

filler particles with various sizes and filler loads have been added to the monomer resin matrix [10]. Moreover, the most common classification system of dental composites is based on filler particle size: conventional (traditional) (20 – 50 μm), macrofilled (1 – 5 μm), microfilled (0.05 – 0.1 μm), hybrid, [10] and more recently ‘nano’ sized particles (20 – 75 nm). Most of the commercial dental composites are hybrid types, having macrofilled and microfilled particle sizes, in an attempt to improve both the mechanical and aesthetic properties. The smaller the particle size and the higher the loading, the better the resulting material properties. However, as filler size decreases, for the same volume percent, surface area increases which limits the maximum volume percent in resin due to surface area to volume effects.

Dental resins are usually cured (hardened) by photoinitiated free radical polymerization. Camphorquinone (CQ) is a commonly used visible-light initiator and ethyl-4-(*N,N*-dimethylamino) benzoate (4EDMAB) is a commonly used co-initiator. It absorbs specific and narrow visible (blue) light wavelengths from 400 to 500 nm with an optimum peak absorbance at 465 nm. The camphorquinone then transfers to an excited triplet state and initiates the polymerisation process in conjunction with a co-initiator to generate free radicals which initiate the polymerisation process [11,12].

The dental nano-materials which are studied in the present paper are provided by 3M ESPE: Filtek Ultimate Universal Restorative [13], Filtek Supreme XT [14]. For comparison the microfilled Filtek Z250 [15] is also analyzed. Next they will be briefly described, according to the producer technical specifications.

In Filtek Z250 restorative, the majority of TEGDMA has been replaced with a blend of UDMA (urethane dimethacrylate) and Bis-EMA(6)1 (Bisphenol A polyethylene glycol diether dimethacrylate) (fig. 2) [15]. Both of these resins are of higher molecular weight and therefore have fewer double bonds per unit of weight. The high molecular weight materials also influence the measurable viscosity, but it results a less shrinkage, reduced aging and a slightly softer resin matrix. Additionally these resins exhibit a higher hydrophobicity and are less sensitive to changes in atmospheric moisture.

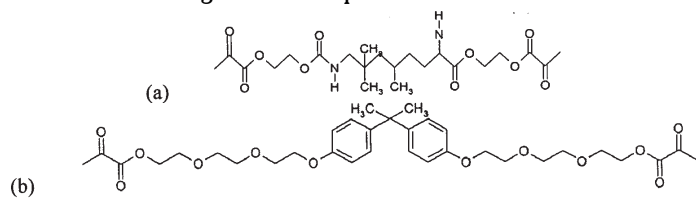


Fig. 2. Chemical structures of UDMA (a) and Bis-EMA(6) (b)

While dental resins have been reinforced with inorganic fillers such as silanized glass/ceramic particles for years, the relatively low strength and durability of the composites have limited their uses [16-19]. For example, in Filtek Z250 composite material, the filler consist in zirconia and silica particles. The particle size distribution is 0.01 μm to 3.5 μm with an average particle size of 0.6 μm . The inorganic filler loading is 60% by volume.

In Filtek Supreme XT Universal Restorative material [14] the resin system is the same reduced shrinkage resin as found in Filtek Z250, but it was discovered a way to modify the sintering process to produce loosely agglomerated nanoparticles, *i.e.* nanoclusters. Although structurally different from densified particles, these nanoclusters behave similarly to the densified particles found in other

composites in terms of providing high filler loading. This resulted in a material with the strength and wear of hybrids with significantly improved polish retention and optical properties. Translucent shades contain a combination of a non-agglomerated/non-aggregated, 75 nm silica nanofiller, and a loosely bound agglomerate silica nanocluster consisting of agglomerates of primary silica nanoparticles of 75 nm size fillers. The cluster size range is 0.6 to 1.4 microns. The filler loading is 72.5% by weight. The Translucent shades are not radiopaque. All of the remaining shades contain a combination of a non-agglomerated/non-aggregated, 20 nm nanosilica filler, and loosely bound agglomerated zirconia/silica nanocluster, consisting of agglomerates of primary zirconia/silica particles with size of 5-20 nm fillers. The cluster particle size range is 0.6 to 1.4 microns. The filler loading is 78.5% by weight.

In Filtek Ultimate Universal Restorative [15] the resin system is slightly modified from the original Filtek Z250 and Filtek Supreme resin. The resin contains bis-GMA, UDMA, TEGDMA, and bis-EMA(6) resins. To moderate the shrinkage, PEGDMA has been substituted for a portion of the TEGDMA resin in Filtek Supreme XT restorative. The fillers are a combination of non-agglomerated/non-aggregated 20 nm silica filler, non-agglomerated/non-aggregated 4 to 11 nm zirconia filler, and aggregated zirconia/silica cluster filler (comprised of 20 nm silica and 4 to 11 nm zirconia particles). The Dentin, Enamel and Body (DEB) 3 shades have an average cluster particle size of 0.6 to 10 microns. The Translucent (T) 4 shades have an average cluster particle size of 0.6 to 20 microns. The inorganic filler loading is about 72.5% by weight (55.6% by volume) for the Translucent shades and 78.5% by weight (63.3% by volume) for all other shades.

Experimental technique

The tested composite materials (Filtek Ultimate, Filtek Supreme XT and Filtek Z250) were prepared in 20 cylindrical samples of 5 mm in diameter and 2 mm in width, for each type measurement, to obtain relevant averaged values. The sample widths were in agreement with the producer specifications. The specimens were polymerized using the high intensity visible light given by two type of lamps: a halogen unit with the spectral range 400 - 520 nm (blue light) and 75 W (EVICROLUX EVL 022) and a LED unit with the emitted wavelengths between 440 and 460 nm (Optilight LD Max). Various photo-polymerization times were used, longer than the minimum exposure time indicated by the technical specifications. For comparison, also non-polymerized samples are analyzed.

The samples were studied by scanning electron microscopy (SEM) using Vega Tescan LMH II equipment. The SEM images were taken in secondary electrons (SE); the acceleration voltage was equal to 30 kV, and the emission current was between 0,5pA and 500nA. The energy dispersive detector for X-rays (QUANTAX - Bruker equipment) was used for chemical composition measurements.

Results and discussions

Chemical composition

In fig. 3a the typical microstructure of non-polymerized Filtek Ultimate is given. It results in uniform particles distribution, and micro-segregates of silica and zirconia particles. From dispersive X-ray spectrum (fig. 3b) the main elements oxygen, silicon, carbon and zirconium are identified. Their mapping (fig. 3c – oxygen, fig. 3d – silicon and fig. 3e – zirconium) allows the filler particle

identification, a good agreement with the observations from fig. 3a resulting. The normalized atomic percents of dominant elements were monitored after the polymerization with halogen and LED lamps at various exposure times – fig. 4a and fig. 4b, where the measurement errors are indicated by vertical bars. An excellent chemical stability is observed for this restorative material. Since the oxygen content does not vary significantly we conclude that OIL is not present for this composite.

Regarding to the chemical compositions of the other two analyzed materials (figs. 5a,b and figs. 6a,b) it results a higher percent of oxygen, both for polymerization with halogen and oxygen lamps. We note a lower relative concentration of zirconium, which can be attributed to the very good affinity for oxygen of the superficial layer. Since the relative atomic percent of oxygen is increasing with the polymerization time for both light sources, we conclude that the time of photo-polymerization process is favoring the formation of oxygen inhibition layer.

Filler content

In a previous work [5] it was shown that OIL thickness depends on the filler content due to the different rates of oxygen diffusion into the resin matrix, by either directly adsorbing oxygen onto the filler surface or by facilitating the diffusion of oxygen between the filler particle/resin matrix interface. The effect of oxygen adsorption of fillers and inhibition thickness within resin composite formulations is not completely understood and only few previous studies were focused on such phenomena [4]. In that study, an inhibitory effect was not present when the filler particles load reached wt. 40 %, compared with the results from [5] wherein an inhibition layer was measured with all resin composite formulations loaded to 70 wt. %.

This discrepancy might be associated with differences in filler type, size and resin-filler interaction. In these circumstances, we considered as useful to study the filler content for each of the previous sample.

Having in view the chemical structure of the tested materials, from the element mapping (for example see figs. 3d-e) it is possible to identify the SiO_2 and ZrO_2 particles using the ImageJ software [20]. Some typical results are given in figures 7a,b for Filtek Ultimate. Moreover, making the ratio between particle area and total image area, the filler particle content can be calculated in volume percents. The resulted data are given in Table 1 for each type of tested materials. It results almost the same filler loading for Filtek Ultimate and Filtek Supreme XT, *i.e.* about 59 volume %, the values being in a good agreement with the producer specifications. We note a slightly higher percent of zirconia particles in the case of Filtek Ultimate than for Filtek Supreme XT. In the case of Filtek Z250, the inorganic filler loading is much lower, *i.e.* 45 volume %, the value being also close to the producer technical data.

In figures 8a-f the histograms of cluster particle distributions are given as function of their size, for each type of particle and tested restorative composites. The average values are presented in table 1. While for zirconia cluster particles no major differences were observed for all analyzed materials, in the case of silica is resulted a higher average cluster particle size for Filtek Supreme XT than for Filtek Ultimate, *i.e.* a higher tendency of nano-sized particles clustering. By comparison, the values for Filtek Z250 are not significantly different, but we note that in this case the micro-sized particles allow a lower filler loading. Regarding to the influence of particle size and filler loading on the formation of OIL no connections were found, *i.e.* in agreement with the results from [4].

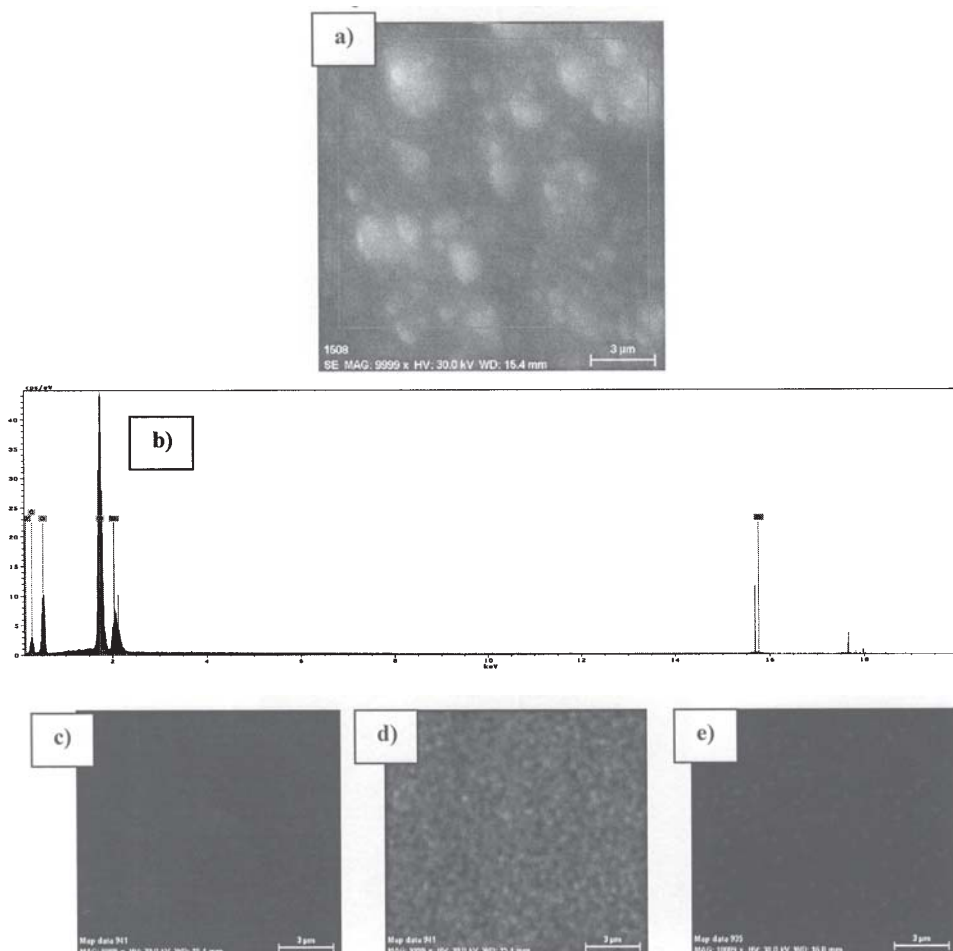


Fig. 3. Microstructural characterization of Filtek Ultimate: microstructure (a), EDAX spectrum (b) and main elements mapping: oxygen (c), silicon (d) and zirconium (e)

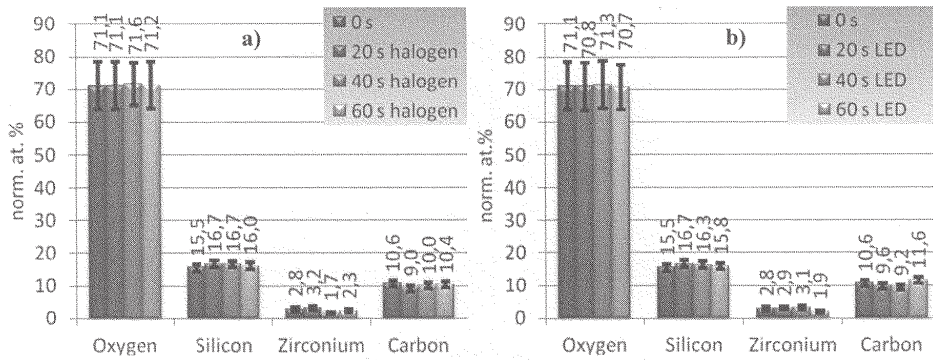


Fig. 4. Chemical composition of Filtek Ultimate photo-polymerized with halogen lamp (a) and LED lamp (b) after various exposure times

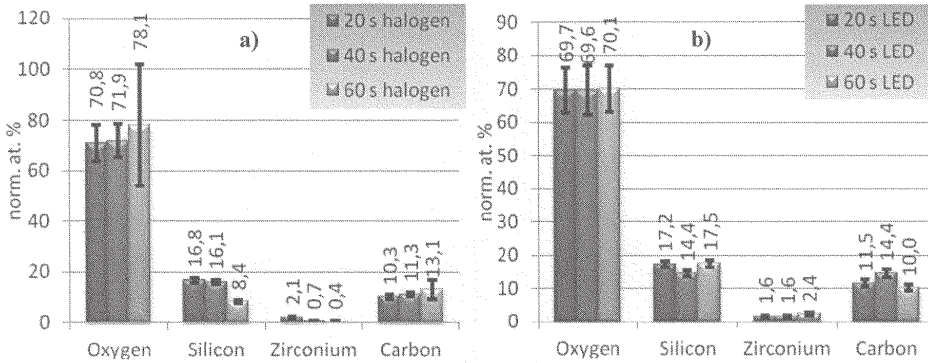


Fig. 5. Chemical composition of Filtek Supreme XT photo-polymerized with halogen lamp (a) and LED lamp (b) after various exposure times

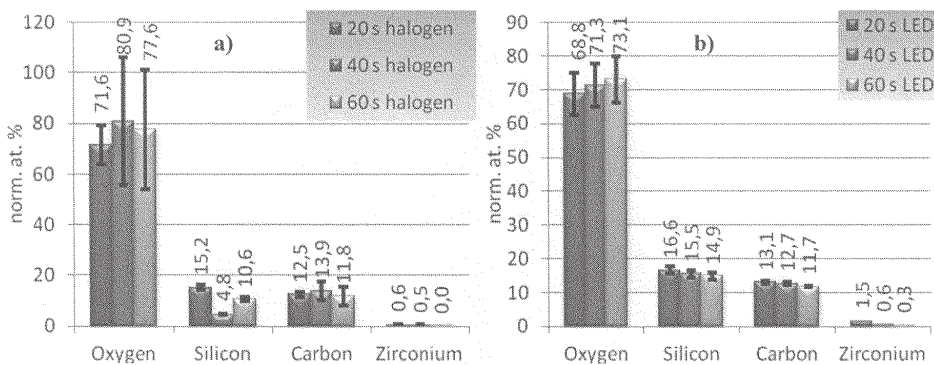


Fig. 6. Chemical composition of Z250 photo-polymerized with halogen lamp (a) and LED lamp (b) after various exposure times

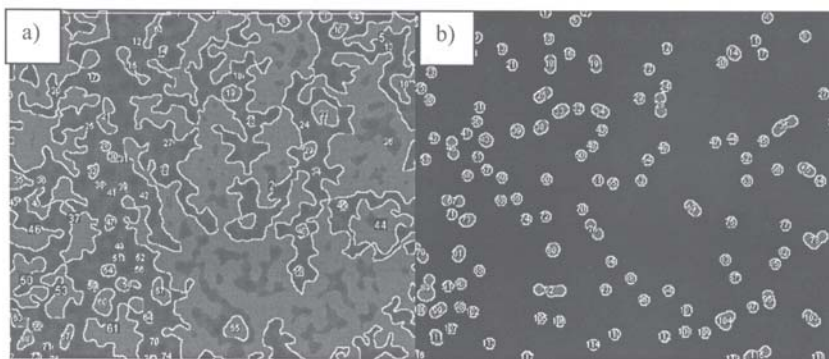


Fig. 7. Particles identification from element mapping (fig. 3d and 3e) in Filtek Ultimate: a) SiO₂; b) ZrO₂

	Filtek Ultimate	Filtek Supreme XT	Filtek Z250
ZrO ₂ particle percent (% vol.)	12,612	9,669	4,004
SiO ₂ particle percent (% vol.)	45,732	48,658	41,048
Average SiO ₂ cluster particle size (µm)	0.26±0.02	0.36±0.02	0.29±0.02
Average ZrO ₂ cluster particle size (µm)	0.206±0.003	0.218±0.004	0.199±0.009

Table 1
FILLER LOADING AND AVERAGED PARTICLE SIZE FOR FILTEK ULTIMATE, FILTEK SUPREME XT AND FILTEK Z250

We note that our values for cluster particle size are about half the ones given by the producer specifications, probably because a spherical shape was considered and not a rectangular one. A possible way to eliminate this disadvantage is to perform a full analysis of cluster particle

shape in the frame of the fractal theory [21-26]. In a future work, the fractal dimensions [23,24] and the shape factors will be calculated, for better describing the microstructure of dental restorative composites.

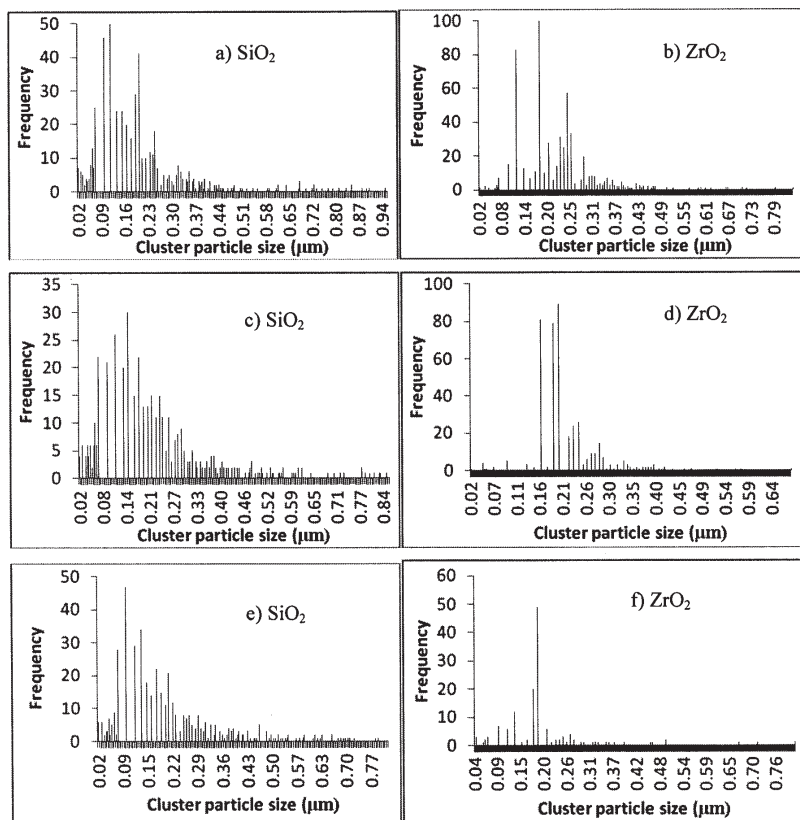


Fig. 8. Histogram of averaged particle size distribution for tested dental composites: a) Filtek Ultimate – SiO₂; b) Filtek Ultimate – ZrO₂; c) Filtek Supreme XT – SiO₂; d) Filtek Supreme XT – ZrO₂; e) Filtek Z250 – SiO₂; f) Filtek Z250 – ZrO₂

Conclusions

The main conclusions of the present paper are:

- the microstructures and chemical compositions of nano-filled Filtek Ultimate and Filtek Supreme XT and microfilled Filtek Z250 were studied in various polymerization conditions to evidence the formation of oxygen inhibition layer;

- an excellent chemical stability results for Filtek Ultimate;

- the superficial content of oxygen is significantly increasing with the polymerization time for Filtek Supreme XT and Filtek Z250, and consequently this process favours the formation of oxygen layer;

- it results almost the same filler loading for Filtek Ultimate and Filtek Supreme XT, *i.e.* about 59 volume %. However, we observed a slightly higher percent of zirconia particles in the case of Filtek Ultimate than for Filtek Supreme XT. In the case of Filtek Z250, the inorganic filler loading is much lower, *i.e.* 45 volume %. These values are close to the producer technical data;

- the histograms of cluster particle distributions were obtained as function of their size, for each type of particle and tested restorative composites;

- regarding to the influence of particle size and filler loading on the formation of OIL, no connections were found.

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References

- SILIKAS, N., KAVVADIA, K., ELIADES, G., *Am. J. Dent.*, **18**, 2005, p. 95
- ZHANG, Y., LIM, C.T., RAMAKRISHNA, S., HUANG, ZM., *J. Mater. Sci. Mater. Med.*, **16**, 2005, p. 933
- MITRA, SB., WU, D., HOLMES, BN., *J. Am. Dent. Assoc.*, **134**, 2003, p. 1382
- GAUTHIER, MA., STANGEL, I., ELLIS, TH., ZHU, XX., *J. Dent. Res.*, **84**, 2005, p. 725
- SHAWKAT, ES., *The effect of the oxygen inhibition layer on interfacial bond strengths and stain resistance of dental resin composites*, Ph.D.

Thesis, College of Medical and Dental SciencesThe University of Birmingham, 2009. p. 76

- BOWEN, RL., *U.S. Pa.* **3,066**, 1962, p. 112
- BOWEN, RL., *J Am Dent Assoc.*, **66**, 1963, p. 57
- ANTONUCCI, JM., STANSBURY, JW., *Molecular designed dental polymer*. In: ARSHADY, R., editor. *Desk reference of functional polymers: synthesis and application*. American Chemical Society Publication, 1997, p. 719.
- REED, BB., CHOI, K., DICKENS, SH., STANSBURY, JW., *Polym. Prepr.*, **38**(2), 1997, p. 108
- LUTZ, F., PHILLIPS, RW., *The Journal of Prosthetic Dentistry* **50**(4), 1983, p. 480
- ANDRZEJEWSKA, E., *Prog. Polym. Sci.*, **26**(4), 2001, p. 605
- COOK, WD., *Polymer*, **33**, 1992, p. 600
- 3M DENTAL PRODUCTS LABORATORY, *Filtek Z250: Technical Product Profile*; U.S.A. 1998
- 3M DENTAL PRODUCTS LABORATORY, *Filtek Supreme XT: Technical Product Profile*; U.S.A. 2005.
- 3M DENTAL PRODUCTS LABORATORY, *Filtek Ultimate Universal Restorative System: Technical Product Profile*; U.S.A. 2010
- LEINFELDER, KF., SLUDER, TB., SANTOS, JFF., WALL, JT., *Oper. Dent.*, **12**, 1980, p. 52
- LACY, AM., *J. Am. Dent. Assoc.*, **114**, 1987, p. 357
- JORDAN, RE., SUZUKI, M., *J. Am. Dent. Assoc.*, **122**, 1991; p. 31.
- O'BRIEN, WJ., *Dental materials and their selection*. 3rd ed. Quintessence Publishing Co Inc., 2002.
- <http://rsbweb.nih.gov/ij/>
- COLOTIN, M., POMPILIAN, G.O., NICA, P., GURLUI, S., PAUN, V., AGOP, M., *Acta Physica Polonica A*, **116**, no.2, 2009, p.157
- IOANNOU, P. D., NICA, P., PAUN, V., VIZUREANU, P., AGOP, M., *Physica Scripta*, **78**, nr. 6, 2008, Article Number: 065101
- AGOP, M., NICA, P.E., IOANNOU, P. D., ANTICI, A., PAUN, V. P., *Eur. Phys. J. D*, **49**, nr. 2, 2008, p.239
- AGOP, M., PAUN, V., HARABAGIU, A., *Chaos Solitons and Fractals*, **37**, nr. 5, 2008, p. 1269
- PAUN V-P., PAUN M-A., TOMA A., CIUCU C., POPENTIU F., *Mat. Plast.*, **45**, no.1, 2008, p. 57
- BORSOS, Z., PAUN, V-P., CASIAN-BOTEZ, I., STOICA, C., VIZUREANU, P., AGOP, M., *Rev. Chim. (Bucuresti)*, **59**, no. 10, 2008, p. 1169

Chemistry of Modern Papermaking
by Cornel Hagiopol and James W. Johnston

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Wood cellulose is one of the oldest natural polymer materials. The processes of refining (pulping) and modifying cellulose fibers to make paper, have also been in use for a long time. Today, given the dramatic increase in the production of synthetic or artificial polymers, rejuvenating old papermaking processes is a daunting challenge. The publication of the "Chemistry of Modern Papermaking" is part of that effort.

This compendium of 9 chapters, is a literature review based on an impressive number of references (over 3400). The authors' work on the effect paper chemicals have on the three-dimensional network of cellulose fibers is aimed at evaluating the main ideas put forward by the scientific community in the last decades.

After a brief review of the papermaking history, an introduction in the organic chemistry of pulping processes and reactions performed on poly-carbohydrates is presented in Chapter 2. Chapter 2 - in which 525 references are reviewed - also refers to polymerization, polycondensation and polymer-analogues reactions used to obtain synthetic polymers as potential paper chemicals.

Chapter 3 discusses the effect of chemical additions on the papermaking process (the fate of paper chemical at the wet end). The authors' investigation goes beyond the technologic effect of paper chemicals (poly-electrolytes, latexes, inorganic particles, non-ionic water-soluble compounds): paper chemical diffusion, ionic interactions, adsorption, migration, re-conformation are presented along with their impact on paper quality.

Chapters 4, 5 and 6 are focused on the temporary wet-strength, wet -strength and dry-strength resins. Their water solubility, molecular weight, cationic charges, multiple reactive functional groups, ability to generate strong or weak chemical bonds with cellulosic fibers are reviewed in minute detail. Special attention has been given to the repulpability potential of paper obtained in the presence of different types of paper chemicals.

Chapter 7 incorporates a highly complex study on internal sizing agents. Sizing agents have the ability to impart a hydrophobic character to cellulose fibers and to ensure a reduction in paper wettability. After the presentation of alum chemistry and of standard sizing agents (rosin and its derivatives), new chemical products are carefully studied: alkyl ketene dimmers, alkenylsuccinic anhydrides, poly-cationic compounds, fluorinated compounds, etc. The more important products are described as dispersions in water. The potential sizing mechanism (reactive and nonreactive dispersions) takes into account their reactivity toward cellulose fibers.

Creping adhesives and softeners are described in Chapter 8, together with the main technological parameters and a comprehensive list of chemical products such as: paper nonreactive creping adhesives, reactive self-crosslinkable creping adhesives, creping adhesives with a cross-linker, etc.

The last chapter (Chapter 9) deals with the chemical treatment of the paper surface. Mention is being made of the fact that chemical polymer products, especially those with high molecular mass that can or cannot contain ionic charges, are particularly useful. Special attention was given to polymer latexes, starches, emulsions of nonreactive small molecules, polymerizable surfactants, fluorochemicals, etc.

The wealth of information included in the book under review validates the authors' efforts to reflect upon and improve the papermaking processes developed during the last century. The authors should be commended for the accurate fashion in which they presented, explained and organized the information contained in their book. The technologically relevant data is analyzed with a focus on the physical and chemical interactions between the cellulose fibers and various other additions. The structures of chemical compounds are studied from the perspective of their potential to improve the final properties of paper.

"Chemistry of Modern Papermaking" will be particularly helpful to researchers and engineers working in the field, and will become required reading for young researchers specializing in the remarkably broad field of papermaking chemistry.

Dan Donescu