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On the Deformation Behavior of Composite "Hen's Eggshell–Polymer Plomb" under Bending

Peter Panfilov [1,2,*], Dmitry Zaytsev [1,2], Maxim Mezhenov [1,2], and Sergei Grigoriev [3]

1 Ural Federal University, Yekaterinburg, Russia; peter.panfilov@urfu.ru
2 Ural State Mining University, Yekaterinburg, Russia; dmitry.zaytsev@urfu.ru
3 Ural State Medical University, Yekaterinburg, Russia; sergeygrig28@gmail.com
* Correspondence: peter.panfilov@urfu.ru

Abstract: Deformation behavior of the composite "hen's eggshell - polymer plomb" under bending is examined. Polymer coating does not change the type of behavior of the composite based on eggshell that continues to be brittle despite the mechanical characteristics of the composite could vary in wide limits for brittle structure. Joining "hen's eggshell – polymer plomb" never crack under loading and, hence, it exhibits the high cohesion strength under stresses applied in these experiments. It seems that the composite "hen's eggshell - polymer plomb" could apply as the substitution of the composite "tooth enamel - polymer plomb" under elaboration of novel restorative materials for dentistry, namely, for estimation of their mechanical properties including cohesive strength.

Keywords: hen's eggshell; polymer coating; mechanical properties

1. Introduction

Restorative procedure in dentistry means that plomb materials replace some part of tooth hard tissues [1]. As a result, treated tooth becomes a composite-like structure, whose mechanical properties should not differ considerably from an intact tooth [2]. The searching for restorative materials in dentistry is complicated problem consisted of many tasks including ethic, biomedical, mechanical, materials science etc. [3]. One of these ones is the experimental estimation of the deformation behavior the composite "tooth hard tissues - plomb", including the cohesive strength between them [2,3]. The main factor, which prevents it's solving, is small volume of hard tissues, especially dental enamel, in human teeth that does not allow carrying out standard mechanical testing of the joining "dentin/enamel - plomb" [4]. Naturally, both ethic and medical aspects of the problem are very important also. Substitution of the tooth hard tissues by a material with close mechanical properties, but not deficit and rare as dentin or enamel, would open a prospect for the solving this actual task for dental materials science.

Hen's eggshell is a mineral of biological genesis or a biomineral [5,6], whose properties including mechanical ones are close to human dentin and enamel under the stress conditions that takes place under the chewing of normal food [7,8]. Eggshell has two natural surfaces, which do not need additional preparation before the testing, while its thickness is almost constant value, and it is easily cut into samples for mechanical testing, for example by the scheme of 3-points bending [9]. Besides, there are many sources of hen's eggs for a legal supply including food markets, farms, and city supermarkets all of them given the governmental guarantee of the quality. These features allow carrying out mechanical testing of the eggshell samples on the 3-points bending scheme without any engineering and ethical problems. Therefore, samples cut from hen's eggshell and covered by a polymer plomb material, which has been glued on their convex surface, could be used for the experimental estimation of the deformation behavior of composites "tooth hard tissues – polymer plomb", including the cohesive strength between them. Indeed, 3-points bending allows effectively examining the mechanical properties of such composites. This applied task has also some fundamental meaning, since the deformation behavior of the composite "brittle material - viscous

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coating" under bending is interesting for the composite science, too [10,11]. The aim of this work is the experimental study of the deformation behavior such composites under 3-points bending on example of the joining of hen's eggshell samples with some polymer plomb materials that used in the international clinical practice including Russia.

2. Materials and Methods

We used hens' eggs obtained from a retail outlet, described as distributed from a hen farm near Yekaterinburg of C1 size inside the dates of guarantee usage. The biological material was stored no more than two days in refrigerator under the recommending conditions by the manufacturer. Liquid biomass was extracted from eggshells by the standard procedure and every eggshell was washed inside by the water and was dried during one day at room temperature. The eggshell was fixed on the substrate from a polyurethane foam before the cutting of procedure (Figure 1a). The samples for mechanical testing were cut with a help of disc diamond saw (diameter 45 mm, thickness 0.5 mm) from the central area of an eggshell along its main axis (Figure 1b). The samples for the bending are shown in figure 1c. The average length of such samples varies from 40 mm to 50 mm. Their width and thickness are 3 mm and 0.3 mm, respectively.

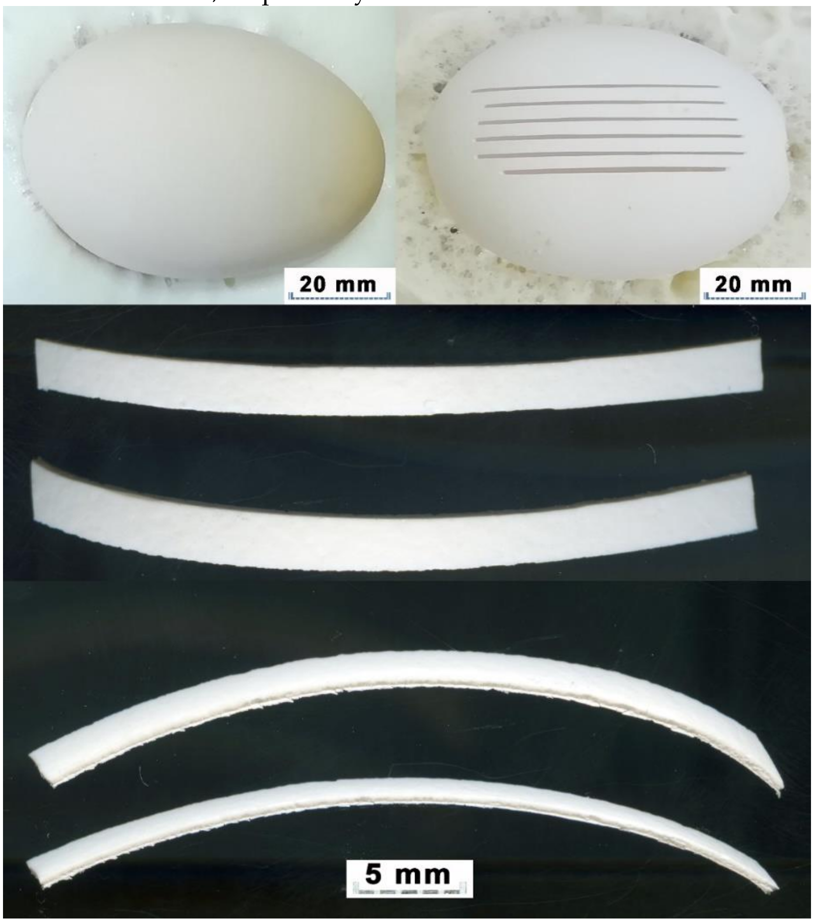

Figure 1. Preparation of samples from hen's eggshell: (1) – eggshell on the substrate; (2) – eggshell after cut off procedure; (3) samples for bending, working surface and end surface.

We carried out mechanical testing on the Shimadzu™ AG-50K XD testing machine (traverse rate was 0.1 mm/min). Shimadzu's device for the 3-points bending was used in experiments: the distance between lower prisms was 10 mm; the length of the sample was 15-20 mm. Software Trapezium™ was applied for processing the data. Our earlier findings on the deformation behavior of the samples cut from hen's eggshell under 3-points bending in air and water are presented in [9]. The preparation of the composite samples "hen's eggshell - polymer restorative material" for the 3-points bending was realized according to the procedure of tooth plumbing from some manufacturers accepted by the Russian Federation Government for the clinical application. The technique include the four stages.

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(1) The etching the convex surface of the sample by the gel contained orthophosphoric acid (H_3PO_4). (2) The inflicting of thin layer of polymer adhesive on the etched convex surface of the sample, namely DX Bond Uni™ and Danova Bond™. (3) The gluing of the polymer plomb material to the convex surface with the adhesive, namely Boston Arkona™, Ceram 1™, Ceram 3M™, DX Flow Composite™. (4) The processing of the polymer plomb by the blue laser was the final stage of the sample preparation procedure. Dentists of the Urals State Medical University at Yekaterinburg carried out these operations with the hen's eggshell samples aimed for 3-points bending.

The set containing 10 samples for each operation was tested in air at room temperature. Deformation behavior of the samples was estimated based on analysis of their deformation (bending) curves. Effective elastic moduli calculated from the inclination of the bending curve, maximal deformation of the sample and ultimate bending strength were used as the mechanical characteristics of the samples in addition to the deformation curve under bending. The working surfaces and end surfaces of the samples before and after mechanical testing were documented with a help of an optical microscope in the reflection mode. Examination of the images of the samples after bending was the basis for the estimation of the cohesion between hen's eggshell and restorative materials.

3. Results

Mechanical testing has shown that the samples from all sets exhibit the brittle deformation behavior under 3-points bending (Figures 2–5 and Table 1). The hen's eggshell samples of set 1 behave (Figure 2a and Table 1) like it was described in our earlier work [9]. The etching of the samples surfaces and the inflicting of adhesives induce the increasing of the deformation prior the fracture and the lowering of the elastic modulus of the samples (Figure 2b and Figure 3, Table 1). The etching and thin layer of adhesive on the surface (set 2 and set 3, respectively) does not cause the changing of the ultimate stress of the samples (Figure 2b and Figure 3a, Table 1), whereas thick adhesive layer on the surface of samples (set 4) leads to considerable rising of the ultimate stress under bending (Figure 3b, Table 1). The thick non-flowing plomb materials glued on the surface (set 5 and set 6), which most frequently used in the clinical practice of Yekaterinburg, induce increasing both ultimate stress and elastic modulus up to the level of a hen's eggshell samples, while their deformation prior the failure decreases in comparison with the samples covered by adhesives (Figure 4, Table 1). The behavior of set 7 and set 8 is differ from described above deformation behavior. There is a plateau of yield in the deformation curves of samples from set 7 (Figure 5a, Table 1). This is the feature of this non-flowing plomb material, which does not completely harden in whole volume of plomb under blue laser processing. The elastic modulus of such samples is the same to the one in hen's samples, but their deformation prior the failure and ultimate stress are considerably higher. The set 8 is the liquid flowing plomb material, which covers all face surface of the sample between the lower prisms of the bending device. The deformation prior the failure does not change in comparison with a semi plastic plomb material of set 7, while both elastic modulus and ultimate stress increase considerably (Figure 5b, Table 1).

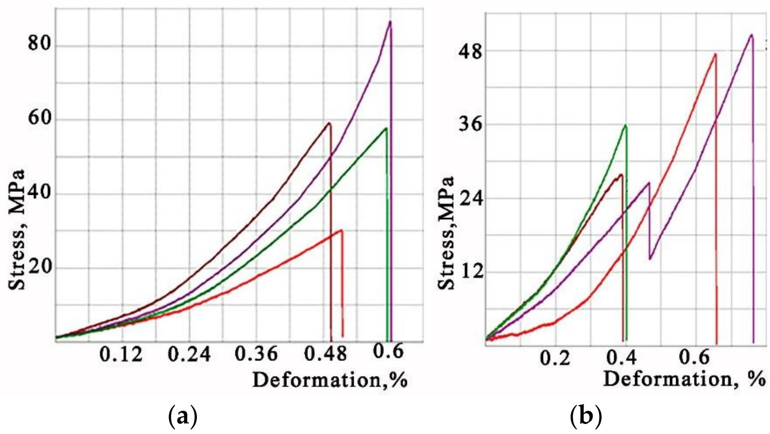

Figure 2. Deformation curves of the hen's eggshell under 3points bending in air: (**a**) – initial state; (**b**) – after the etching.

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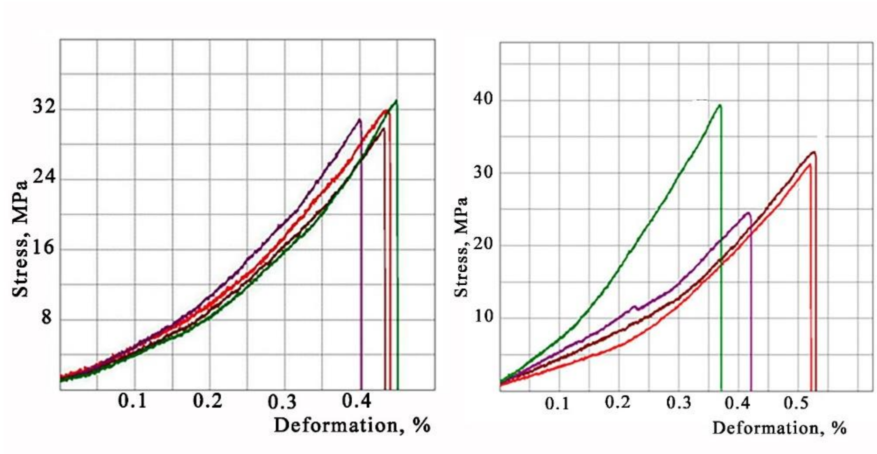
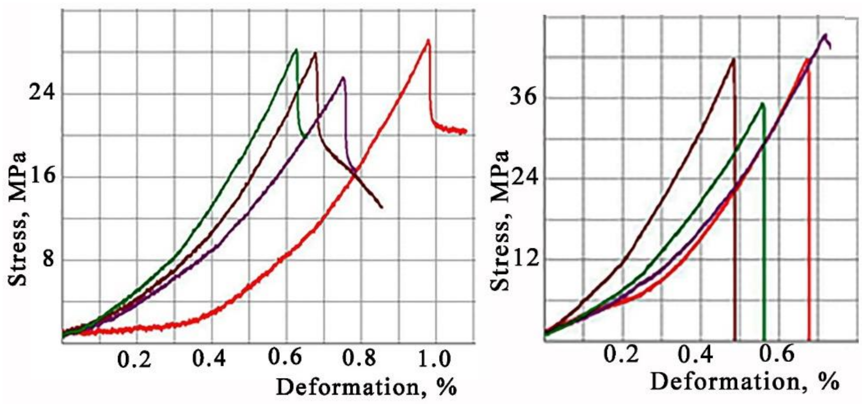


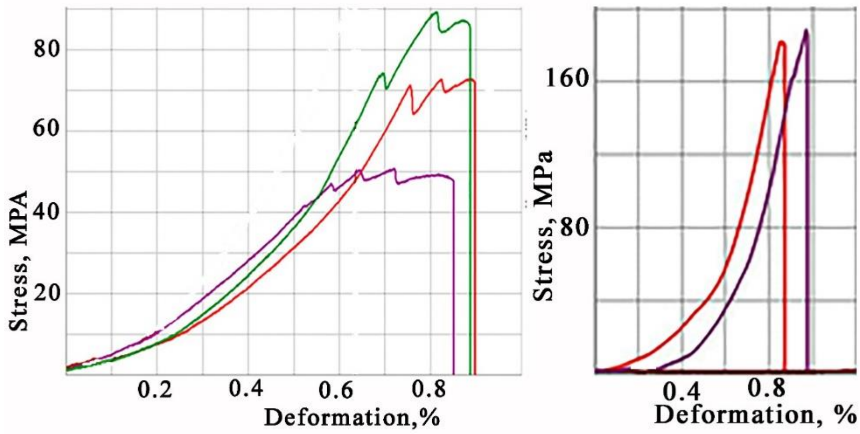
(**a**) (**b**)

Figure 3. Deformation curves of the hen's eggshell under 3points bending in air: (**a**) - adhesive «DX Bond Uni™»; (**b**) - adhesive «Danova Bond™».



(**a**) (**b**)

Figure 4. Deformation curves of the etched hen's eggshell under 3points bending in air: (**a**) - polymer plomb «Boston Arkona™»; (**b**) - polymer plomb «Ceram 1™».



(**a**) (**b**)

Figure 5. Deformation curves of the etched hen's eggshell under 3points bending in air: (**a**) - polymer plomb «Ceram 3M™»; (**b**) - polymer plomb «DX Flow Composite™».

Table 1. Mechanical properties of hen's eggshell with polymer plomb materials under bending.

№	Samples	Elastic modulus, GPa	Deformation, %	Ultimate stress, MPa
1	Hen's eggshell 1	10	0.5	30
2	Etched hen's eggshell	8	0.6	30
3	Hen's eggshell + adhesive «DX Bond Uni™»	6	0.8	30
4	Hen's eggshell + adhesive «Danova Bond™»	8	0.8	50
5	Hen's eggshell + plomb «Boston Arkona™»	10	0.6	60
6	Hen's eggshell + plomb «Ceram 1™»	9	0.6	40
7	Hen's eggshell + plomb «Ceram 3M™»	10	0.8	80
8	Hen's eggshell + plomb «DX Flow Composite™»	14	0.8	180

Metallographic examination of the samples after the bending has shown that of the geometry of applied stress governs the trajectory of dangerous crack, as it should be in a brittle isotropic solid. The dangerous crack appeared under the loading prism in the following sets of samples: (1) hen's eggshell samples, which were not processed before (Figure 6a); (2) etched hen's eggshell samples (Figure 6b); (3) hen's eggshell samples covered by adhesives (Figure 6c). The motion of the dangerous crack did not always lead to the failure of these samples if the loading was plugged off as soon as kink appeared on the engineering curve, as it was mentioned in [9]. Dangerous cracks appeared and moved exclusively on the boundary between plomb and eggshell in the samples covered by plomb material (Figure 6d–f). Non-flowing plombs were in areas near the contact of the loading prism with the sample (Figure 6d,e), while liquid flowing plombs covered the sample between the lower prisms (Figure 6f). The dangerous crack in the sample with non-flowing plomb could be braked when the testing was stopped, whereas the one never braked in the samples with liquid flowing plombs and, therefore, such samples al-ways failed. No decohesion between the eggshell and plombs was observed in the experiments despite the geometry of loading stimulated the cracks on the boundary between them (Figure 6b–f).

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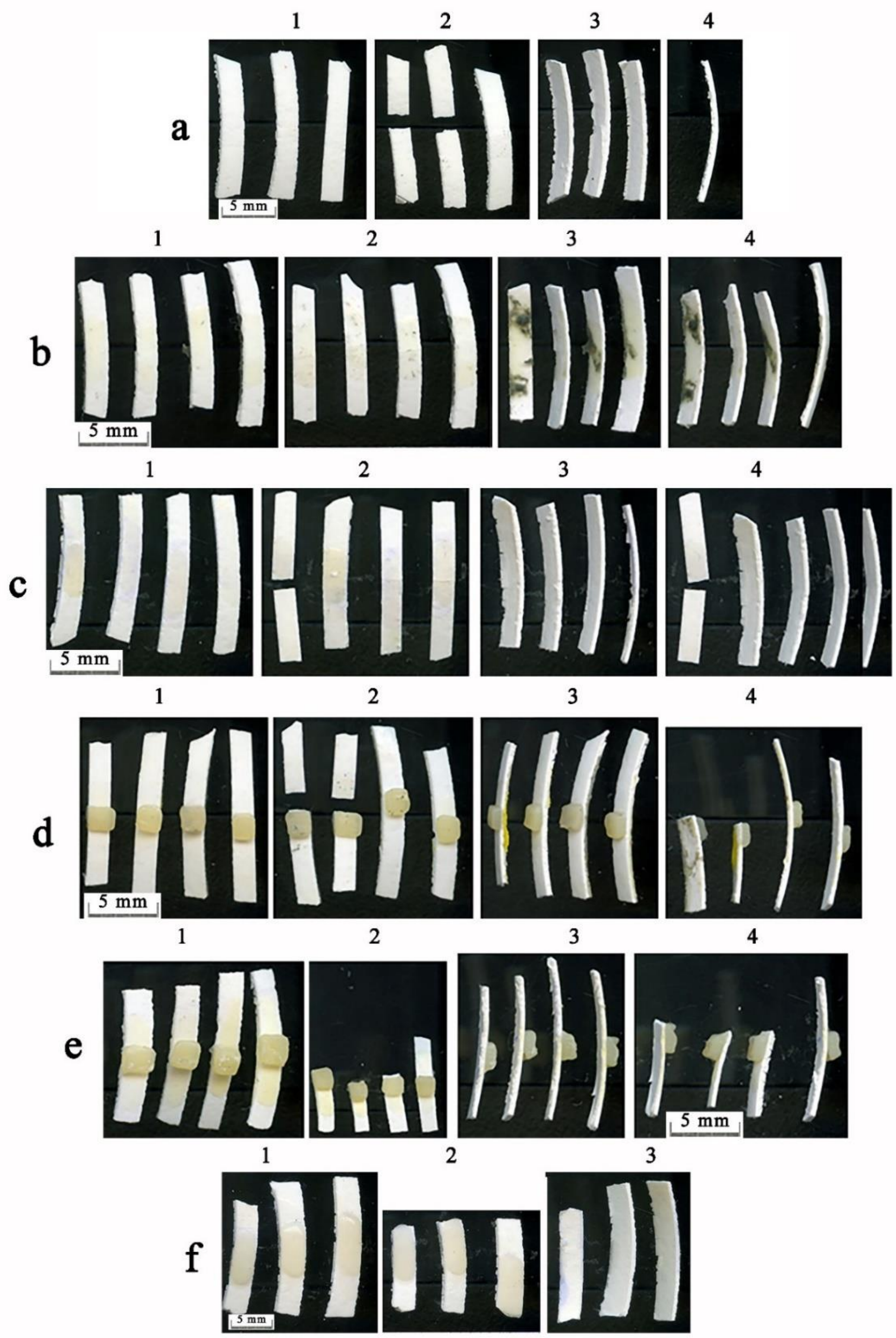

Figure 6. Samples cut from hen's eggshell: (1 – Initial state, working surface; 2 - Bending in air, working surface; 3 – Initial state, end surface; 4 – Bending in air, end surface): (**a**) – initial state; (**b**) – etched state; (**c**) - adhesive «Danova Bond™»; (**d**) – polymer plomb «Ceram 1™»; (**e**) - polymer plomb «Ceram 3M™»; (**f**) – polymer plomb «DX Flow Composite™».

4. Discussion

Testing has shown that deformation behavior of the samples cut from hen's eggshell under bending continues to be brittle despite the polymer coatings because in all cases the total deformation before the failure was less than 1% [12]. Additional argument is the course of the de-formation curves for majority of samples, which could approximate by a linear dependence [13,14]. This is expected result because hen's eggshell is a natural inorganic biomaterial with covalent chemical bonding and, hence, it should not exhibit any other behavior than the brittle one [15]. At that the composites "hen's eggshell - polymer plomb" possess mechanical characteristics that varied in wide limits, but always inside the brittle behavior. This finding seems very important because it was obtained on the samples possesses the native surfaces and, hence, the influence of such random factor as the preparation of samples on experimental data is minor.

The main factors governed mechanical properties of the composite "hen's eggshell - polymer plomb" under bending is geometry of the polymer coating and its mechanical properties. Indeed, polymer plomb materials in the modern dentistry are in majority of cases viscous flow polymer materials, which are strengthened with the surface by a blue laser in the final stage of the restoration of teeth [3]. Sometimes, viscoelastic nature of the polymer coating [16] could display in the engineering curve (figure 5a), but this small plasticity does not change the brittle character of response of the composite, because its total plasticity is always less than 1%. Cohesive strength of the joining between hen's eggshell and polymer plomb is homogeneous and quite powerful in all examined composites because the joining never cracks under bending.

Procedure of the restorative treating of damaged teeth, namely the montage a plomb in a tooth, could be successfully applied to preparation of the composite "hen's eggshell - polymer plomb" for the mechanical testing by the 3-points bending scheme. Of course, hen's eggshell is not equivalent to the human tooth enamel [17], but it would be considered as the substitution of this tooth hard tissue under examination of novel plomb materials. The experiments that were carried out allow estimating the deformation behavior of the biomineral on the different stages of the restorative procedure. The main features of the behavior of modern dental restorative materials were pointed without usage of composite samples based on a tooth enamel. In addition, 3-points bending is more appropriative loading scheme for routine mechanical testing in comparison with the uniaxial compression of small-size cuboid composite samples based on tooth enamel. This result could open an opportunity for accelerative elaboration of novel restorative materials for dentistry.

Yes, of course, the conclusion that a polymer coating does not change the brittle behavior of an inorganic material sounds as a negative prognosis for the composite as a structural material. However, for a substitution of the hard tissues of damaged tooth, especially tooth enamel, such composite has a future. Indeed, (1) human teeth are working under average loading in the limits of one dozen MPa and (2) their deformations under the chewing of food are considerably less than 1% of compression. Therefore, examined composites should be working without any damaging under these conditions, since a brittle material is damaged under limit loading only.

5. Conclusions

It was shown that viscous polymer coatings do not change the deformation behavior of samples cut from hen's eggshell under bending, which continues to be brittle despite their mechanical characteristics could vary in the wide limits. Joining "hen's eggshell - plomb" never crack and, hence, it exhibits quite powerful cohesion strength. It seems the composites "hen's eggshell - polymer plomb" under bending could serve as the substitution of the joining "tooth enamel - polymer plomb" during examination of novel restorative materials for dentistry, namely for estimation of their mechanical properties including the cohesive strength.

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Conflicts of Interest: The authors declare no conflict of interest.

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