phase. Due to the high viscosity of PE, CB is unable to penetrate the PE phase and thus settles preferentially at the surface [11,10]—until the percolation threshold of CB is reached so that the CB regions also

become continuous. Given the similarities between CB and graphite, we have expected a lubricating effect of the former. If this were the case, settling of CB at the surface would be a desired effect.

While the present paper is devoted to tribology, we have already mentioned the electric resistivity of our materials. A sharp resistivity increase with increasing temperature is observed near the melting region of the semicrystalline polymer matrix [12,13]. A common explanation is breaking up conductive paths because of expansion which accompanies approaching melting. Materials with this property can be used as self-regulating heaters, current limiters, over-current protectors, microswitches and sensors—as discussed for instance by Boiteux et al. [14]. The materials we investigate exhibit reproducibility of their electrical conductivity in heating/cooling cycles [15,10], an effect which can be related to crosslinking and the resulting inhibition of rearrangement of filler particles. The temperature ranges in which the resistivity increases with increasing temperature are seen are quite wide [10].

Tribological and other surface properties are significantly affected by the surface morphology [1,3,16]. Blending, chemical modification, irradiation and the use of additives can be looked upon as ways to affect that morphology.

2. Experimental

2.1. Sample preparation

Crosslinking of PE was performed by means of gamma irradiation with a ^{60}Co source at the Department of Chemical Engineering of Technion [17,10]. A combination of γ irradiation of the UHMWPE powder prior to blending (0.064 MRad/h) and of the sample after blending was applied to create samples which we denote XL-UHMWPE.

Blends were prepared by mixing an electrically conductive dry CB and UHMWPE or XL-UHMWPE + PVDF in a Brabender Plastograph at 235 °C. Samples with varying CB content levels were thus made: 1.0, 1.33, 1.67, 3.0 and 4.0 phr (parts per hundred) CB for 70% PVDF + 30% UHMWPE; 0.5, 1.0, 1.5 and 4.0 phr CB for 70% + 30% XL-UHMWPE.

2.2. Friction determination

Tests were performed in the same way as before [4] with a friction attachment to a SINTECH II mechanical testing machine. A 4.5 kg load cell and a sled with the nominal weight of 700 g were used. The testing speed was 150 mm/min. A polished stainless steel surface was used. Resistance to initial and then continuous movement were determined as static and dynamic friction, respectively (the term friction coefficients is often used). The results reported here are the

averages of at least six tests per sample surface conducted at 24 °C.

2.3. Scratch resistance determination

In the beginning of this paper we have argued the vital importance of improving wear resistance of relatively soft and thus easily scratched surfaces of PBMs. We apply two techniques for determination of the effects involved. In both cases we use a Swiss micro-scratch tester with the depth resolution of ± 7.5 nm. The scratch speed is 5.33 mm/min with the length of 5.00 mm. A diamond indenter with the point radius of 200 μm is applied. All results reported are averages obtained at 24 °C. Details are provided in [5] and [18]. The first type of testing we perform is a single pass scratch. It consists of a pre-scan at a very low load (0.03 N) which shows the topology of the surface and provides a baseline; a scratch proper which provides the instantaneous penetration depth R_p ; and a post scan 5 min later, again at 0.03 N, which provides the residual depth R_h . In all viscoelastic materials investigated we have found scratch recovery or scratch healing, so that $R_p > R_h$. The final depth value, that is R_h , is reached inside of 3 min in all PBMs. We have defined [5] the extent of the viscoelastic recovery as

$$\phi = (1 - R_h/R_p)100\% \quad (1)$$

A multiple scratch test along the same groove is used to determine sliding wear [17]. Fifteen scratches at a constant force (5.0, 10.0, 15.0 and 20.0 N) in the same location were applied continuously to each sample in the wear test. Test points from every 0.5 mm of the scratch length were averaged to achieve the value representing each of the 15 runs.

3. Friction results

Fig. 1 shows the results for 70% PVDF+30% UHMWPE as a function of the CB concentration. It is

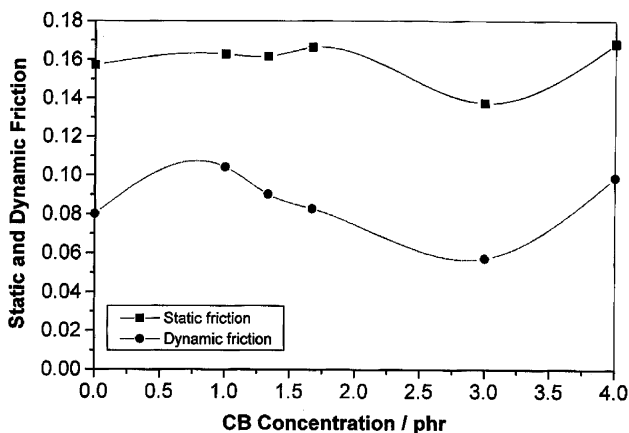


Fig. 1. Friction results for 70% PVDF+30% UHMWPE as a function of CB concentration.

obvious that the simple rule ‘put in more additive to get better results’ does not work. The addition of up to 1 phr CB (for dynamic) and up to 1.5 phr (for static) only increases both kinds of friction. However, around 3 phr minima are seen. Further addition of carbon black causes again the increase of friction.

The results in Fig. 1 can be explained by various surface morphologies created at the different concentrations of CB. When first adding CB, tiny bumps, grooves, and ridges appear on the surface—what is reflected in higher friction values. We recall that, due to the high viscosity of UHMWPE, CB is unable to penetrate and consequently settles at the surface [10,11]. Scanning electron microscopy (SEM) results show a shell 3–5 μm thick consisting of CB particles embedded in the PE surface while the PE inner core is completely free of CB [10]. At the same time, electric conductivity results for the UHMWPE containing materials show the percolation threshold around 1.8 phr [10]. It is at this concentration that both static and dynamic friction in Fig. 1 begin to fall; carbon black at the surface apparently begins to perform its job of lubrication. However, above 3 phr both static and dynamic friction increase again. We recall here the results for an epoxy+a fluoropolymer such that the minority phase becomes the matrix [4]. A possible explanation of the ascending regions on the right hand side of Fig. 1 is that now UHMWPE forms the bumps, grooves and ridges between the CB regions.

Fig. 2 shows similar graph curves as Fig. 1 but now for crosslinked PE. In comparing the static friction from Figs. 1 and 2, the curves qualitatively are similar. The descending region, however, appears much earlier, around 0.6 phr of CB. Fig. 2 in [10] is important here; it shows that the percolation threshold for XL-UHMWPE appears at the same concentration. A redrawing of Fig. 2 from [10] is shown below as Fig. 3. Comparing Figs. 2 and 3, we see that also here there is the chain of connections between formation of a continuous CB phase: drop in electrical resistivity is accompanied by a drop in static friction. For higher CB concentrations the drop is followed by an

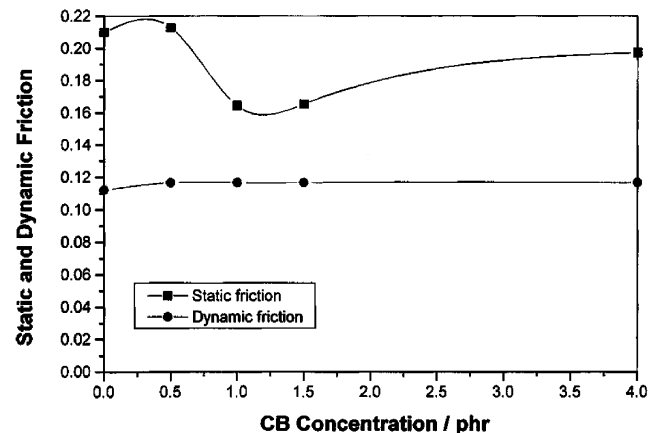


Fig. 2. Friction results for 70% PVDF+30% XL-UHMWPE as a function of CB concentration.

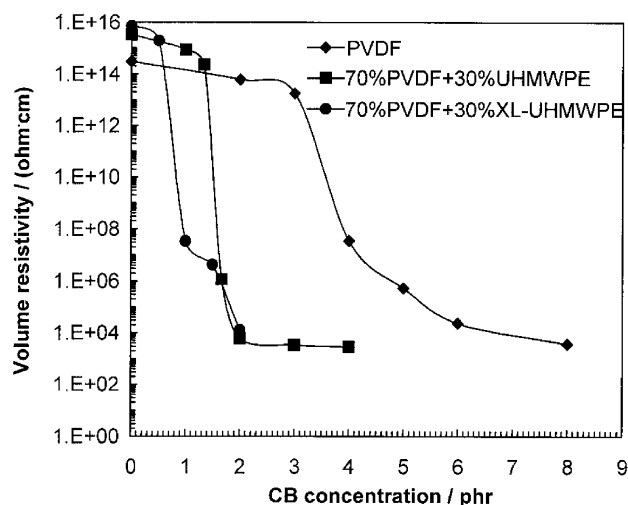


Fig. 3. Volume resistivity of various PVDF+PE blends as a function of CB concentration.

ascending part of the curve—again as we have seen for un-irradiated PE. In other words, the connection between electric resistivity and static friction is independent of irradiation—or otherwise—of the samples.

In the case of the dynamic friction the changes with CB concentration in Fig. 2 are slight. Apparently, once the movement on the crosslinked surface has been initiated, the presence of CB makes very little difference, while overall the values are higher than for the uncrosslinked PE. Higher values for XL-UHMWPE are also observed for the static friction.

Given effects of crosslinking seen comparing Figs. 1 and 2, we need to consider them more in detail. Accordingly, in Fig. 4 we display friction curves vs. the γ irradiation dosage for the 1.67 phr CB sample. Up to 10 MRad or so the dynamic friction remains virtually unchanged—while the static friction increases slightly. At too high a dosage such as 20 MRad the friction is significantly higher than for the un-irradiated material. As discussed for instance by Dawes

and Glover [19], there are two main structural effects of irradiation: bond cleavage and crosslinking. The former is detrimental, the latter beneficial for the structural integrity and dimensional stability of the material. Large amounts of bond cleavage are also known to cause brittleness—what can explain the increases in both static and dynamic friction seen in Fig. 4. The figure includes also points represented by asterisks corresponding to a material treated differently: UHMWPE alone was first crosslinked at 15 MRad and then melt-blended. We see that this different procedure results in lower dynamic friction, while the static friction lies below the curve for the samples which were irradiated after blending. Since PE is the component that undergoes crosslinking, apparently the irradiation effect is stronger when applied to PE alone before blending with PVDF, and the resulting friction lowering is larger too. We have thus learned one more useful lesson; the results such as displayed in Fig. 4 give us the capability to optimize the blend properties with respect to the CB content, the irradiation dose and the stage at which irradiation is applied.

4. Single scratching results

Fig. 5 shows the average penetration depth of the samples as a function of the applied force. The results shows that the blend containing 1.67 phr CB irradiated at 10 MRad was penetrated the least by the indenter. The worst results are seen for the 1.0 phr CB 20 MRad irradiated sample. The high irradiation dose which causes high friction values also causes the deepest penetration. We recall again the discussion in [6] showing that low friction is accompanied by low scratching depths. As already mentioned, that study was performed for epoxy+fluoropolymer systems, this given a very wide range of applications of epoxies [20]. Apparently the friction—scratching connection appears in the systems presently studied also. The second deepest

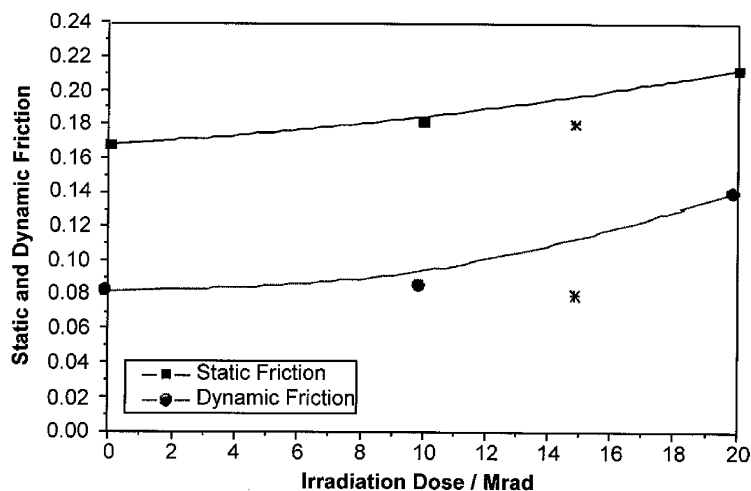


Fig. 4. Friction results vs. the γ irradiation dosage.

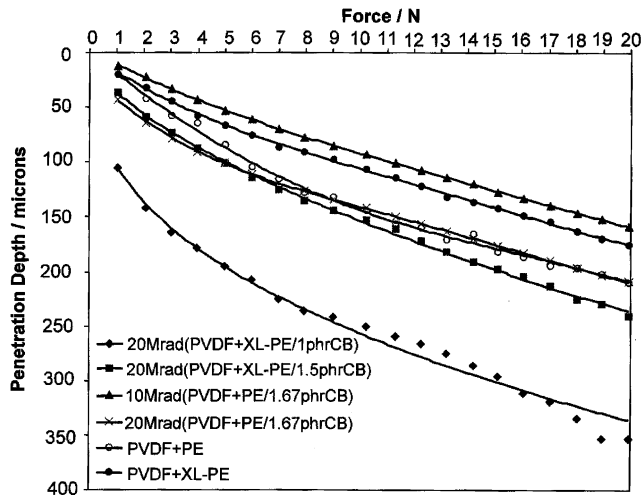


Fig. 5. Single scratch penetration depths as a function of the applied force.

curve is for the 1.5 phr CB 20 MRad sample; more CB helps, but the high irradiation dose still hurts.

In Fig. 6 we show the healing or residual depths, also vs. the applied force. We find that the same 1.67 phr CB and 10 MRad irradiated sample has also the shallowest R_h . The deepest values are also here for the samples which received the highest irradiation dose of 20 MRad.

As already noted, crosslinking can harm the sample through polymer degradation or do the opposite by improving properties such as our scratch resistance—depending on the material, the irradiation source and dose. We compare the XL samples with the uncrosslinked ones in Fig. 7. A significant result is seen: crosslinking does in fact improve scratch resistance. The pure uncrosslinked sample shows the deepest R_h values practically for the whole range of applied forces. The XL samples have significantly lower residual depths.

However, also here the irradiation is a two-edged sword.

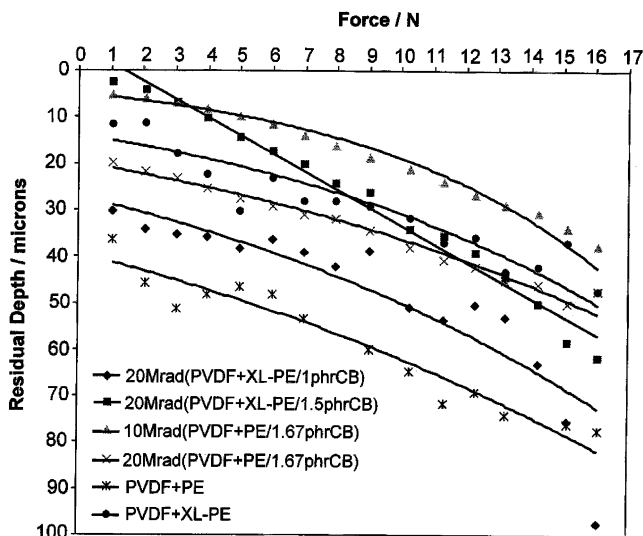


Fig. 6. Single scratch residual depths as a function of the applied force.

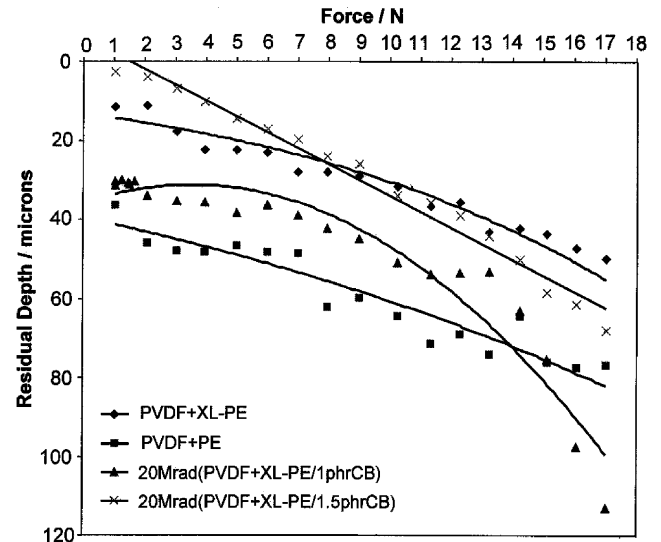


Fig. 7. Effects of crosslinking on the single scratch residual depths as a function of the applied force.

Thus, the curve in Fig. 7 for 1.0 phr CB and 20 MRad has deeper residual values than the crosslinked sample without CB, but over most of the force range shallower than the sample which received no irradiation. Addition of 1.5 phr CB to the blend irradiated at 20 MRad results in shallower R_h values than the curve for crosslinked PE with 1.0 phr CB. Starting with the deepest curve for uncrosslinked and no CB sample, we find we have two ways of improving the scratch resistance: moderate crosslinking and/or CB addition. Combination of both approaches produces either better or else worse results than crosslinking by irradiation alone. Thus, each of these two variables can be useful if manipulated with caution.

5. Sliding wear results

We have reported in [18] a discovery of strain hardening in sliding wear for three polymers. Multiple scratching along the same groove results in less and less penetration and residual depth changes between the consecutive scratches. After 8–10 scratches, both R_p and R_h plotted as a function of the number of tests performed reach horizontal asymptotes for a given applied load; further scratches do not affect the depth. It was of course quite interesting to find out whether the phenomenon is widespread. Subsequent investigation of five more polymers have shown strain hardening in four of them, with polystyrene as the only exception [21,22]. In the preceding paper [9] we have demonstrated that the addition of only 1 wt% of a MLC makes PS to fall into line, that is to show strain hardening also. To continue this, we have subjected the samples studied in the present work also to sliding wear multiple scratch tests.

We have determined sliding wear under the applied loads

of 5.0, 7.5, 10.0, 12.5, 15.0 and 17.5 N. For brevity we present here results for 5.0 N in Fig. 8 and for 15.0 N in Fig. 9. Inspection of Fig. 8 tells us that the pure blend (70% PVDF+30% UHMWPE, no CB, no irradiation) shows the worst wear resistance by far, with the residual depth values between 160 and 190 μm . However, this sample—as well as curves for all the samples investigated—show strain hardening.

The sample with the least wear contains 1.67 phr CB and was irradiated at 20 MRad. The 1.67 phr CB sample irradiated at 10 MRad follows closely, its sliding wear resistance W for the applied force F which we have defined [18] as

$$W(F) = \lim_{n \rightarrow \infty} R_h(F) \quad (2)$$

is almost the same; here n is the number of tests.

At 15.0 N in Fig. 9 we see something not seen in Fig. 8: addition of 1.0 phr CB combined with 20 MRad irradiation results in sliding wear worse than for the un-irradiated and 0 phr CB blend. Thus, once again irradiation and CB addition constitute two-edged swords. As in Fig. 8, irradiation at 10 MRad with 1.67 phr CB contents provide significant improvement over other samples, including the blend without CB. In this case the 1.67 phr CB and 20 MRad sample shows worse wear resistance than the irradiated blend without CB. Again here as well as under other constant force values we have applied (results not displayed for brevity), all curves exhibit strain hardening in sliding wear tests.

6. General discussion

Interesting connections between electrical, tribological and mechanical properties begin to emerge. It was noted in [10] that the addition of carbon black results in increased

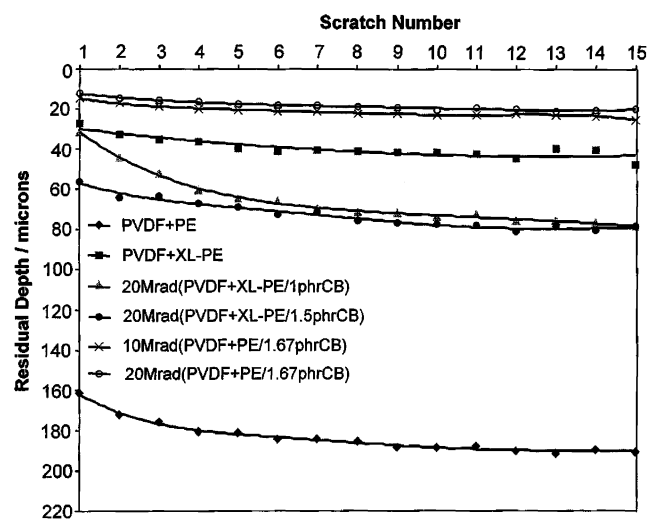


Fig. 8. Residual depths as function of the number of tests in sliding wear determination for 5.0 N.

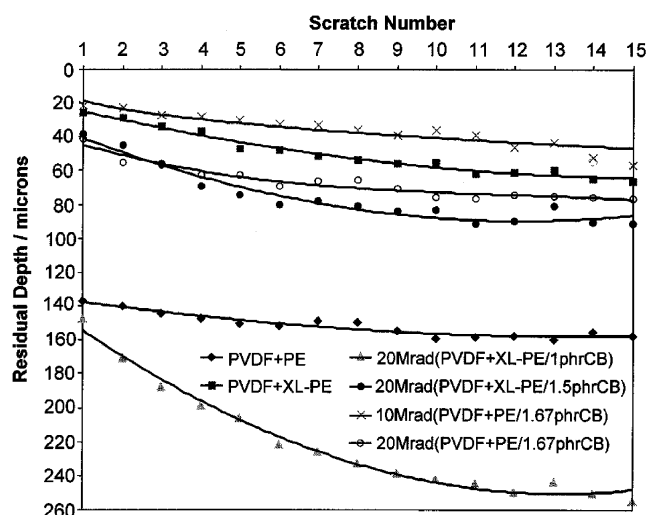


Fig. 9. Residual depths as function of the number of tests in sliding wear determination for 15.0 N.

stiffness of PVDF+UHMWPE blends. Similarly, Barrios and Garcia-Ramirez [23] report that addition of CB to styrene/butadiene rubber (SBR) copolymers results in between 100 and 300% increase in tensile modulus. We have demonstrated above that at the electric conductivity threshold the formation of a continuous surface CB phase results in a lubricating effect and a drop of friction.

In Fig. 6 we see shallower residual depths in single scratch tests for 1.67 phr CB and 10 MRad sample compared to the 20 MRad sample with the same CB concentration. Return now to Fig. 4 which pertains also to materials containing 1.67 phr CB. We see higher static and dynamic friction values for 20 MRad compared to 10 MRad. A similar connection between friction and scratching results has been pointed out above discussing Fig. 5—and fits again with results for a commercial epoxy with a fluoropolymer additive [4–6].

The phenomenon of strain hardening in sliding wear determination, discovered for three polymers in [18] and confirmed for four more in [21,22] appears in all PBMs investigated in the present work: crosslinked and uncrosslinked, with and without CB addition, and for all forces applied. Thus, polystyrene without a lubricant [21] remains the only exception.

Experimental determination of behavior under application of a scratching indenter provides us with two numbers, as discussed above: the instantaneous or penetration depth R_p and the residual or healing depth R_h . By performing molecular dynamics computer simulations [24] it is possible to obtain a continuous dependence of the scratching depth R as a function of time t . Each $R(t)$ curve includes necessarily R_p (the lowest point) and R_h (the asymptote). It is by a combination of experiment and understanding coming from computer simulations that we shall be able to obtain PBMs with lower friction and higher scratching and wear resistance.

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