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Comparative evaluation of addition of different nanoparticles on the mechanical properties of maxillofacial silicone elastomer: an in vitro study."

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ABSTRACT: Facial disfigurement can be the result of congenital anomaly, trauma or tumour surgery that can be restored using prostheses. Silicone elastomer is most used material for facial restoration. Mechanical properties and colour degradation are the most common reasons for failure of maxillofacial prosthesis. Concentration of fillers, additives, and their types determine required mechanical properties of the silicone prostheses.The objective of this study is to comparatively evaluate the addition of zinc, silver, and surface treated silica nanoparticles on the mechanical properties of maxillofacial silicone elastomer.

KEYWORDS: Nanoparticles, Maxillofacial Silicone Elastomer, Tear Strength, Tensile Strength, Hardness, Percent Elongation

I. INTRODUCTION

Maxillofacial prosthetics is a branch of prosthodontics concerned with the restoration and / or replacement of stomatognathic (jaws) and craniofacial (facial) structures with prostheses that may or may not be removed on a regular or elective basis.[1]Maxillofacial prosthodontics currently finds itself undergoing more transformation than at any other time in its existence. Silicone elastomers have been used for over 50 years to fabricate prosthesis and the most preferred material because of its chemical inertness, durability, ease of manipulation, and biocompatibility.[2]

Despite this, the most common reason for re-fabrication of maxillofacial prosthesis are the expected half-life and degradation of colour and mechanical properties of silicone maxillofacial prostheses. Thus, it is necessary to have a material with satisfactory tear strength, tensile property, and appropriate hardness. The ideal material should be like the missing facial tissue to optimally match a patient's articulate features of mastication, speech resonance, and facial gesture. Consequently, there is a need for improved materials with superior physical and mechanical properties that are comparable to those of human tissues and skin.[2]In the past few decades, most material research in this area has focused on optimizing prosthesis performance by improving the physical and mechanical properties of prosthesis material so that it more closely resembles human skin and has longer service life. The optimization of mechanical properties can be carried out by incorporating nanoparticles that act as fillers.[6]

Fillers are nano sized particles added to the silicone elastomer to improve the mechanical properties and viscosities of silicone elastomers. The fillers fulfil the task of supporting the crosslinked matrix by diffusing to the matrix.[5] Nano-oxide particles are rigid and have a higher shear modulus than the pure silicone elastomer. The enhanced properties discovered in adding nanoparticles into a polymeric matrix may be attributed to the higher surface energy and chemical reactivity of the particles, allowing them to interact with the silicone elastomer matrix and form a 3-dimensional network within the silicone polyethylene backbone. [6]Several studies[3,7,8]have confirmed the effectiveness of nanoparticles like silicon dioxide, silver oxide and zinc-oxide in protecting silicone against colour deterioration, as nanoparticles block the ultraviolet rays and so increase its durability in terms of colour. The properties of hardness, tear strength and tensile strength help to assess material durability.[3]

Some studies[2,3,4,5,6]assert that nanoparticles may provide benefits, including the improvement of the physical properties of polymers, the number of published studies is scarce related to changes in hardness, tear strength, and permanent deformation when nanoparticles are added to facial silicone.

Hence, the purpose of this in vitro study is to comparatively evaluate the influence of the addition of nanoparticles on the hardness, tear

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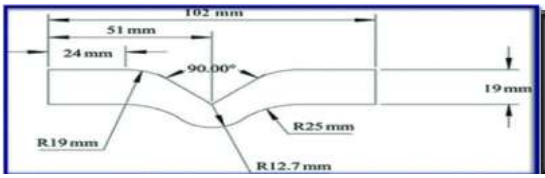
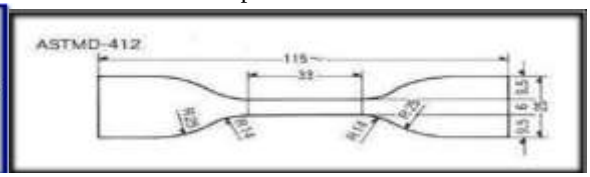
strength, tensile strength, and percentage elongation of a facial silicone. The null hypothesis is that the addition of nanoparticles would not influence these properties of the silicone.

II. MATERIALS AND METHODOLOGY

Specimen preparation and material manipulation

A trouser and dumbbell shaped brass metal die (Fig 1 &2) was fabricated in accordance to specifications given by American society for testing and material (ASTM No. D2240, No. D624 and No. D412).AutoCAD was used to design the dimensions of specimens as follows.





A total of seventy-two specimens were used in this study that were divided into three main groups (based on mechanical property) with four subgroups in each group (based on nanoparticles) Twenty-four specimens each were used to test hardness, tear strength, tensile strength, and percentage elongation respectively. Tensile strength and percentage elongation were evaluated using the same specimens.

TABLE 1a:Distribution of specimens

PROPERTIES	CONTROL GROUP	ZINC NANOPARTICLES	SILICA NANOPARTICLES	SILVER NANOPARTICLES
HARDNESS	H_C	H_Z	H_S	H_A
TEAR STRENGTH	T_C	T_Z	T_S	T_A
TENSILE STRENGTH	Tn_C	Tn_Z	Tn_S	Tn_A
PERCENTAGE ELONGATION	P_C	P_Z	P_S	P_A

Silicone elastomer specimens (M511Technovent Ltd, USA) containing different nanoparticles including silver: 0.002%,[19] zinc :2%[1] and surface treated silica: 3%[11] were prepared by adding above mentioned percentage of nanoparticles to the base of the pre-weighed silicone elastomer separately.

Test specimens containing nanoparticles were fabricated by adding weighed nanoparticles to the base paste i.e part A of elastomer .The mixture was kept on the vibrator for the proper distribution of nanoparticles. Then the mixed part A was added to the part B on a wider glass slab to minimise incorporation of air bubbles. The mix was kept in vacuum chamber at 360 rpm for 5min under -10 bar vacuum pressure to remove air bubbles incorporated during mixing. The mixing steps were performed at a relative humidity of 50%+10% and temperature of 23^0± C.

The metal die was coated with petroleum jelly to facilitate easy removal of test specimens after polymerisation. The mixed elastomer was then placed in the dumbbell and trouser shaped die which was closed with a metal lid and allowed to polymerise for 24 hours. After polymerization the specimens were carefully removed and excess flash was trimmed.

Testing of specimens for:

Hardness: A total of 24 trouser shaped specimens of group H_A, H_z, H_S, H_C were subjected to shore A hardness test by using durometer in accordance with ASTM D2240. As per the dimensions of mould, each specimen was of 3mm thickness; three specimens were stacked on one another to obtain thickness of 9mm. The digital durometer was placed in a vertical position with the point of indenter tip at least 12mm from any specimen edge and pressor foot was applied parallel to the surface of the specimen as rapidly as possible. Readings were made one second after firm contact was achieved. Five sites were

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measured for each specimen with a 6mm distance between each site. The specimen at the top was removed and new specimen was added. The mean value of five was considered as the hardness of material.

Tear strength:

A total of 24 trouser shaped specimens of group T_A,T_Z,T_S,T_C were subjected to tear strength test using the computer controlled universal testing machine in accordance with ASTM D624. The thickness of the specimen was measured in three locations across the width of the specimen, near its centre, and the average measurement was used. The specimen was placed in the plate grips provided with the universal testing machine and stretched at a rate of 500mm/min, during which time the force applied was be recorded.

From these measurements, the tear strength of the specimen was calculated using the formula:

$T=F/d$

Where F is the maximum force in newtons and d is the thickness of specimen in millimetres.

Tensile strength: A total of 24 dumbbell shaped specimens of group Tn_A,Tn_Z,Tn_S,Tn_C were tested according to ASTM D412. The thickness and width of each specimen was measured three times with a calliper, and the average value was used in calculating the specimen cross sectional area. The specimen was placed in the grip of the universal testing machine using care to adjust the specimen symmetrically to distribute tension uniformly over the cross section.

The lower member remained fixed while upper member moved at constant rate of 500mm/min cross head speed. The maximum load prior to breaking was obtained and tensile strength was calculated using the following formula:

$Tn=F/A$ Where Tn is the tensile strength; F is the force magnitude prior to breaking; A is cross sectional area of unstrained specimen.

Percent Elongation

A total of 24 dumbbell shaped specimens were tested for percentage elongation. The original length was measured before testing using the digital calliper by placing benchmarks on the specimen 25 mm apart, equidistant from centre and perpendicular to its long axis. The additional distance between the benchmarks upon sample failure, was recorded by computer software. The percentage elongation was calculated from following equation:

$E=100(L_b-L_0)/L_0$

where L_b is the length after rupturing and L_0 is the original length.

III. STATISTICAL ANALYSIS

Normality of the data was assessed using Shapiro Wilkinson test.The data of hardness, tear strength and tensile strength followed normal distribution so the difference between the groups was evaluated using parametric tests such as, One way ANOVA test (Within group) and Post hoc Tukey test (between group).Since the data of percent elongation was not following normality, the difference between the groups was evaluated using non parametric tests such as, Kruskal Wallis ANOVA (within group) and Mann Whitney U test (between group).

IV. RESULTS

HARDNESS

The highest mean value of hardness was found for group incorporated with zinc nanoparticles. The other two groups containing silver and silica nanoparticles respectively had hardness comparable to the control group without any nanoparticles with no statistically significant difference observed. Although the hardness increased significantly for specimens containing zinc it was found within acceptable range of 25-40 Shore A hardness. Comparing means of all groups showed high statistical significance ($p < 0.01$) Post hoc Tukey HSD test was conducted to compare mean values (of each group) with all other groups. All groups showed high significant difference to each other.

International Journal Dental and Medical Sciences Research
Volume 5, Issue 2, Mar - Apr 2023 pp 01-07 www.ijdmsrjournal.com ISSN: 2582-6018

Table 1b: One-way ANOVA for shore A hardness test

Groups		N	Mean	Std. Deviation	F	p value
Hardness	H_C	6	26.6667	1.03280	23.55	0.000 HS
	H_Z	6	31.2333	1.24847		
	H_A	6	25.5667	1.62193		
	H_s	6	26.7333	1.08566		

Statistical test applied: One Way ANOVA; HS – Highly significant at p<0.01

Table 1c: Tukey HSD test between all study groups of shore A hardness test

Dependent Variable	(I) group	(J) group	Mean Difference (I-J)	p value
Hardness	H_C	H_Z	-4.56667*	.000 HS
		H_A	1.10000	.455
		HS	-.06667	1.000
	H_Z	H_A	5.66667*	.000 HS
		H_S	4.50000*	.000 HS
	H_A	HS	-1.16667	.405

TEAR STRENGTH

Comparison of mean Tear strengths (in N/m^2) between these study groups was done using one-way ANOVA test (table 2b). A statistically significant difference was found between the groups ($P < 0.01$). Highest tear strength was recorded for T_Z, followed by T_C and the tear strength of other two groups i.e T_A and T_S are comparable.Further, individual comparisons were done using Tukey's Post hoc Analysis. The Post hoc test demonstrated that GroupT_Z showed significantly highest mean Tear strength compared to other study groups at P<0.01, this was followed by Group T_C showing significantly higher mean impact strength compared to groups T_A and T_S at P<0.01

Table 2b: One-way ANOVA for Tear strength test

Groups		N	Mean	Std. Deviation	F	p value
Tear strength	TC	6	14.1650	2.37437	23.55	0.000 HS
	TZ	6	17.8950	2.88935		
	TA	6	10.2700	1.61624		
	Ts	6	9.0367	.51267		

Statistical test applied: One Way ANOVA; HS – Highly significant at p<0.01

Table 2c: Tukey HSD test between all study groups of Tear strength test

Dependent Variable	(I) group	(J) group	Mean Difference (I-J)	p value
Tear strength	Tc	Tz	-3.73000*	.024 S
		T_A	3.89500*	.018 S
		T_s	5.12833*	.002 HS
	Tz	T_A	7.62500*	.000 HS
		T_S	8.85833*	.000 HS
	T_A	T_s	1.23333	.728

TENSILE STRENGTH

Comparison of mean Tensile strengths (in MPa) between these study groups was done using one-way ANOVA test (table 3b). A statistically significant difference was found between the groups ($P < 0.01$).

The test results demonstrated that the highest tensile strength was recorded for Tn_A, followed by Tn_z, $Tn_s$and Tn_CFurther, individual comparisons were done using Tukey's Post hoc Analysis. Table no.3c.The Post hoc test demonstrated that Group Tn_A showed significantly highest mean Tensile strength compared to other study groups at P<0.01, this was followed by Group $Tn_z$and Tn_s showing significantly higher mean tensile strength as compared to control groupat P<0.01. However no statistical significant difference was found among groups incorporated with nanoparticles at p >0.01 .

International Journal Dental and Medical Sciences Research
Volume 5, Issue 2, Mar - Apr 2023 pp 01-07 www.ijdmsrjournal.com ISSN: 2582-6018

Table 3b: One-way ANOVA for Tensile strength test

Groups		N	Mean	Std. Deviation	F	p value
Tensile strength	Tn_C	6	9.8167	.26583	7.75	0.001 HS
	Tn_Z	6	10.6167	.31898		
	Tn_A	6	10.9200	.28107		
	Tn_S	6	10.5300	.65115		

Statistical test applied: One Way ANOVA; HS – Highly significant at p<0.01

Table 3c: Tukey HSD test between all study groups of Tensile strength test

Dependent Variable	(I) group	(J) group	Mean Difference (I-J)	p value
Tensile strength	Tn_C	Tn_Z	-.80000*	.015 S
		Tn_A	-1.10333*	.001 HS
		Tn_S	-.71333*	.032 S
	Tn_Z	Tn_A	-.30333	.586
		Tn_S	.08667	.983
	Tn_A	Tns	.39000	.378

PERCENT ELONGATION

Comparison of mean Percentage elongation between these study groups was done using Kruskal Wallis ANOVA test. A statistically significant difference was found. Highest percentage elongation was recorded for P_Z , followed by P_S,P_A and P_C Further, individual comparisons were done using Mann Whitney U test Post hoc Analysis. Table no:4c The Post hoc test demonstrated that Group P_Z showed significantly highest mean percentage elongation compared to other study groups at P<0.01(p= 0.007), this was followed by Group P_S, P_A and P_C. Statistical significance difference in percentage elongation was found in groups containing nanoparticles in comparison to control group. However no statistically significant difference was found among groups incorporated with nanoparticles at p >0.01.

Table 4b: Kruskal Wallis ANOVA for percentage elongation

		N	Mean	Std. Deviation	Median	Chi square	p value
Elongation	PC	6	371.5000	2.81069	372	12.20	0.007 HS
	PZ	6	380.0000	4.19524	380.5		
	PA	6	376.6667	3.93277	378		
	PS	6	378.6667	2.06559	380		

Statistical test applied: Kruskal Wallis ANOVA; HS – Highly significant at p<0.01

Table 4c: Mann Whitney U test between all study groups of percentage elongation test

Dependent Variable	(I) group	(J) group	Mean Difference (I-J)	p value
Percentage elongation	P_C	P_Z	-8.50000*	.006 HS
		P_A	-5.16667	.03 S
		P_S	-7.16667*	.005 HS
	P_Z	P_A	3.33333	.132
		P_S	1.33333	.394
	P_A	P_S	-2.00000	.403

V. DISCUSSION

The properties that are considered essential for maxillofacial silicone elastomers are high tear strength, high tensile strength, adequate hardness, and good level of elongation at break. Results from various studies indicate that none of trading materials tested can meet all these criteria.[2]

The aim of this study is to comparatively evaluate the effect of addition of zinc, silver, and surface treated silica nanoparticles on the hardness, tear strength, tensile strength, and percentage elongation of maxillofacial silicone elastomer. Fillers are nanosized particles added to the silicone elastomer to improve the mechanical properties and viscosities of silicone elastomers. The fillers fulfil the task of supporting the crosslinked matrix by diffusing into the matrix[5].To achieve the significant improvement in mechanical properties, the degree of filler addition and degree of reinforcement is one of the main requisites. The reinforcement depends to a large extent on filler loading (amount of filler), filler characteristics, polymer properties and processing conditions.[2] In the present study Zinc oxide (2%), silver oxide (0.002%) and silicon dioxide (3%) nanoparticles are used as fillers in maxillofacial silicone elastomer.

The hardness is the ability of a material to resist permanent surface indentation. [9]The resistance to indentation and penetration makes the material harder. Shore A hardness is a measure of the texture of silicone elastomer, with a value between 25 and 35 indicating similarity with soft tissue, according to the defect area.[7] The increase in hardness values after addition of nanoparticles can be caused by the spreading of the nanoparticles inside the polymer matrix and between the

polymeric chains thus filling the inter-aggregate areas. This can increase the resistance to indentation and penetration making the material harder.Nobrega et al., in their study found that addition of TiO2 at concentration of 1% and 2% decreased the hardness values, as the TiO2 particles tend to agglomerate. Nobrega et al also mentioned that, incorporation of Nano size oxides of Ti, Zn, or Ce at concentrations of 2.0 to 2.5% by weight into a silicone-based elastomer, improves hardness, but when the concentration was increased to 3.0%, the hardness decreased.

Tear strength is the ability of the material to resist tearing forces that act at right angle to the surface flaw.Generally, the degradation of facial prosthesis starts at the edges that need to be thinned as possible for aesthetic reasons.[9]

The increase in tear strength may be attributed to the action of nanoparticles in the continuous phase of the silicone elastomer that leads to increased cross-linked structure formation of the silicone material.[7]

Li et al.;in their study found that silicone elastomers with ZnO nanoparticles as fillers is associated with strengthening of the material The strain energy will spread by the polymer near and around the growing cracks, and this explanation could be behind the increase of tear strength. The energy within the polymer matrix will dissipate by nanofillers astearing progress, thus increasing its resistance to tearing such that a higher force and load will be needed to completely break the polymer matrix.[5] Han et al., in their study found that incorporation of nanoparticles at concentration of 2.0% improved tear strength, but, when the concentration was 3.0%, the tear strength decreased. Although nanosized oxide particles can reinforce the silicone elastomer matrix, it is important to maintain the filler content at a proper level because of their higher surface energy and chemical reactivity. This fact helps to explain the observed decrease in tear strength when the concentration of nano-oxides exceeded the certain amount.[3]

Tensile strength refers to the maximum stress that material can resist before it begins to fail under localized accelerated deformation. Tensile strength can be considered based on the catastrophic tearing of cracks from voids. A small amount of elastic energy can break the polymer network when the elastomeric network can dissipate input energy into heat. Filler addition is a good source of energy dissipation.

Andreopoulos et al ; in their study found that the nano-ZnO aid in polymerization and increasing the polymer's total cross-linking density, making it stronger and stiffer. It also prevents the polydimethylsiloxane chains from breaking, thus increasing the tensile strength. ZnO nanoparticles increase the contact surface area between elastomer chains, producing better tensile strength with a more rigid structure. The nanoparticles adsorb to polymer chains and create numerous crosslinking sites due to their high surface energy. As a result, the polymer's total crosslinking density increased, resulting in greater stiffness, which prevents the polymer chains from breaking. Moreover, the physical interconnection that occurred between nanoparticles and silicone matrix, when the tensile forces are applied, the nanoparticles and polymer chains start sliding over each other, thus preventing failure and breakage of the polymer chains.[9]

Elongation indicates a material's capacity to stretch before it breaks.[9] It is more useful in rehabilitate defects of the head and neck with extending undercuts.The elongation of cured silicone elastomer is greatly dependent on the crosslinking system, cross-linking density and the interaction between fillers and polymer chain. Also, the elasticity and strength of maxillofacial silicone are greatly dependent on the molecular weight and the degree of cross-linking of polymers.[7] Han et al., in their study concluded that the incorporation of ZnO nano-sized oxide improved tensile strength and percent elongation up to 2.5 percent. According to the study conducted by Singh et al., there was an increase in tensile strength and percentage elongation upon addition of different nanoparticles with M-511 silicone.

LIMITATIONS OF THE STUDY

The present in vitro study had following limitations:

- The study used only the single concentration of different nanoparticles.
- The effect of ageing on the mechanical properties of maxillofacial silicone elastomer was not evaluated.
- The uniform distribution of nanoparticles was not confirmed using scanning electron microscopy.

VI. CONCLUSION

Within the limitations of this in vitro study, the following conclusions were drawn:

- The silicone elastomer specimens containing zinc nanoparticles (Group H_Z) shows highest hardness. There is no statistically significant difference in hardness between the control

group (Group H_C), the group with silver nanoparticles (Group H_A) and the group with silica nanoparticles (Group H_S).

- The tear strength significantly improved in silicone elastomer specimens reinforced with zinc nanoparticle (Group T_Z). However, silicone elastomer specimens reinforced with silver (Group T_A) and silica nanoparticles (Group Ts) showed decrease in tear strength in comparison to the control group.
- The tensile strength significantly improved in silicone elastomer specimens reinforced with zinc nanoparticles (Group Tnz,). A significant increase in tensile strength was also found in silicone elastomer specimens reinforced with silver nanoparticles (Group Tn_A) and in silicone elastomer specimens reinforced with silica nanoparticles (Group Tn_S).
- The percentage elongation increased significantly in silicone elastomer specimens reinforced with zinc nanoparticles (Group Pz). The highly significant increase was found in group of zinc and silica nanoparticles.
- Hence, the maxillofacial silicone elastomer incorporated with zinc nanoparticles had a significant increase in mechanical properties in terms of hardness, tear strength and percent elongation in comparison to other study groups.

BIBLIOGRAPHY

[1]. Glossary of prosthodontics terms-GPT-9
[2]. Shakir DA, Abdul-Ameer FM. Effect of nano-titanium oxide addition on some mechanical properties of silicone elastomers for maxillofacial prostheses. J. Taibah Univ.Medical Sci. 2018 Jun 1;13(3):281-90.
[3]. Chowdhary R. Effect of adding silver nanoparticle on physical and mechanical properties of maxillofacial silicone elastomer material-an in-vitro study. J.Prosthodont.Res. 2020;64(4):431-5.
[4]. Zayed SM, Alshimy AM, Fahmy AE. Effect of surface treated silicon dioxide nanoparticles on some mechanical properties of maxillofacial silicone elastomer. Int. J.Biomater. 2014 Oct;2014.
[5]. Cevik P, Eraslan O. Effects of the addition of titanium dioxide and silaned silica nanoparticles on the mechanical properties of maxillofacial silicones. J.Prosthodont.2017 Oct;26(7):611-5.
[6]. Han Y, Kiat-amnuay S, Powers JM, Zhao Y. Effect of nano-oxide concentration on the mechanical properties of a maxillofacial silicone elastomer. J. Prosthet.Dent. 2008 Dec 1;100(6):465-73.
[7]. Wang L, Liu Q, Jing D, Zhou S, Shao L. Biomechanical properties of nano-TiO2 addition to a medical silicone elastomer: the effect of artificial ageing. J.Dent. 2014 Apr 1;42(4):475-83.
[8]. Akash RN, Guttal SS. Effect of incorporation of nano- oxides on color stability of maxillofacial silicone elastomer subjected to outdoor weathering. J.Prosthodont.2015 Oct;24(7):569-75.
[9]. Ali Saad Ahmed, Mohammed Moudhaffer Mohammed Ali, Effect of Strontium Titanate NanoPowder Addition on Some Mechanical Properties of Room Temperature Vulcanized Maxillofacial Silicone, J Res Med Dent Sci, 2021, 9(12): 59-65
[10]. Karaman G, ALTINTAŞ E. Investigation of the effects of different nanoparticle additionals on the mechanical properties of silicone elastomer used in maxillofacial prosthesis. Journal of Health Sciences and Medicine. 2020 Jan 23;5(6):1654-60
[11]. Andreopoulos AG, Evangelatou M, Tarantili PA: Properties of maxillofacial silicone elastomers reinforced with silica powder. J Biomater Appl 1998;13:66-73
[12]. Tukmachi MS, Moudhaffer MA. Effect of nano silicone dioxide addition on some properties of heat vulcanized maxillofacial silicone elastomer. IOSR - JPBS 2017; 12(3): 37-43.
[13]. Nguyen CT, Chambers MS, Powers JM, Kiat-Amnuay S. Effect of opacifiers and UV absorbers on pigmented maxillofacial silicone elastomer, part 2: mechanical properties after artificial aging. J Prosthet Dent 2013;109:402-10.
[14]. ASTM Standard D624. Standard test method for tear strength of conventional vulcanized rubber and thermoplastic elastomers. West Conshohocken: American Society for Testing and
[15]. Materials; 2007. Available at: http:// www.astm.org