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EFFECT OF PARTICLES SIZE OF CRT GLASS WASTE ON PROPERTIES OF POLYMER CONCRETES

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Abstract

The research has been focused on concretes in which the continuous phase is some kind of polymeric resin and the discrete phase is some type of mineral aggregate. Such composite materials are known as Polymer concretes (PC) and boast several advantages such as lower weights, higher resistance to corrosive environments and chemical attacks, faster curing and lower permeabilities. In PC the inorganic fraction can reach up to 90% of the total and is made up of aggregates such as sand and gravel. The aim of this work is to study how to use glass waste CRT to replace sand and gravel, from to made a recycled glass polymer concretes. In particular it has been investigated the effect of particle size distribution of CRT recycled glass on properties of PC obtained. The first step is the chemical/physical characterization of recycling materials through XRF, XRD, particle size and microstructural analysis (SEM). This is followed by the realization and optimization of laboratory prototypes prepared with glass wastes and unsaturated polyester resin. The performances of material have been evaluated with different tests: microstructural analysis (SEM, packing factor), chemical/physical analysis (chemical resistance, water adsorption), and mechanical analysis (bending test, impact test, scratch test). The results obtained showed how it is possible to obtain a concrete polymer composed only of recycled glass. The results also showed the structural limits of the materials obtained allowing the relative percentages between coarse and fine fractions of glass to use to achieve PC with recycled glass.

Key words: glass waste, polymer concrete, recycling, unsaturated polyester

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1. Introduction

Polymer concretes (PC) are composite materials formed by incorporating inorganic aggregates into polymers, they are used in a range of civil and structural applications such as bridge decking, concrete crack repair materials, pavement overlays, hazardous waste containers, sewer pipes and decorative constructional panels. Due to their specific properties including; higher mechanical strengths, and lower weights, excellent bonding to different substrates, higher resistance to corrosive environments and chemical attacks, faster curing and lower permeabilities. The aggregates can be silicates, quartz, quartz sand, crushed stone, gravel, limestone, calcareous, granite, clay, etc. In the composition different types of fine materials such as: fly ash, silica fume, glass fiber, carbon fiber, etc. can be used to improve the properties of polymer concrete. The aggregates in weight percentages between 60% and 95% are used, for example are used sand and gravel between 60 and 80% to produce pipes and structural components, while is used quartz sand in percentage up to 95% to produce kitchen tops, desks tops, and worktops. Various polymers have been used in fabrication of PCs such as unsaturated polyesters, epoxies, acrylics, polyuretan (Agavriloaia et al. 2012). During hardening, the polymer react through their unsaturated groups, the chemical reaction is isothermal and is called cross-linking (Lipovsky, 2006). The production process associated with it is referred to as curing, and the resulting polymer binder is a thermosetting polymer (Elalaoui et al., 2012). In concrete polymers the use of recycled materials is

widely studied, both with the introduction of inorganic and organic recycled materials (Barbuta et al., 2016; Hodul et al., 2016; Shi-Cong et al., 2013; Pozzi et al., 2013; Taurino et al., 2015; Saribiyik et al., 2013; Shao et al., 2000). This research has investigated on how to use waste glass ground from cathode ray tubes (CRT panel glass) for the realization of polymer concretes. CRT glass originate from the treatments carried out on television sets and computer monitors permit the separation of the cathode-ray tube (CRT) which is two thirds of the entire weight of these apparatus and consists for 85% of glass (Andreola et al., 2010). Color CRTs generally are composed by four different glasses each one having a particular chemical composition. Panel (screen, the front part) a very homogeneous barium (9-11 wt%) –strontium (8-10 wt%) glass, of a greenish-blue color whose weight is about two-third of the whole CRT. Cone (the hidden part inside the TV set) a lead (18-20 wt%) glass, whose weight is about one-third of the whole CRT. Neck a glass with a very high lead content enveloping the electron gun. Frit (the junction between the panel and the cone) a low melting lead glass, included only in color CRTs. The separated glasses after reclaiming process become a not dangerous residue and represent a useful raw material not only in closed-loop recycling but also in open-loop one.

In the polymer concretes both glass from screens (panel) are potentially acceptable even if they must be supplied with particular characteristics of homogeneity, cleanliness, etc. The research was developed in collaboration with Stena Technoworld, a company specializing in the recycling of waste glass from cathode ray tubes. Analyzing the recycled glass produced by Stena, it was decided to direct research into the production of kitchen tops, desk tops and worktops using Stena glass instead of quartz sand. These materials industrialmente classificati come quartz composites are produced whit unsaturated polyester resins (5-8% by weight), quartz (95-92% by weight) and colored pigments (Fugazzi,1999; John, 2006). The choice of working on these products was made because the recycled glass produced by Stena has a particle size distribution compatible with the quartz sand used for quartz composites.

2. Case studies

2.1 Materials

The materials used for the realization of new polymer concretes are the unsaturated polyester resin, glass wastes from cathode ray tube and quarz sand. Unsaturated polyester resin (UP) is a category of thermosetting polymers which is widely used in fabrication of quartz composites.

Such due to their suitable processing characteristics, thermal stabilities, chemical resistance and comparatively low prices. The polymeric matrix is an unsaturated polyester resin dispersed in styrene and methacrylate, provided by Carlo Riccò Company (Correggio Italy). Table 1 shows the characteristics before curing.

Table 1. Characteristic of the unsaturated polyester resin before curing

Content methacrylate	5±1 %
Content styrene	27-31 %
Viscosity at 25°C	450–550 mPa·s
Appearance liquid resin	Limpid, Green
Stability at 80°C	24hours

This unsaturated polyester is accelerated with a complex of cobalt, and catalyzed with methyl ethyl ketone peroxide (MEKP) therefore the crosslinking occurs at room temperature with the simple addition of a peroxide. In Table 2 are reported the Gel Time and Curing of the resin and the temperature range in which the reaction exothermic peak may occur.

Table 2. Gel time and curing of unsaturated polyester resin

Gel time	20 – 38 (min.)
Exothermic peak	185° – 205 °C
Curing time	28 – 53 (min.)

For glass wastes, two granulometric fractions obtained by dry milling of CRT glass were used, one with a coarse granulometry and one with fine granulometry. Stena Technoworld, a factory in Angiari (It), has provided the coarse and fine CRT panel glass wastes. The composition of glass fractions of CRT panel glass has been obtained by XRF analysis, the data show a barium glass with a low concentration of dangerous elements (Table 3).

Table 3. Chemical composition (% in weight) of the CRT panel glass by XRF analysis

Oxides	***% in weight***
SiO_2	**56.87**
Na_2O	**12.89**
SrO	**8.52**
BaO	**7.95**
K_2O	**7.29**
Al_2O_3	**3.76**
ZrO_2	**1.41**
ZnO	**0.63**
TiO_2	**0.38**
Fe_2O_3	**0.22**
NiO	**0.03**
PbO	**0.02**
CoO	**0.01**
CaO	**0.01**
MgO	**0.01**
Tot.	**100**

Coarse CRT panel glass has been used to produce the coarse fraction of the filler, used to make the composites. The particles size distribution of the coarse CRT panel glass is resulted to be a monomodal (Fig. 1), with a peak around 200 microns. The particles size distribution has achieved with the use of a Micromeritics MASTERSIZER 2000 laser particle

analyzer. The fine CRT panel glass is used to produce the fine fraction of the filler, used to make the samples. In this glass the particles size distribution shows a peak around 20 micron (Fig.2) and the microstructure of the particles are visible in Fig. 4, where the presence of very fine particles is very high. The quartz sand used show a bimodal particles size distribution (Fig. 3) with the peaks at 300 and 35 microns.

The first peak represents particles size the coarse fraction that gives the main structure to the composite. The second peak represents particles size the fine particles that gives to the structure a good level of compaction. The chemical analysis carried out with XRF showed a content of SiO_2 of 99.98%.

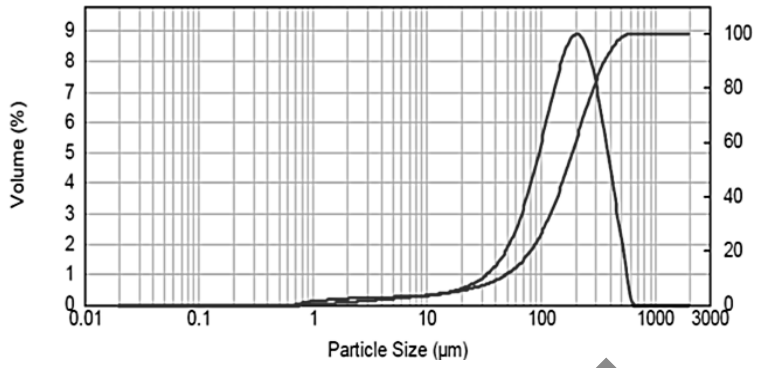


Fig. 1. Particle size distribution coarse CRT panel glass, is show a peak at 200µm

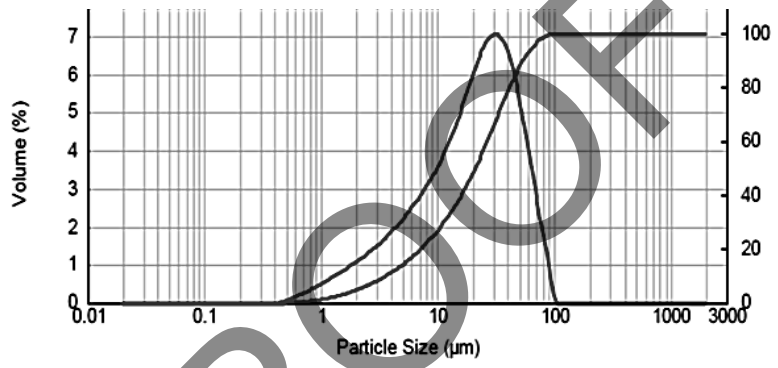


Fig. 2. Particle size distribution of fine glass CRT

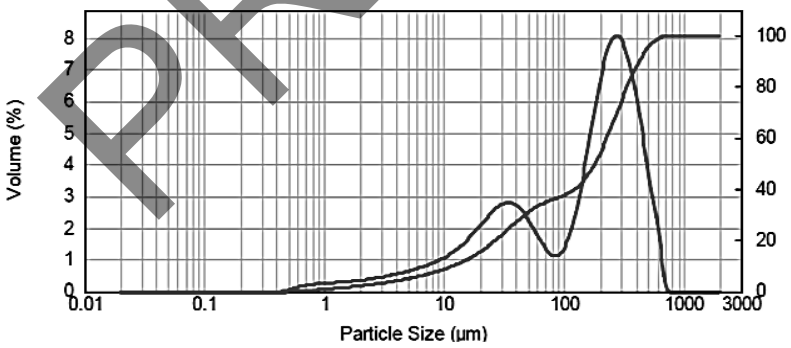
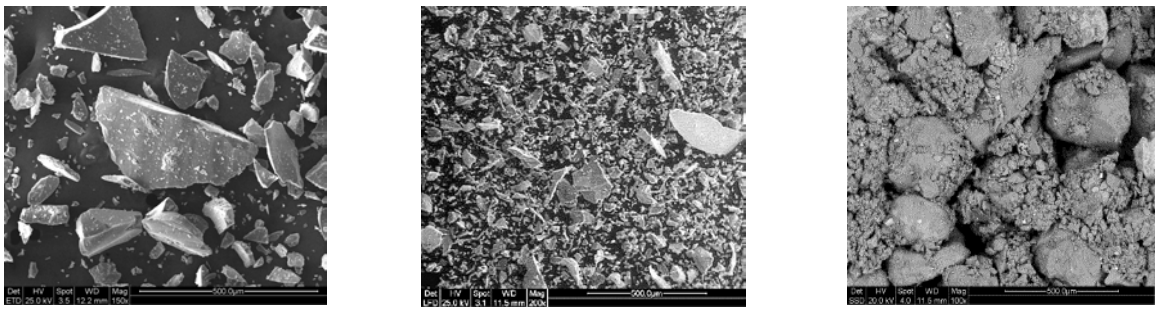


Fig.3. Quartz sand particle size distribution, peaks at 300 and 35µm



(a) (b) (c)

Fig. 4. ESEM micrographs of coarse (a), fine (b) CRT panel glass and quarz sand (c)

On the glasses and sand used, a morphological analysis was performed using an electron microscope (ESEM).The micrographs (Fig. 4) they showed that the glass is made up of particles with heterogeneous diameter and morphology with sharp edges of the grains, due to the dry grinding of the glass carried out in the CRT treatment plant. On the other hand, the quartz sand has a more rounded morphology of the particles, evident effect of the different processing phase to which it is subjected.

2.2. Sample preparation

Four sets of CRT glass samples were produced for the work, and a series of quartz sand was used as reference (code samples QSL). Samples with the glass were prepared by adding the fine CRT glass to the coarse CRT glass up to a percentage of 30%. Samples prepared with quartz sand were made to reproduce quartz compounds in the laboratory, these samples were used as reference samples. In consideration of the average percentage used in industrial quartz composites, the samples were made with a ratio between filler and unsaturated polyester resin to 92/8 by weight. The samples have been prepared by mixing the filler with resin using a mechanical mixer. The suspension obtained has been casting at 25°C into a 10x10x2.5 cm metal mold, and for cross-linking pressed at 10 bar at 25°C for 1 hour, using one Carver hydraulic press. After the hardening phase the samples have been cured to 80°C for 4 hours in a stove to complete cross-linking. To improve the adhesion between polymer and filler, a silane coupling agent (vinyltriethoxysilano) has been added to the samples. This addition has been made at 1% in weight on the filler. The composition of samples is shown in Table 4, with percentages in weight of glass, quartz sand and unsaturated polyester resin. Five samples have been made for every composition.

2.3 Testing on samples

On the produced samples we have carried out the following analyzes:

- Water absorption by immersion test in distilled water for 24 hours at 25° C.
- Chemical resistance in hydrochloric acid (10% w/w) and potassium hydroxide (10% w/w) by immersion test for 24 hours at 25° C.
-True density measured with the helium pycnometer ACCUPYC 1330, Micromeritics instrument.
- Packing factor
- Drop weight test performed to the standard ASTM D3029 using Dynatup 9250HV, Instron.
- Three points bending test performed to the standard UNI EN ISO 178, using a testing machines Instron 3340.
- Microstructural analysis with ESEM-Quanta200-FEI.

3. Results and discussion

3.1. Microstructural analysis

As we expected, the first result we have observed that the addition of fine fraction up to 30% in weight creates samples with a good level of compaction. The microstructural analysis with SEM (Scanning Electron Microscope) to show us the gradual addition of fine fraction (with particle size around 35 microns) decreases the porosity with a good compaction in the sample, with 30% in weight of fine fraction (sample Vg*/Vf/R 62/30/8) (Fig.5).

If we compare the particles size distribution of the quartz sand samples (QSL) with the glass samples we can see that only the sample Vg*/Vf/R 62/30/8 (Fig. 6) has a particles size distribution similar to the quartz composite, while the other samples have a smaller fine fraction.

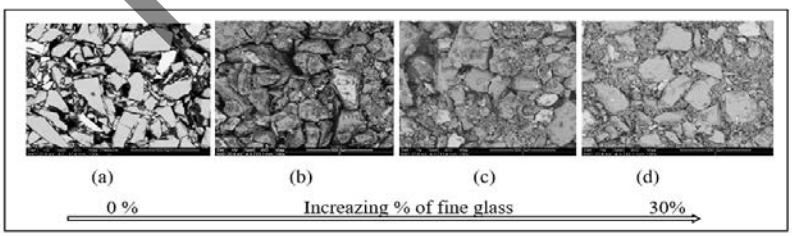


Fig. 5. ESEM micrographs of glass samples: (a) 0%; (b) 10%; (c) 20%; (d) 30% of fine glass

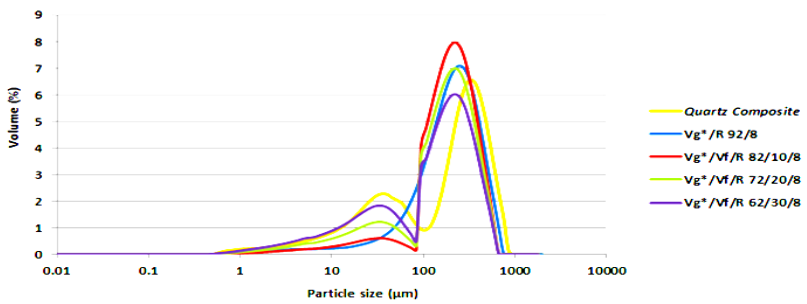


Fig. 6. Comparison particle size distribution of samples glass and quartz composite

3.2. Packing factor

The packing factor indicates the fraction of the volume of the structure occupied by particles. It is a dimensionless number and its values run between 0 and 1. The packing factor is calculated by assuming that each particle is represented as a rigid sphere and in particular, it is obtained from the ratio between the apparent density and the real density of the powder. Table 5 shows the data obtained from the density measurement and the value of the packing factor. The packing factor reaches the highest value with the sample at 30% of fine glass and the values are similar to those observed for the QSL samples.

Table 5. Density data and packing factor

Samples	***Apparent Density (g/cm^3)***	***True Density (g/cm^3)***	***Packing factor***
QSL	2.91	2.93	0.99
Vg*/R 92/8	1.98	2.60	0.76
Vg*/Vf/R 82/10/8	1.99	2.57	0.78
Vg*/Vf/R 72/20/8	2.08	2.57	0.81
Vg*/Vf/R 62/30/8	2.81	2.87	0.98

3.3. Chemical resistance and water adsorption

The chemical resistance has been evaluated in hydrochloric acid and potassium hydroxide with an immersion test of 24 hours at 25°. Table 6 shows the weight loss data obtained with the samples and other values, added as a comparison, obtained with a sample of pure resin. The increase of glass fine fraction in the glass composites decreases the chemical resistance, in contrast, the chemical resistance observed for the QSL samples was the highest.

All the samples have a better resistance in acidic medium (HCl), with lower removal rates compared to the attack in the basic environment (KOH). The unsaturated polyester resins, in fact, have a low resistance in a basic environment. It should be noted that with 30% of fine glass there is a strong increase in weight loss, especially in an acid environment.

Table 6. Chemical resistance data

	% weight loss HCl	***% weight loss KOH***
Resin	**0.04**	**0.45**
QSL	**0.05**	**0.49**
Vg*/R 92/8	**0.13**	**1.14**
Vg*/Vf/R 82/10/8	**0.33**	**2.31**
Vg*/Vf/R 72/20/8	**0.40**	**3.18**
Vg*/Vf/R 62/30/8	**2.35**	**7.87**

The most interesting data have been the increase of water absorption that is observed by adding fine glass in the samples (Table.7). This data is not related to the improvement of the packing factor, which increases with the growth in the percentage of fine glass in the samples.

Table 7. Water absorption of samples

	Water absorption %
QSL	2.54
Vg*/R 92/8	3.08
Vg*/Vf/R 82/10/8	4.97
Vg*/Vf/R 72/20/8	8.84
Vg*/Vf/R 62/30/8	9.79

The increase of the fine fraction glass makes possible to increase the level of compaction and the paking factor. The result is a very low residual porosity and consequently the decrease in water absorption. It is evident that this mechanism is valid for the samples produced only with quartz sand, while for the glass composites it is necessary to consider the interaction with the resin. The resin penetrates into the pores of the composite and the cross-linking closes the pores, sealing the composite and making it waterproof. When the cross-linking is blocked or the resin does not bind the particles, the porosity remains open and the composite results permeable. The data of water absorption on chemical degradation seem to indicate that the fine glass fraction interferes with the cross-linking mechanism, while with quartz sand there is no interference with the cross-linking reaction.

3.4. Mechanical analysis

The mechanical analysis data confirm the strong correlation with the percentage of fine glass used in the glass samples. The increase in the fine glass fraction leads to a decrease in the values observed in the bending tests (Fig. 7) and in the drop weight test (Table 8) compared to the QSL samples data. Only samples without fine glass present interesting results, with bending load values and impact energy better than the QSL samples. these results can be interpreted using the considerations made previously on the block of the mechanism of cross-linking. Only the development of a good cross-linking of the thermosetting resin allows obtaining good results in the mechanical tests.

Table 8. Data drop weight test

Sample	***Maximum load (N)***	***Energy at maximum load (J)***
QSL	1608 ± 25	1.51 ± 0.85
Vg*/R 92/8	1633 ± 30	1.56 ± 0.86
Vg*/Vf/R 82/10/8	1198 ± 24	1.02 ±0.10
Vg*/Vf/R 72/20/8	862 ± 9	0.44 ± 0.16
Vg*/Vf/R 62/30/8	852 ± 10	0.49 ± 0.23

3.5. Optimization polymer concrete

The observed behaviors of the mechanical and chemical properties are related to the partial inhibition of the formation of the lattice structure, that must bind the resin to the fine glass particles, with a consequent decrease of the chemical/physical and mechanical parameters. This is because the structure and chemical composition of the CRT panel glass particles do not allow an effective interaction between the glass surface and the polyester resin. To solve this problem, we have decided to increase the percentage of coupling agent from 1% to 4% in weight on glass. In this way, the compatibility between the glass surface and the resin tends to increase, allowing the formation of the lattice structure between particles and resin.

The results obtained show an increase in the chemical and mechanical properties of the samples obtained by increasing the silane (as observed in Table 9 for the KOH attack, Table 10 for the HCl attack, e Table 11 for water absorbption). The table shows the percentage change between the measured values before and after the percentage increase of the coupling agent. In particular, it is interesting to analyze this datum by observing that the major variations are recorded with the attack in KOH, while they are very limited in case of water absorption. The marked improvement in KOH resistance is an indication of an improvement in resin crosslinking, but the result of water absorption indicates that the porosity is not influenced.

Table 9. Chemical resistance in KOH.

Sample	***weight loss % (1% silane)***	***weight loss % (4% silane)***	***percentage variation***
QSL	0.49	/	/
Vg*/R 92/8	1.14	0.98	**14%**
Vg*/Vf/R 82/10/8	2.31	1.64	**29%**
Vg*/Vf/R 72/20/8	3.18	1.97	**38%**
Vg*/Vf/R 62/30/8	7.87	3.58	**54%**

Table 10. Chemical resistance in HCl.

Sample	***weight loss % (1% silane)***	***weight loss % (4% silane)***	***percentage variation***
QSL	0.05	/	/
Vg*/R 92/8	0.13	0.06	**54%**
Vg*/Vf/R 82/10/8	0.33	0.24	**27%**
Vg*/Vf/R 72/20/8	0.40	0.36	**10%**
Vg*/Vf/R 62/30/8	2.35	1.97	**16%**

The exception is the sample with 10% of fine glass, which shows a reduction in the absorption of 44%. Therefore, the increase in the percentage of coupling agent increases crosslinking in all the samples, but it develops a greater interaction between glass and resin only at a low percentages of fine glass. In the mechanical tests, we have an increase of the properties in the bending tests (as shown in Table 12), due to the fact that increases crosslinking.

Table 11. Water absorbption data

Sample	***absorbed water % (1% silane)***	***absorbed water % (4% silane)***	***Percentage variation***
QSL	2.54	/	/
Vg*/R 92/8	3.21	3.08	**4%**
Vg*/Vf/R 82/10/8	8.80	4.97	**44%**
Vg*/Vf/R 72/20/8	9.57	8.84	**8%**
Vg*/Vf/R 62/30/8	11.27	9.79	**13%**

Table 12. Stress bending data

Sample	***Stress bending 1% Silane (MPa)***	***Stress bending 4% Silane (MPa)***	***Stress Increasing %***
QSL	31 ± 3	/	/
Vg*/R 92/8	34 ± 4	39 ± 3	**13%**
Vg*/Vf/R 82/10/8	17 ± 1	22 ± 4	**23%**
Vg*/Vf/R 72/20/8	9 ± 3	15 ± 2	**40%**
Vg*/Vf/R 62/30/8	4 ± 1	6 ± 1	**33%**

4. Conclusions

The results obtained allow us to make the following conclusions.

The first conclusion is that it is possible to develop polymer composites loaded with CRT glass only if the percentage of fine glass is limited (<100μm). Comparing the results obtained with the specifications required for the various types of commercial composites, we can assume that it is possible to use our produced composites as thin panels usable as coatings. The composites for internal and external coatings have, as only requested property, a good resistance to bending, that can obtain by using only coarse CRT glass panel.

The second conclusion concerns the use of CRT fine glass. The data show a considerable criticality related to the interaction that this material develops with the resin. The use of coupling agents can partially solve the problem, in particular if the percentage of fine glass is used in low quantity (about 10%).

The third consideration points out that the structure of the glass particles is very irregular and because of it, it interferes with the formation of the lattice particles resin. This is a limiting factor,

especially for the use of fine glass.

Finally, the fourth consideration regards the possibility of improving the properties of CRT glass/polymer composites. We believe that this is possible by working on crosslinking catalysts and coupling agents specifically selected to solve the criticality observed in the glass resin interaction.

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