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New Nanoindentation and Nanoscratching Parameters of Thermoplastics

M. R. Naimi-Jamal,[1] *G. Kaupp*[2]

Summary: The determination of hardness and modulus values from unloading curves in nanoindentations is particularly troublesome with thermoplastic polymers and the values can strongly depend on the maximal normal force. Quantitative analysis of the loading curves provides reliable nanoindentation coefficients k (μN nm$^{-3/2}$) as the slopes of linear plots that reliably characterize the pristine polymers and are potent interpolation tools. Kinks in the linear plots (here not observed with isotactic polypropylene (PP-it)) indicate plastic-viscoelastic transformations and separate the characterization of the degraded polymer with the smaller nanoindentation coefficients from the pristine polymer. The quantitative analysis of the correct relation between lateral and normal force in nanoscratching reveals the coefficient K (μN$^{-1/2}$) as a basic extrapolation tool with direct and quantitative access to scratch resistance as a measure for wear that replaces the unfounded and never constant so-called "friction coefficient F_L/F_N". The linear plots of the correct relation between lateral and normal force reveal the occurrence of plastic-viscoelastic transformations most distinctly by a kink and two linear ranges.

Keywords: atomic force microscopy (AFM); chain breakage; mechanical properties; nanoindentation; nanoscratching; thermoplastics

Introduction

Nanomechanical parameters such as hardness H and reduced elasticity modulus E_r of thermoplastic polymers are difficult to obtain according to the ISO 14577 norm[1] and they contain large undefined systematic errors.[2] The analysis of unloading curves is only possible after several unload/reload cycles that change the polymer until an apparently stable state is reached and the initial "noses" with negative initial slope have disappeared. The area function of the diamond indenter, which is needed for the calculation of H and E_r, is determined on fused quartz and applied to the indentation of the polymer with totally different indentation geometry and despite totally different properties of the unrelated materials. The values of H and E_r must be calculated with both a three- and an eight-parameter iteration step. They are not constant at some thermoplastics but depend on the maximal normal force F_N and the scatter of the values is large. Furthermore, the ISO norm does not care for the size of the exponent in the iterated power function for the corrected unloading curve. This exponent assumes values between 1 and 3 and even changes in that range when the final end-point of such iteration is changed. This lack of physical meaning of the unloading curves has also been shown in the absence of viscosity effects with the ceramic SrTiO3 in Reference [2]. Much better procedures are the quantitative analysis of the loading curves or the correct analytical treatment of nanoscratching results. It is important that new quantitative

[1] Faculty of Chemistry, Iran University of Science and Technology, 16846 Tehran, Iran
E-mail: naimi@iust.ac.ir
[2] University of Oldenburg, Diekweg 15, 26188 Edewecht, Germany
E-mail: gerd.kaupp@uni-oldenburg.de

relations between normal forces F_N and the penetration depths h of the loading curves in nanoindentations (equation (1)) and between lateral force F_L and normal force F_N in constant-force nanoscratchings (equation (2)) have been found and multiply validated. These relations allow for linear analyses in terms of universal indentation coefficients k ($\mu N\ nm^{-3/2}$) and scratching coefficients K ($\mu N^{-1/2}$) that are potent extrapolation tools and do not rely on assumptions or iterations. Furthermore, the linear plot analyses allow for detections of phase transformations if kinks occur in the linear plots, most sensibly in the nanoscratching experiments. Previous assumptions used an exponent 2 for the nanoindentation loading curve that was never experimentally found, and an exponent 1 for the nanoscratching curve (by defining the so called ''friction coefficient F_L/F_N'') that never was a constant. Unfortunately these invalid assumptions were nevertheless used for various mathematical deductions of further parameters that were challenged in Reference[2]. We apply the new experimentally secured equations (1) - (3) to common thermoplastics and discuss the chain breaking under mechanical stress of linear PMMA, PC, PP-it, and crosslinked CR39.

Experimental Part

A Hysitron Inc. TriboScope® Nanomechanical Test Instrument with a two-dimensional transducer, leveling device and complete software in combination with a blunt ($R = 200$ nm) three-sided diamond indenter was used. The indented surface was firmly mounted on an AFM stage of a Nanoscope III instrument for direct measurement of the initial surface (suitability and slope correction) and of the final impression, using the same indenter tip (though with some tip sample convolution). The Triboscope recording unit with transducers and leveling device was placed on top of the NanoScope III E $164 \cdot 164\ \mu m^2$ XY piezo scan base for that purpose. More detailed AFM images were obtained with Si_3N_4 cantilever tips. Load and unload times were 10 s, holding times 30 s at the indentations. Constant force edge-in-front nanoscratchings of 5 μm length were performed in 30 s at constant rate after the initial indentation. Test experiments indicated no significant changes of results if the times were halved or doubled. The F_L, effective F_N and depth values were averaged with Excel software from the central 67% of the scratching traces that were automatically recorded. The polymers were air-conditioned injection molded polymethyl methacrylate (PMMA) and polycarbonate Makrolon® (PC) or molded CR39 (polymer from diethyleneglycol bisallylcarbonate) lens materials from Leitz, Wetzlar, and a grade 080 isotactic polypropylene (PP-it) from Imam Khomeini Petroleum Co, Tehran.

Nanoindentation

It is important that quantitative relations between normal forces F_N and the penetration depths h of the loading curves have been experimentally found and multiply validated in nanoindentations. The common previous assumptions of an exponent 2 for the load – penetration depth curve have never been experimentally realized in nanoindentations with pyramidal and conical tips. The experimental result is consistently the relation of equation (1) with the exponent 3/2 in nanoindentations with pyramidal diamond tips on all kinds of solid materials.[2–3]

$$F_N = k\, h^{3/2} \tag{1}$$

Thermoplastic polymers are soft and experience much creep, sagging, and plastic flow. The nanoindentations into these polymers are therefore best performed very rapidly and with a blunt cube corner exhibiting a sharper effective taper than a Berkovich indenter. The initial unloading curves in Figure 1 of the three polymers start with ''noses'' (negative slopes) that are

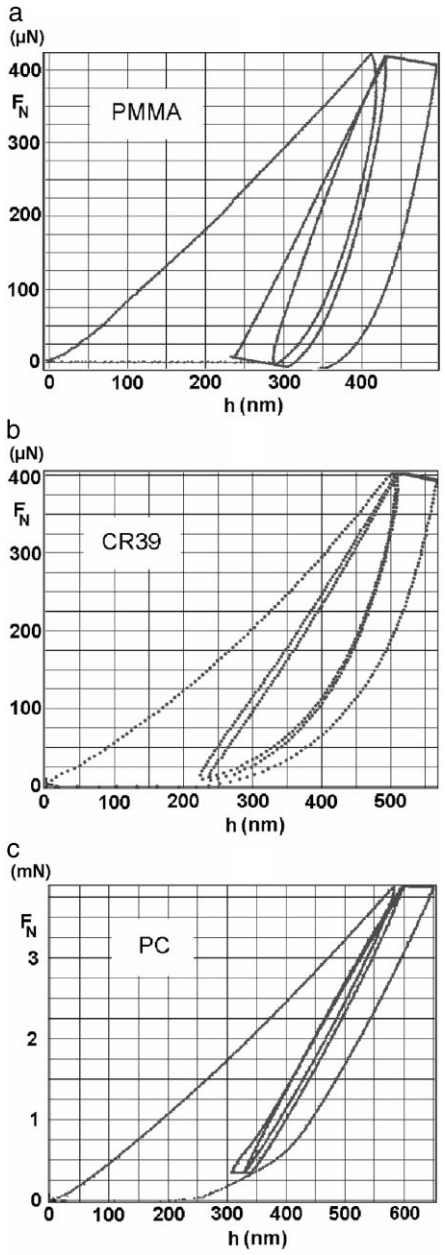

Figure 1.
Load and multiple unloads/reloads to/from 10% of the maximal load on the linear PMMA (a) and PC (c) or cross-linked CR39 (b) in F_N–h diagrams; load and unload times are 10 s, waiting times after second reload are 30 s.

impossible for the iteration of H and E_r values. Positive slopes are only obtained after several hysteretic unload/reload cycles and after holding periods until a ''stable viscoelastic behavior'' is reached. However such usage is still troublesome, as longer holding times would further change the initial slope of the unloading curve due to the sagging and creep features during the holding period, rendering any H and E_r values of the changed polymers additionally uncertain. All of these features show that the polymers are chemically changed by chain breakings[4–5] and stabilizations of the macroradicals by disproportionation to give shortened chains,[6] until these become too short for further mechanical chain breaking. Such local plastic-viscoelastic transformations will be distinctly revealed by the analyses of the loading and scratching curves below, if they occur by main chain or polymer network ruptures due to mechanical stress. The unloading and reloading curves are dissimilar in PMMA, PC and CR39 but the shape of the final unloading curve of PP-it (Figure 2) resembles the one in Figure 1b (smooth approach

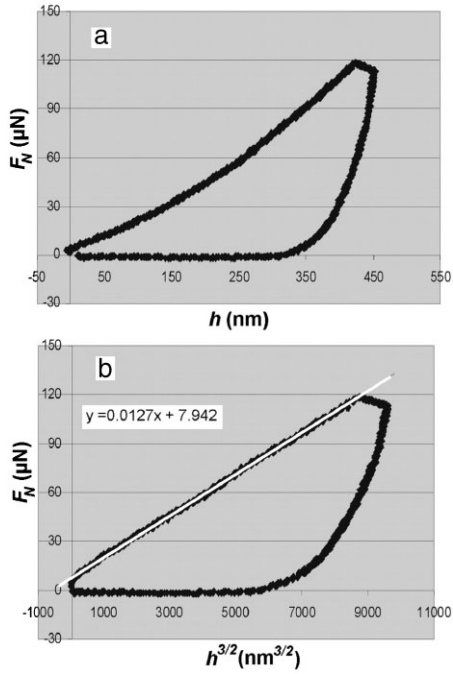

Figure 2.
Load and unload curves (a) and F_N–$h^{3/2}$ plot (b) on PP-it of the 10/30/10 s cube corner nanoindentation.

of the baseline without going below it as in Figure 1a where adhesion occurs). Interestingly the penetration depth of linear PC differs strongly from linear PP-it (Figure 2), PMMA and cross-linked CR39. This is certainly related to the readiness for mechanical bond breaking and mobility of the chains, but not easily predicted.

If the mechanical properties of pristine polymers (but not of their changed viscoelastic states at maximal load as mostly with H and E_r) are to be compared, the loading curves must be analyzed, but we also report here the more common H and E_r values according to the ISO 14577 norm, despite their questionable reliability.

Quantitative Nanoindentation

The loading curve of PP-it is most easily analyzed according to equation (1), as it does not exhibit a kink in Figure 2b. The excellent linearity of the F_N–$h^{3/2}$ loading plot almost through zero indicates very low disturbance by uppermost surface effects and the slope is the small indentation coefficient k of 0.0127 μN nm$^{-3/2}$ that reflects deep penetration, high work of indentation and absence of phase transformation in that range.[2] The iterated values of H and E_r under these conditions are 0.10 GPa and 1.8 GPa, respectively.

The nanoindentation on PC under the same conditions gives a F_N–$h^{3/2}$ plot with a kink. Two ranges of linearity exhibit different slopes: $k_1 = 0.441$ for the pristine polymer and $k_2 = 0.295$ μN nm$^{-3/2}$ for the transformed polymer (Figure 3a). This detects the plastic-viscoelastic phase transformation due to chain breakages[2] at a comparatively high normal force F_N and a penetration depth h of only 112 nm. The invalid non-linear trial plot (Figure 3b) with the incorrect exponent 2 is curved.

A similar situation than in PC is encountered with PMMA in its F_N–$h^{3/2}$ plot, though with the kink at a much lower F_N value and a penetration h of 140 nm (Figure 4a). The indentation coefficient for the pristine polymer is $k_1 = 0.0714$ the

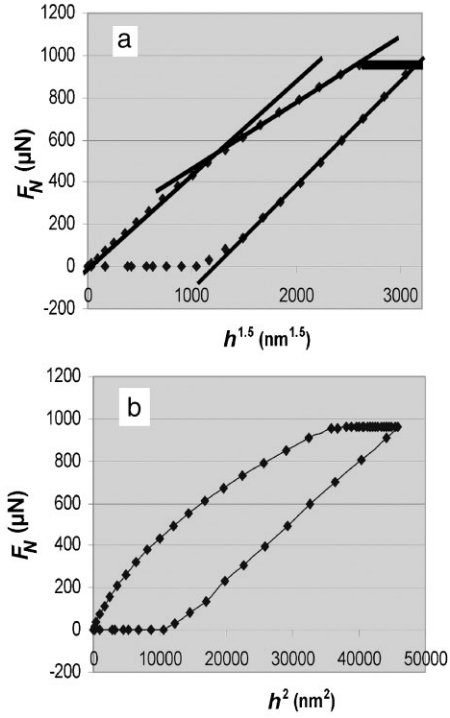

Figure 3.
Loading and unloading plots of a cube corner nanoindentation on PC; (a) F_N–$h^{3/2}$ plot exhibiting two straight lines and a kink in the loading curve that is not seen in the invalid F_N–h^2 trial plot.

one for the transformed polymer $k_2 = 0.0536$ μN/nm$^{3/2}$. Again the invalid trial plot (Figure 4b) with incorrect exponent 2 cannot trace the important plastic-viscoelastic phase transformation due to chain breakages.

Interestingly, the cross-linked polymer CR39 exhibits its kink at still smaller normal force F_N and lower penetration depth of 119 nm (Figure 5a) than PMMA. This is a consequence of less flexibility in the cross-linked than in the linear polymer. The pristine CR39 gives $k_1 = 0.0489$ and the transformed polymer $k_2 = 0.0339$ μN/nm$^{3/2}$. Again the invalid trial plot (Figure 5b) fails due to the incorrect exponent.

The Figure 2–5 clearly show the validity of equation (1) by linear plots also for thermoplastic polymers, despite creep and sagging at rapid indentation, while trial plots with the incorrect exponent 2 for

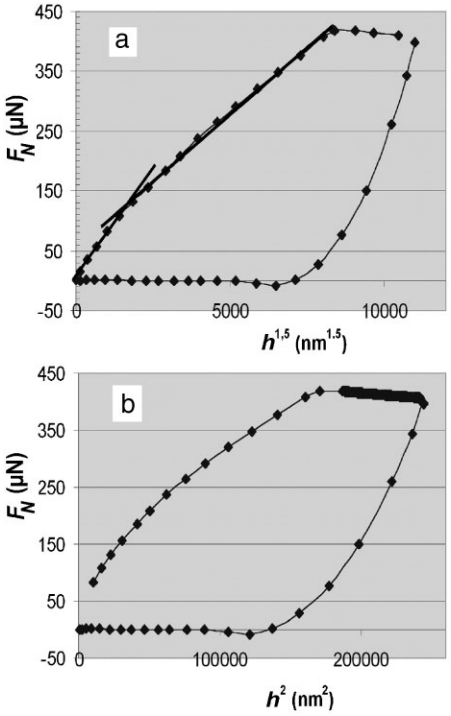

Figure 4.
Loading and unloading plots of a cube corner nanoindentation on PMMA; (a) F_N–$h^{3/2}$ plot exhibiting two straight lines and a kink in the loading curve that is not seen in (b) the invalid F_N–h^2 trial plot.

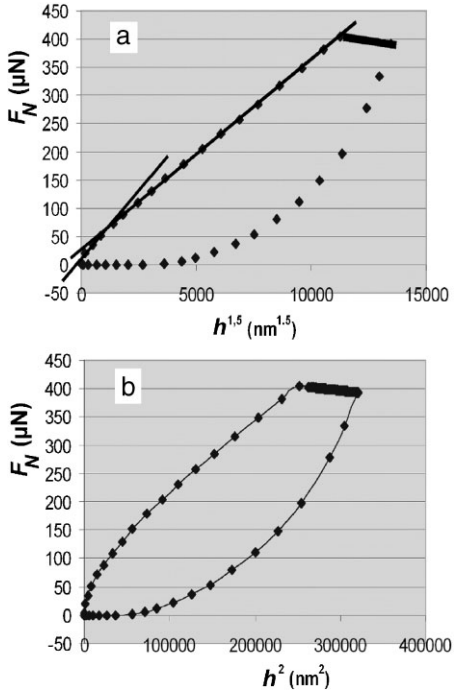

Figure 5.
Loading and unloading plots of a cube corner nanoindentation on CR39; (a) F_N–$h^{3/2}$ plot exhibiting two straight lines and a kink in the loading curve that is not seen in the invalid F_N–h^2 trial plot.

nanoindentations totally obscure the plastic-viscoelastic transformation feature as detected by two linear ranges with different slopes in the correct plots. The nanomechanical data are collected in Table 1 that contains also the still more common (though unreliable for the reasons given) values of H and E_r according to the ISO norm. The assumptionless k-values allow linear extrapolations for the penetration depths as a function of the normal force for the given indenter, but it is also possible to transfer the extrapolation capability to other indenters with different opening angles (e.g. Berkovich indenter), if the respective k-values are divided by the tangent of the effective cone angle and minor empiric corrections are made for the final tip radius and other imperfections.[2] The variation of the k_1 values of the pristine polymers is considerable (factor 35). This reflects the flexibility of the chains, the partial crystallinity, and the varying readiness for bond breakage as the tip is forced to penetrate. The highest flexibility is available in the hydrocarbon PP-it, which does not require significant bond cleavages up to more than 400 nm penetration depths. The k_2 values after local breakage of chain bonds and disproportionation are smaller than the k_1 values, because the shorter chains or broken networks provide easier penetration.

Table 1 also contains the total work of indentation as obtained by integration of the loading curve up to the given F_N values for comparisons. PP-it without significant chain breakage has a low value upon deep penetration, while PC, PMMA and CR39 providing kinks in their F_N–$h^{3/2}$ plots exhibit an almost linear relation between W_{Ntot} and penetration depth h at the same F_N value.

Table 1.
Comparison of cube corner nanoindentation parameters on thermoplastic polymers.

Polymer	F_N (μN)	$H^{a)}$ (GPa)	$E_r^{a)}$ (GPa)	h (nm)	W_{Ntot} (μNμm)	k_1 (μN/nm$^{3/2}$)	k_2 (μN/nm$^{3/2}$)	Kink position F_N (μN)/h (nm)
PC	900	3.11	17.9	178	71.02	0.441	0.295	539/112
PC	400	3.16	21.9	93	15.28	0.441		539/112
PMMA	400	0.34	5.25	395	71.69	0.0714	0.0536	122/140
CR39	400	0.285	2.3	500	87.71	0.0489	0.0339	72.6/119
PP-it	120	0.10	1.8	426	22.68	0.0127	–	

[a)]Obtained by the ISO 14577 standard data treatment.

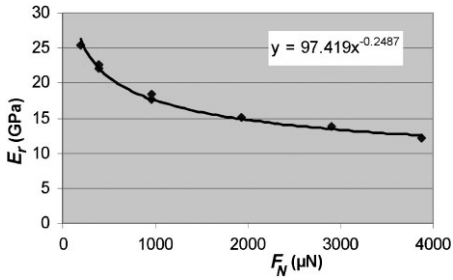

Figure 6.
Dependence of the elastic modulus E_r of injection molded PC (Macrolon®) from F_N in cube corner indentations.

The variations of k_1 in Table 1 reflect the mechanical properties of the pristine polymers. The k_2 values reflect the viscoelastic states. This is also largely the case for the standard H and E_r values. PC is exceptional in both states. Importantly, the H and E_r values as obtained by the standard procedure can be very dependent on the load because of the amount of polymer degradation when starting the unloading experiments at different maximal forces F_N. For example, the E_r-values of PC (as determined by the iterative standard technique) decrease according to a power function when the load is increased (Figure 6) whereas the H-values decrease linearly from 3.18 (200 μN) to 2.88 GPa (4000 μN). Such relations might be of theoretical interest and can serve to eliminate single deviating measurements from consideration.

An exponential behavior was not found with PMMA and CR39 where both standard H and E_r decreased linearly from 200 to 1250 μN load: $H = 0.346$–0.328, E_r 5.28–5.24 for PMMA and $H = 0.286$–0.284, $E_r = 2.5$–2.1 GPa for CR39. The assumption of independence of E_r from the load (standard procedure) is far from being obeyed, particularly with injection molded PC.

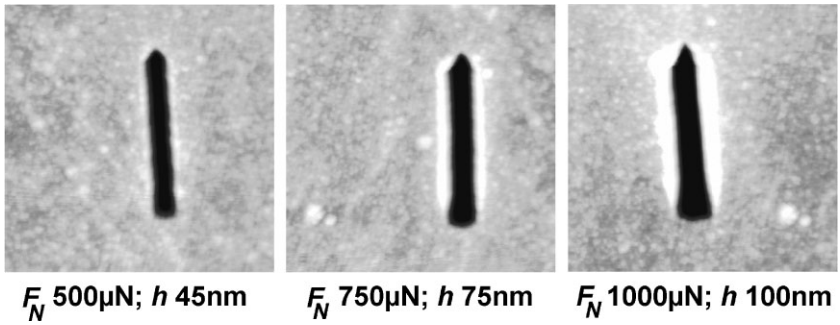

Figure 7.
AFM topologies of PC upon cube corner edge-in-front nanoscratching (5 μm, z-scale 200 nm) at the indicated normal forces F_N and resulting depths h.

Nanoscratching

The thermoplastic polymers exhibit elastic, plastic, viscoelastic, viscoplastic and brittle properties that influence their mechanical properties. Numerous studies on macro- and microscratching have been performed in terms of wear and scratch resistance,[2] however, an understanding at the molecular level has not been advanced. Quantitative nanoscratching provides more information and supplements the results of nanoindentation. Again rapid scratching is essential and a blunt cube corner gives best results for the comparison of the polymers. Figure 7 shows how pileup develops as a function of normal load and thus depth of the scratches on PC (Makrolon®). It can be seen that persistent grooves are formed and that pileup forms increasingly at the higher normal loads. Apparently no or little abrasion occurred under these conditions. Strong mechanical interaction with the long-chain or cross-linked polymers leads to bond breaking creating flow, pileup and abrasion. Despite of that the new general law of equation (2) has been

found for constant force nanoindentations with pyramidal tips and validated for all kinds of solid materials.[2,7] The lateral force F_L (in scratch direction) is sensed by the 2D-transducer of the Triboscope instrument and recorded. The constant K with dimension $[1/\sqrt{\text{force}}]$ and unit $\mu N^{-1/2}$ is obtained as slope from linear plots. It is this scratch coefficient that replaces the previously preferred so-called ''friction coefficient F_L/F_N'', which is not a constant, due to equation (2). Only the quantitative treatment with K from equation (2) is an extrapolation tool that characterizes the mechanics upon nanoscratching (e.g. nonlinearity between normal force and lateral force; scratch work; scratch resistance). The nanoscratching work is lateral force times scratch length; the specific nanoscratching work spec W_{sc} ($\mu N\ \mu m$) is a characteristic parameter. It is equal to F_L times 1 μm according to equation (3). The full scratch resistance $(R_{sc})_{tot}$ is the scratch work divided by the cross-section of the scratch, which can be calculated from the recorded depth and the geometry of the indenter tip leading to proportionalities of $(R_{sc})_{tot}$ and $F_L^{1/3}$ or $F_N^{1/2}$.[2]

$$F_L = K\, F_N^{3/2} \tag{2}$$

$$\text{spec } W_{sc} = F_L \cdot 1 = K \cdot F_N^{3/2} \tag{3}$$

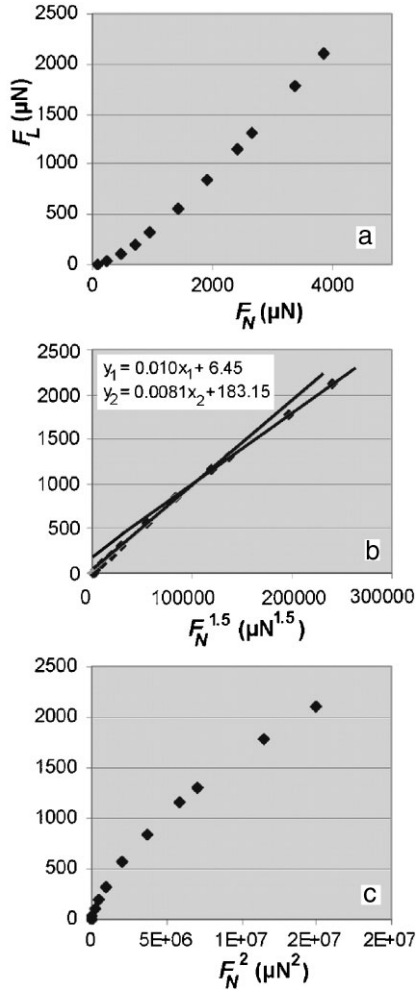

Figure 8.
Edge-in-front cube corner nanoscratching results on PC at various preset constant normal forces F_N; (a) invalid trial F_L–F_N plot; (b) valid F_L–$F_N^{3/2}$ plot with a kink indicating plastic-viscoelastic transformation beyond this point; (c) invalid trial plot with exponent 2 exhibiting curvature.

Importantly, the specific universal nanoscratching coefficient of the materials becomes a different value if a phase transformation (here plastic-viscoelastic transformation) occurs at nanoscratches that are executed beyond a characteristic threshold normal load. Figure 8b shows the validity of the exponent 3/2 in equation (2) because two linear ranges of data points are observed for pristine polymer and after the kink transformed polymer. The corresponding nanoscratching coefficients are the slopes $K_1 = 0.010$ and $K_2 = 0.0081$ $\mu N^{-1/2}$. The kink at $F_N = 2.4$ mN occurs very late. This polymer is very resistant towards mechanical chain breaking, abrasion and wear.

PMMA and CR39 have their kinks in the linear F_L–$F_N^{3/2}$ plots at much lower normal forces of 560 μN and 310 μN, respectively, and the K_1 and K_2 values of Figure 9a and Figure 9b are larger than the ones of PC.

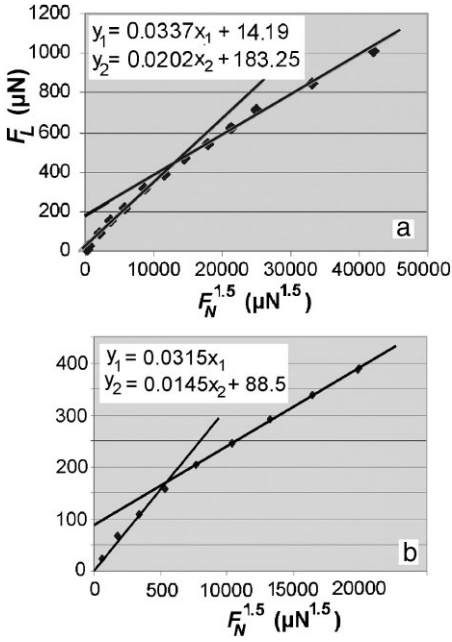

Figure 9.
Edge-in-front cube corner nanoscratching; F_L–$F_N^{3/2}$ plots on (a) PMMA and (b) CR39 showing validity of equation (2) by two linear ranges with the kink indicating plastic-viscoelastic transformation beyond that point.

Table 2.
Edge-in-front cube corner nanoscratching results with PC, PMMA and CR39 with F_N and F_L values at the kink point.

Polymer	F_N (μN)	F_L (μN)	K_1 ($\mu N^{-0.5}$)	K_2 ($\mu N^{-0.5}$)	$b^{a)}$ (μN)
PC	2390	1280	0.0101	0.0081	183
PMMA	570	460	0.0337	0.0202	183
CR39	310	170	0.0315	0.0145	88.5

[a)] intersection of the high pressure line with F_L axis.

This confirms the validity of the results of the nanoindentations with these polymers.

The K values are the basis for extrapolations and ratings. Table 2 collects the data for comparison. PC is very different from PMMA and CR39. The nanomechanical values can be used for extrapolations in the low and high force regions. The intersections b with the F_L axes are also required as the additional terms to equation (3) for the calculation and quantitative extrapolation of the specific nanoscratching work. Further applications and deductions are found in Reference [2].

Conclusion

The still common nanomechanical data of hardness H and modulus E_r are particularly questionable for thermoplastic polymers (also no constancy due to degradation), and the so-called ''friction coefficient'' (F_L/F_N) is not a constant, due to the universal power law of equation (2). Thus wear and scratch resistance remained very qualitative on the basis of wrong assumptions and multiparameter iterations of unloading curves. A much better way is the correct analysis of the loading curves in nanoindentations and the acceptance of the correct relation between lateral and normal force in nanoscratching. Both new approaches provide linear plots with highest reliability. The new nanoindentation coefficient k ($\mu N\ nm^{-3/2}$) and the nanoscratching coefficient K ($\mu N^{-1/2}$), as well as the total nanoindentation work and specific nanoscratching work, allow for quantitative treatments without assumptions and without multiparameter iterations for the first

time.[2] This has now also been validated for thermoplastic polymers. Their plastic-viscoelastic transformation under mechanical stress can be easily detected by both nanotechniques that exhibit two ranges with kink in the linear plots, if it occurs. The reason for such transformation has been discussed in terms of the different readiness of the polymers for chain breaking at the site of mechanical stress until the chains are short and flexible enough for losing their ability of being broken. The cross-linked polymer CR39 suffered bond breakages within its 3D-network at lower applied forces than the linear chain polymers PP-it, PMMA and PC that have their different flexibilities, when the indenter tip goes down or forward. As the viscoelastic effects are time dependent, fast measurements all at the same rate were performed and no significant alterations were observed in test experiments if the rate was halved or doubled. This would however change if massive deviations from these rates were chosen. The numerical data of the parameters are of course dependent on the tip taper, finite radius, and other imperfections. But they can be reasonably transformed to the results with other tips,[2] if comparison with data from other research groups is required.

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