بسم الله الرحمن الرحيم

in the name of

God

the Compassionate

the Merciful

AN INVESTIGATION INTO THE SHRINKAGE BEHAVIOR (KINETICS) OF MICROFILLED HYBRID AND NANO DENTAL COMPOSITES.

DISSERTATION

Presented in Fulfillment of the Requirements for the Degree of Doctor of Dental Surgery (DDS) in the graduate of Dental School of Kerman University of Medical Sciences

By

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ABSTRACT

Aim and Background: This study investigated the shrinkage strain rate, shrinkage strain percentage and post curing shrinkage of different dental composites including Microfilled, Hybrid and Nanofilled composite systems. It also investigates the effect of light curing method (ramp and conventional) on the shrinkage behavior.

Materials and Methods: Since commercially Microfilled composites are not available anymore, an experimental Microfilled composite was prepared in laboratory. The other composites, Hybrid and Nano, were selected from the most common commercially available composites (which are used to restore decay cavities, core build-ups, *etc.* in restorative and cosmetic dentistry).

Four Nanocomposites, six Hybrids, two Flowables and one microfilled composite were evaluated. The samples, in five replicants, were photopolymerised at 640 mW/cm^2 in normal mode (40 seconds), and in ramp irritation mode, an increasing intensity of 100 mW/cm^2 to 730 mW/cm^2 (total 20 seconds) was applied at 23 °C. The shrinkage strain measured up to 2000 seconds using the bonded-disk technique of Watts and Cash, and initial shrinkage-strain rates were obtained by numerical differentiation of shrinkage strain with respect to time. Shrinkage-strain rates increased rapidly to a maximum, and then rapidly decreased upon vitrification.

To analyze the data, the composites were categorized into four groups: I) Nano composites, II) Microhybrids (and hybrids), III) Flowable composites, and IV) Microfilled composite. Nanocomposites exhibited lower shrinkage rates. Microfilled composite and Flowables showed the highest shrinkage strains. In post-polymerization shrinkage measurement, Nanocomposites and Flowables exhibited higher rates, while Microfilled composite showed the lowest rate. There was no significant statistical difference in the final shrinkage applying normal or ramp curing modes, however, a difference was observed in the early seconds of curing in ramp mode. There were higher post polymerization shrinkages in the specimens which were cured using the ramp mode, this is the result of an initial lower and immature shrinkage while the composite is being ramp cured. In the ramp mode the time to reach the maximum shrinkage strain rate was postponed, this is clinically important as the materials would have more time for stress relaxation before being gel.

The multiple regression model indicated that the shrinkage strain between four groups was significantly different (while other variables were adjusted). These variables can be truly situated in a linear model, as the three variables of shrinkage in 40^{th} second, composite type and light-curing method can predict 98.6% of shrinkage strain behavior in 2000^{th} second. The multiple regression analyses model was also conducted with respect to the post-polymerization shrinkage, in which either the composite type and light-curing method can be a significant predictive factor, however only 14.5% of post-polymerization shrinkage strain was related to these variables. Regarding the time to reach the maximum shrinkage strain rate, the model reveals that composite types and curing methods can be the significant predictor factors, with 81.4% accuracy. Data were analyzed by conducting one-way ANOVA and Tukey test at the significance level of 0.05.

Results: Regarding the shrinkage behavior of the samples, our results suggest the application of Nanofilled dental composites in tooth restorations. Since all composites revealed a relatively high post-polymerization shrinkage (10–38%, even when the patient has left the dentist clinic), respecting composite light irradiation method, we suggest an initial curing using the ramp mode for 20 seconds and after that irradiate the composite for 10 more seconds in normal mode.

ELS ® as a micro-hybrid composite exhibited the lowest shrinkage strain and shrinkage strain rate and the highest post-polymerization shrinkage. These are probably due to the special initiator system and monomers in this composite.

Keywords: Dental composites, Shrinkage strain, Shrinkage strain rate, post curing shrinkage, light curing method

چکیده

مقدمه و زمینه هدف: هدف از این مطالعه بررسی میزان کرنش انقباض (جمع شدگی) و سرعت کرنش انقباض و میزان انقباض پس از پخت کامپوزیت های میکروفیلد، هیبرید و نانو میباشد. این مطالعه همچنین رفتار انقباض کامپوزیت را در دو روش پخت با نور رمپ و نرمال بررسی میکند.

مواد و روشها: بدلیل عدم استفاده از کامپوزیت های میکروفیلد، این کامپوزیتها به منظور تجاری تولید نشده و در نتیجه در بازار موجود نمیباشد. از همین رو، برای مطالعه این گروه کامپوزیت ها، یک کامپوزیت با ساختار میکروفیلد در آزمایشگاه تولید و به عنوان نماننده کامپوزیت های میکروفیلد مورد مطالعه قرار گرفت. سایر کامپوزیتها (هیبرید و نانو) از کامپوزیت های رایج در بازار تهیه شدند. جمعا ۱۳ کامپوزیت در مطالعه مورد بررسی قرار گرفت. چهار نانو کامپوزیت، شش کامپوزیت هیبرید (و میکروهیبرید)، دو کامپوزیت فلو و یک کامپوزیت میکروفیلد. برای مطالعه، کامپوزیتها با پنج مرتبه تکرار مورد تابش نور قرار گرفتند و میزان انقباض تا ثانیه ۲۰۰۰ با استفاده از تکنیک متصل به دیسک ثبت شد. در روش تابش نرمال نور با شدت ثابت ۶۴۰ mW/cm^2 به مدت ۴۰ ثانیه و در روش رمپ، نور با شدتی از زیر ۱۰۰ mW/cm^2 شروع شده و تا حد اکثر ۷۳۰ mW/cm^2 به مدت ۲۰ ثانیه به نمونه تابانده میشد. دما در تمام نمونه آزمایشها ثابت و در حد ۲۳ درجه سانتی گراد بود. سرعت انقباض کامپوزیت ها در ثانیه های ابتدایی تابش نور افزایش یافته تا به حداکثر خود برسد و سپس به علت پدیده شیشه ای شدن کامپوزیت کاهش پیدا میکرد.

بمنظور آنالیز داده ها، کامپوزیتها در چهار گروه نانو کامپوزیت ها، هیبرید (میکروهیبرید)، فلو و میکروفیلد تقسیم بندی شدند. در بین گروه ها، نانو کامپوزیت ها کمترین میزان انقباض را نشان دادند. در میزان انقباض پس از پخت، نانو کامپوزیت ها و کامپوزیت های فلو بیشترین میزان و گروه میکروهیبرید کمترین میزان انقباض پس از پلیمره شدن را داشتند. اختلاف معنی داری در انقباض نهایی کامپوزیت پس از تابش نور در ثانیه های ۴۰ و ۲۰۰۰ با دو روش تابش نور مورد مطالعه دیده نشد. با این حال، در ثانیه های ابتدایی تابش اختلاف بین دو روش دیده میشد به طوری که روش رمپ زمان رسیدن به حداکثر سرعت انقباض را افزایش میدهد. همچنین میزان انقباض پس از پلیمریزاسیون در روش رمپ بیشتر از روش نرمال بود که به دلیل انقباض ابتدایی کمتر در روش تابش رمپ است. این یافته از این جهت اهمیت دارد که در این حالت کامپوزیت زمان بیشتری برای آزاد سازی استرس های ناشی از انقباض خواهد داشت.

آنالیز مدل regression چند متغیره نشان داد که میزان انقباض در بین گروه ها با یکدیگر اختلاف معنی داری دارند بطوریکه این متغیر ها بخوبی در یک مدل خطی جای گرفته و سه متغیر انقباض در ثانیه ۴۰، نوع گروه ماده و روش تابش نور ٪۹۸/۶ تغییرات انقباض ثانیه ۲۰۰۰ را پیش گویی میکنند. در مورد میزان انقباض پس از تابش نور نیز این آنالیز نشان داد که هم نوع ماده و هم روش تابش اشعه میتوانند پیش گویی کننده های معنی داری باشند. اما فقط ٪۱۴/۵ تغییرات انقباض پس از تابش نور ناشی از این دو متغیر است. در رابطه با زمان به حداکثر رسیدن سرعت انقباض کامپوزیتها، آنالیز داده ها نشان داد که ٪ ۸۱/۴ تغییرات این زمان را میتوان از روی نوع مواد و روش تاباندن اشعه پیش گویی کرد. آنالیز داده ها با استفاده از آزمونهای رگرسیوی چند متغیره، one-way ANOVA و Tukey انجام شد.

نتایج: نتایج این مطالعه استفاده از نانو کامپوزیت ها را (در مورد میزان انقباض) پیشنهاد میکند. در مورد روش تابش اشعه، از آنجا که تمام کامپوزیتها درصد انقباض پس از تابش نور تقریبا بالایی در هر دو روش داشتند (٪۳۸-۱۰) و نیز روش رمپ میزان انقباض اولیه ماده را کم میکند (استرس بیشتری آزاد میشود)، پیشنهاد میشود که برای کیورینگ کامپوزیتها، ابتدا ۲۰ ثانیه نور رمپ تابانیده شود و سپس ۱۰ ثانیه نور عادی (روش نرمال) استفاده شود.
کامپوزیت ELS®به عنوان یک کامپوزیت میکروهیبرید، کمترین میزان کرنش و سرعت انقباض و بیشترین میزان انقباض پس از پلیمریزاسیون را در کل نمونه های تست شده نشان داد. این یافته ها احتمالا بدلیل سیستم های خاص شروع کننده و مونومری این کامپوزیت است.

کلمات کلیدی: کامپوزیت دندان، کرنش انقباض، سرع کرنش انقباض، میزان انقباض پس از پخت، روش تابش نور

DECLARATION

I hereby declare that *An Investigation into the Shrinkage Behavior (Kinetics) of Microfilled, Hybrid and Nano Dental Composites* is my own work, that it has not been submitted before for any degree or examination at any university, and that all the sources I have used or quoted have been indicated and acknowledged by complete references.

Mohammad Rashid Shahidi Bonjar

Signed:_____

The work reported in this thesis was carried out in the Department of Polymer Science, Iran Polymer and Petrochemical Institute (IPPI), Tehran, Iran.

DEDICATION

I must thank Almighty God for giving me the strength and diligence to overcome in times of difficulty and the humility to accept my shortcomings and still succeed as a man among many.

This work was performed in dedication to those who gave their time and love to support me and my efforts. My parents, whom my existence is regarded to their devotion, and loved ones believed in me and respected my pursuits and quests in life, even when we didn't see eye to eye. No words can describe my gratitude to them and no deed I can do ever to repay them for their numerous sacrifices and generosities in my life.

In memorial, this work is dedicated to Mr. Ali Reza Afzali Pour and Mrs. Fakhereh Saba, the founders of Universities in Kerman, who taught us the value of sacrifice and achievement in this world. May God bless them.

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I would like to truly admire from all my university professors for their scientific and practical advices and instructions throughout my academic studies and training. I will always adore their patience and guidance versus my inconvenience and ignorance.

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Chapter 1

1.1 Introduction:

Operative dentistry has been transformed in recent years and is expecting to undergo further and far reaching changes in years to come. Composite resins have been introduced into the field of conservative dentistry to minimize the drawbacks of the acrylic resins that had replaced silicate cements in the 1940s (the only aesthetic materials previously available). In 1955, Buonocore used orthophosphoric acid to improve the adhesion of acrylic resins to the surface of the enamel [1].

To improve the physical properties of acrylic resins, Bowen developed Bis-GMA monomer in 1962. These early and chemically cured composites required the base paste to be mixed with the catalyst, leading to problems with the proportions, mixing process and color stability [2].

The acrylate based composites have been used in dentistry for over 40 years. Developments in filler technology and initiation systems have considerably improved composite's physical properties and expanded their clinical applications. Since early composites, the volumetric shrinkage resulting from conversion of dimethacrylate monomers into the long and cross-linked polymeric chains has been identified as a critical limitation that needed to be addressed [3, 4].

For many years dental amalgam was the first and only choice of restorative materials especially in posterior teeth. Used for more than 150 years, dental amalgam showed safe, affordable and durable, to restore the teeth of hundreds millions of people. Although amalgam has a certain safety record and has been widely reviewed by different public health services, due to public concerns of possible environmental hazards of mercury and also as a result of its disability in aesthetic and cosmetic afford, dentists and patients have been looking for some sort of tooth colored restorative substitute.

From 1970, composite materials polymerized by electromagnetic radiation were introduced. These materials were promising because mixing and its drawbacks were omitted. At first, an ultraviolet light source (365 nm) was used to provide the required

light energy [5], but its shallow polymerization and iatrogenic side-effects led to its replacement by visible light (427 - 491 nm), which is currently in use and undergoing further development [6, 7].

Composites used in today dentistry, suffer from some restrictions and disadvantages which can be classified in four groups as follows:

I. Material related limitations: a) Due to resin and monomer polymerization nature (dental composites base), polymerization shrinkage is inevitable. Although various techniques have been presented to decrease the shrinkage, but polymerization shrinkage still remains as one of the main defects for dental composites, b) Inhomogeneous linear coefficient of thermal expansion (LCTE) between teeth structure and composite restoration. This means that under identical temperature variation, the composite and tooth do not behave alike and their expansion/shrinkage is not homogeneous, and c) Biocompatibility of some components is still unknown.

II. Clinical composite application requires more time and precision than an amalgam restoration.

III. Composite application is more technique sensitive. More irritable steps can lead to more possibility of treatment failure. Isolation, etching, priming, bonding and adhesive placement, composite insertion, finishing and polishing are the steps which requires much care than other restorative materials [8].

IV. The life span and longevity of composite fillings may be less than dental amalgam fillings [8, 9].

V. One of the most important properties which determine the durability of a dental restoration is its resistance against biodegradation, through exposure to plaque acids, foods and enzymes that can cause material softening. It has been assumed that one of the problems of composite in the oral environment is chemical degradation, which may result in reduction of physico-mechanical properties [8, 10].

VI. Finally, composite restorations are more expensive than amalgam restorations. Surface wearing through time, restoration fracture within the body and at the margins, marginal leakage, secondary caries incidence at the margins and post operative sensitivity (due

to polymerization shrinkage) are the other restrictive factors. Clinical behavior of composites depends on their physical, mechanical and aesthetic properties which in turn are related to their structure [11, 12].

Beside these limitations, there are some advantages known for composites which can be listed as:

I. Compared to murky amalgam restorations, composites can comply a grate natural color and tooth-like surface texture. As an esthetic restoration, composites are widely applied in cosmetic and restorative dentistry (Fig. 1.1).

Fig. 1.1 - The tooth-colored appearance of composite filings is more cosmetically appealing than dental amalgam.

II. Conservative tooth structure removal has been always an important point in cavity preparation, which can be accomplished in composite fillings. This means that a completed composite filling will often be smaller in size than a comparable dental amalgam filling.

III. Easier and less complex tooth preparation (in comparison with amalgam). Vertical line angles, undermined enamel removal and *etc.* soon are no more required.

IV. Compared to porcelain crowns and indirect tooth colored restorations, a composite restoration is more economical and can be done in one session treatment.

V. Composites are insulator materials, therefore, they possess less heat exchange between the tooth pulp and oral cavity (low thermal conductivity), and therefore, these filings usually have less post treatment thermal sensitivity [8].

VI. As bonding systems are used to employ composites, boding benefits like dentine tubules sealing (and pulp protection) and high cohesion force are achieved [13, 14]. Composite fillings can also support the undermined enamel and can have a strengthening effect on teeth [15].

VII. Composite filling are ready to be used immediately after the dental appointment has been completed. In comparison, dental amalgam fillings require several hours before they can approach their full strength.

1.2 Dental Composites

Direct restorative resin composites have gained a permanent position on the dental market. Their superior aesthetics and less destructive tooth preparation (than amalgam) have been instrumental in this success. Simple application and less toxicity are some of their advantages which lead to their wide application in dentistry and cosmetic dentistry. Besides, improved mechanical and physical properties such as weight, fatigue life, wear resistance, thermal insulation, thermal conductivity, corrosion resistance, micro mechanical retention and so on have made them as a wide spread dental material for various purposes in dentistry.

1.2.1 Types and Classification

There are several classifications for composites. Regarding the curing system which starts the polymerization in composites, there are 3 types of composites: light cure, heat cured (self or chemically cure) and dual cure (light and heat cure) composites. The light-activated composites are the standard for clinical use, whereas chemically activated composites are proposed for some specific applications such as core buildups [16].

Traditionally, dental composites are classified into three groups according to their filler particle size distribution, quantity and composition of inorganic fillers, but recently there has been introduced a forth group. These groups are: I) traditional macrofilled (mean diameter 5-30 μm), II) microfilled composites (mean diameter 0.04 μm), III) hybrid composites which combine the characteristics of macrofilled and microfilled composites [16] and IV) nanofilled composites (mean diameter 20 nm) [17, 18].

1.2.1.1 Conventional compoites:

Approximately 70% to 80% weight (60% to 70% by volume) of conventional composites contains inorganic filler. The terms "conventional" and "traditional" are

related to materials that were developed in the 1970s but are less used in nowadays (also known as large particle macrofilled resins). The average filler size in 1980 was approximately 8μm. Because of the large filler size and high filler rigidity, conventional composites indicate a non polishable rough surface. Surface roughness increases with the lifespan of the material because of the "plucking" effect caused by loss of filler particles from the matrix. How ever, this surface roughness can be a suitable background for stains and pigments resulting superficial restoration discoloration [19].

1.2.1.2 Microfilled composites:

This composite was designed to have a polishable surface resulting to be similar to the nearby enamel (decreased surface roughness in comparison of conventional composites). These materials have a very fine particle size of colloidal or fumed silica (< 0.04 μm) dispersed in a resin matrix.

The very large surface area of the fumed silica filler (130 m^2/g, 1,000 to 10,000 times as much surface area as filler particles in conventional resins), must be wetted by the resin matrix and this results in a significant increase in viscosity and therefore significantly limits the volume of filler that can be incorporated (about 35% to 50%). In an attempt to maximize filler loading while minimizing increase in viscosity, manufacturers have applied pre-polymerized particles. This process involves the addition of 0.04 μm size silicon dioxide particles to a heat polymerized resin in concentrations of up to 60% by weight. Following polymerization, the monomer is ground into 5 to 50 micron size pieces (pre-polymerized filler) which, along with more 0.04 μm silicon dioxide particles, are added to the resin matrix. This efficiently maximizes the percentage filler content and minimizes the increase in viscosity [19]. A schematic view of microfilled composites is indicated in Fig. 1.2.

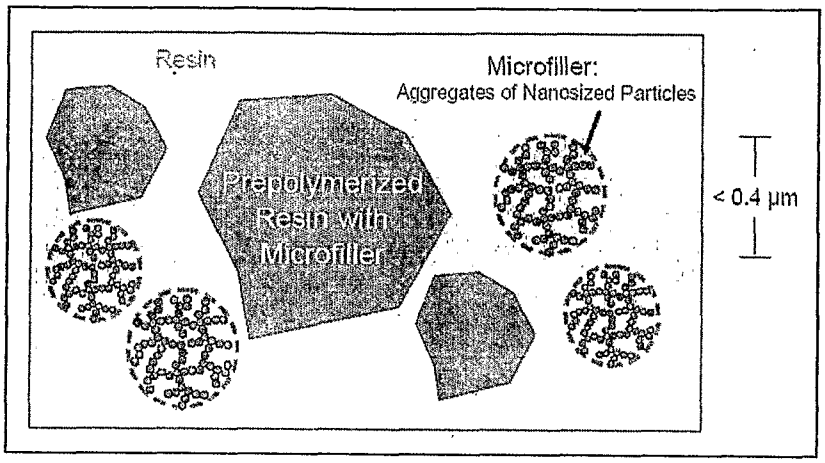

Fig. 1.2 - Schematic illustration of a microfilled composite.
(image from Ceram.X® scientific compendium, Dentsply DeTrey)

The microfilled composites have lower mechanical properties due to the larger volume of resin. They possess higher coefficients of thermal expansion, greater water sorption, higher polymerization shrinkage, lower module of elasticity, lower tensile strength and lower fracture toughness [19].

1.2.1.3 Hybrid & Micro-Hybrid composites:

Hybrid composites are so called because they are made up of polymer groups (organic phase) reinforced by an inorganic phase, including 60% or more of the total content (volume). Composed of glasses of different compositions and sizes (instead of pre-polymerized resin particles), with particle sizes ranging from 1 to 10 micrometers, and containing ≤ 0.4 µm sized colloidal silica [18] (Fig. 1.3.A).

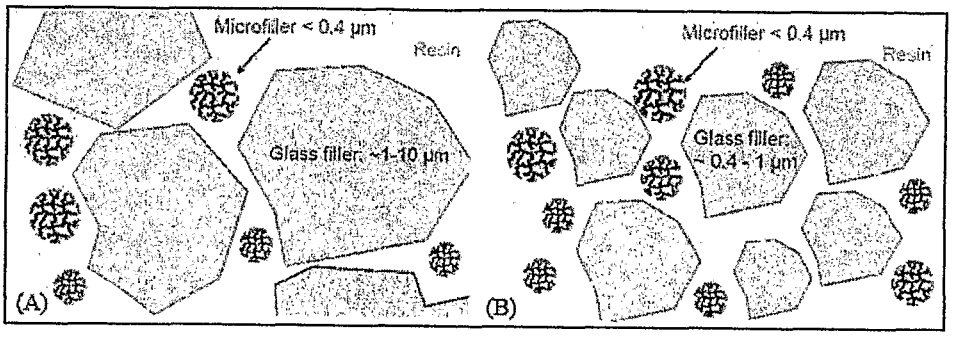

Fig.1.3 - (A) Schematic illustration of a hybrid and (B) a microhybrid composite. (image from Ceram.X® scientific compendium, Dentsply DeTrey)

Recent developments lead to smaller sizes of the glass filler fraction with an average particle size of about 0.4 - 1 µm resulting in the so called Micro-Hybrid Composites (Fig. 1.3.B). The majority of today composites used in dentistry are included in this group [18].

As shown in Fig. 1.3, hybrids and microhybrids contain a broad range of particle sizes. A wide range of particle sizes can lead to high filler loading which results a high strength. While they may contain a small fraction of filler particles in the nanomer particle size range, they also contain a range of substantially larger filler particles which influences the optical properties of these composites and detracts from polish retention. The average particle size of hybrids and microhybrids is typically below 1 µm but above 0.4 µm (0.4 µm $\leq$ hybrid filler size $\leq$ 1 µm) [17].

The characteristic properties of these materials are: availability of a wide range of colors and ability to mimic the dental structure, less curing shrinkage, low water absorption, excellent polishing and texturing properties, similar abrasion and wear to that of dental structures, closer thermal expansion coefficient to that of teeth, universal recipe for both the anterior and posterior sector, different degrees of opaqueness and translucency in different tones and fluorescence [20]. Fig. 1.4 indicates a schematic scale for filler sizes.

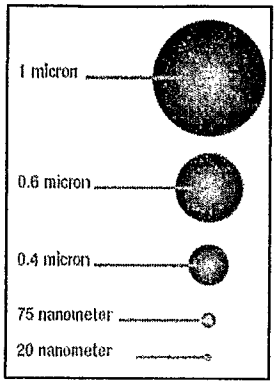

Figure 1.4 - a schematic scale indicating filler sizes used in dental composites (image from Filtek Supreme Plus ® technical product profile, 3M EPSE).

Flowable composite resins have lower filer volumes than the other high viscous composite resin restorative materials. As a result of this lower filler volume, these materials have decreased in viscosity, which makes them a good choice as a pit and fissure restorative. However, they also have increased shrinkage and wear along with decreased strength. They have been recommended as a class V restorative or as a liner under other posterior composites [21]. Their main advantages are: high wetability of the tooth surface, ensuring penetration into every irregularity, ability to form layers of minimum thickness, so improving or eliminating air inclusion or entrapment [22], high flexibility and less displacement in stress concentration areas (cervical wear processes and cavitated dentine areas), radio-opaqueness and availability in different colors. The drawbacks are: high polymerization shrinkage (due to lower filler load) and weaker mechanical properties [21, 22, 23].

Some of the indications for these materials that may be highlighted are: preventive resin restorations (minimally invasive Class I), pit and fissure sealants, base or liner, small/angular Class V abfraction lesions, sealing ditched amalgam margins, repair of small porcelain fractures in non-stress-bearing areas, enamel defect repair, repair of crown/composite resin margins, luting porcelain and composite resin veneers and small class III restorations [23].

Packable or "condensable" composites have recently been introduced to the profession as an amalgam substitute to remedy some of posterior composite restorations. They contain a higher filler load as well as better filler distribution. This will result in a