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ABSTRACT

Title of Thesis : The Influence of Aggregate Grading with Two Different Binders on Mechanical Strength of Polymer Concrete

Pei-yuan Gao, Master of Science in Chemical Engineering

Thesis directed by : Dr. R. H. Wang

The scope of this research is to study the influence of grading of the aggregate on the mixing design and the strength of polymer concrete .

Also, the curing conditions, the modification of polymer and the application of coupling agent were investigated.

Based on the experimental results, two numerical methods were developed to be used in combining the aggregates to obtain the desired specific surface area and the grading of the aggregate.

A computer program was developed for one of the methods to give all the possible compositions of the aggregate.

Theoretical explanation is offered and a numerical example is worked out which illustrates the application of these methods. THE INFLUENCE OF AGGREGATE GRADING WITH TWO DIFFERENT BINDERS ON MECHANICAL STRENGTH OF POLYMER CONCRETE

BY

PEI-YUAN GAO

Thesis submitted to the faculty of the Graduate School of the New Jersey Institute of Technology in Partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering

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ACKNOWLEDGEMENT

The author wishes to acknowledge the helpful discussions and encouragment offered by author's advisor Dr. R. H. Wang, and also wishes to acknowledge the helpful corrections by Dr. C. R. Huang, Prof. I. Hundert. In addition support from his friends and relatives are gratefully acknowledged.

TABLE OF CONTENTS

SECTION	No.	PAGE	No.

T.	INTRODUCTION		
2.	LITERATURE REVIEW	7	
3.	EXPERIMENT	16	
	3-1 MATERIALS	16	
	3-2 PROCEDURE	18	
4.	RESULTS AND DISCUSSION	53	
5.	CONCLUSION	57	

APPENDIX 1.	Computer program and output	
	for organic system 1.	59
APPENDIX 2.	Computer program and output	
	for organic system 2.	63
SELECTED B	IBLIOGAPHY	67

LIST OF TABLES

TABLE	PAGE	NO.
1. ASTM C33 grading limits	27	
 Size distribution of aggregate used in the experiment 	28	
3. Specific surface area of aggregate	28	
4. Size distribution of aggregate groups	29	
Bulk density and specific surface area of aggregate groups	30	
6. Mechanical strength of polymer concrete (organic system-1, binder content 13%)	31	
 Compressive strength of polymer concrete (organic system-1, binder content 11.5%) 	32	
 Density of polymer concrete and specific surface area of aggregate 	33	
 Mechanical strength of polymer concrete (organic system-2) 	34	
10. Grading groups with specific surface area of 180 and 190 Sq cm/g	35	
11. Example of combining aggregate	36	
12. Compressive strength of polymer concrete with aggregate having specific surface area of 180 Sq cm/g (organic system-1)	37	
13. Compressive strength of polymer concrete with aggregate having specific surface area of 190 Sq cm/g (organic system-2)	37	

LIST OF FIGURES

	FIGURES	PAGE NO
1.	Grading curve for Empirical formula	38
2.	The limite region for specific surface area in 170 - 200 Sq cm/g	39
3.	Tipical Young's Modulus of composite material	40
4.	Idealization of stresses around a single aggregate partical	41
5.	Distribution of strain and stress in the mortar and aggregate phases	42
6.	Size distribution of aggregate for Table 2	43
7.	Size distribution of aggregate for Table 4	44
8.	Bulk density vs specific surface area of aggregate	45
9.	Compressive and tensile strength of polymer concrete (organic system-1)	46
10.	Compressive strength of polymer concrete (organic system-2)	47
11.	Some grading curves with specific surface area of 180 Sq cm/g	48
12.	The grading curve of aggregate for example in Table 12	49
13.	The effect of curing temperature on tensile strength of polymer concrete	50
14.	The effect of curing temperature on compressive strength of polymer concrete	51
15.	The effect of curing time on tensile strength of polymer concrete	52

SECTION 1

INTRODUCTION

Polymer concrete is prepared by mixing the aggregate with polymer which is used as a binder and it has become a material for practical use in the field of construction works and as an insulation material in the electric power industry.

However, the mixing proportions of polymer concrete have not been studied systematically.

The compressive strength is an important characteristic of polymer concrete. The general assumption is that an improvement in compressive strength of polymer concrete will improve its other properties as well.

The factors that can affect the strength of polymer concrete can be classified into three categories: (1) constituent materials, (2) methods of preparation, (3) curing procedures. The category(1) include the polymer, the aggregate and the mechanisms of the interface between the polymer and the aggregate.

The influence of the aggregate on the strength of the

polymer concrete is due to (a) the shape of particles, (b) size and size distribution of the particles, (c) concentration and concentration distribution of the particles, (d) orientation of the particles, and (e) composition of the aggregate.

The purpose of this study has been to explore the relationship between the strength of polymer concrete and the grading of the aggregate, i.e. the size distribution of the aggregate.

Ideally, the strength of a solid depends on the strength of its atomic bonds. Thus, to obtain an approximation to at least the order of magnitude of the fracture strength, we can consider the interaction between two atoms. The total energy required to separate these two atoms depends on the relationship between the force and the displacement and may be equated to twice the surface energy of the new surface area created. The equation to calculate the maximum stress σ is

$$\sigma = (Er / b_0)^{0.5}$$

where b_o is atomic spacing and E is the Young's modulus and r is the surface energy. [1][4]

Based on thermodynamic considerations, Griffith arrived at a similar solution of the theoretical cohesiven stength. The Griffith equation is:

 $\sigma = (2Er/\pi C)^{0.5}$

Where C is one-half the crack length.[1][4]

It is easy to see from Griffith's equation that if the length of the cracks is less or equal to b_0 , the strength of the material will reach its maximum value, which is impossible. However the Griffith's equation has pointed out the way to increase the strength of material, that is increase the Young's modulus and surface energy and decrease the length of the crack as much as possiple.

We are able to model the polymer concrete as a twophase material with aggregate particles embedded in a matrix of polymer.

From the composite theory, the modulus of the twophases composite material is between the modulus of the individual phases.

There are several models to analyse the composite material. Parallel model, series model, Hirsch's model and Counto's model [1][2]. As a more realistic model for polymer concrete, a two-phase material consisting of spherical particles in a continuous polymer, and assume that Poisson's ratio is the same for the composite material and each of the two phases, then E can be expressed as

$$\mathbf{E} = \mathbf{E}_1 \mathbf{V}_1 + \mathbf{E}_2 \mathbf{V}_2$$

Where 1 : polymer phase. 2 : aggregate phase

In general, the Young's modulus E of aggregate is much higher than that of the polymer phase. Therefore it is clear that the modulus of the composite material will increase as the volume of the aggregate increases. The typical figure for the relationship between E and volume fraction is shown in Figure 3.

The highest mechanical strengths are achieved with polymer concrete that has a very high loading of aggregate. The upper limit of aggregate content occurs when the mixing become unworkable. The high loading of aggregate is achieved by carefully chooing the various aggregate used in the mixing. From the traditional point of view, a high loading of the aggregate is achieved by decreasing the void volume in the aggregate mass as much as possible. However, in the case of fine aggregates, the void volume in the aggregate is no longer the primary factor. Instead of the void volume, the specific surface area of the aggregate played more important role in influencing the binder needed. The amount of the polymer should only be enough to wet all the surfaces of the aggregate and it decreases as the specific surface area decreases.

Obviously we can not decrease the specific surface area without any restriction because a smaller specific surface area means a larger size of the aggregate particle. In this case, the void volume becomes important. In addition to a void volume increase, a particle with large size will

create a longer crack around the particles due to the shrinkage during the polymerization process.

The interface is another important consideration. Actually the polymer concrete should be considered as a three-phase composite material, the three phases are the binder, the aggregate and the interface between the aggregate and the binder. In many ways, the properties of the interface are very different from the other two phases. The volume fraction of the interface phase, or interface area per unit volume of polymer concrete, will become greater as the specific surface area increases.

Lipatov proposes a relationship for these three phases composite material : [5]

E = E E E / (E E V + E E V + E E V) 123 123 231 132

where 1,2,3 express the aggregate, the binder and the interface respectively. The real relationship between E and volume fraction is much more complicated than that has shown in Figure 3. The interface usually is a weak spot in the composite material. Its Young's modulus is the lowest of the three. But it does not mean the volume of the interface should be made as small as possible. Because the energy requirements for crack propagation are increased by any new microcrack surface, as the crack grows around aggregate particles the energy demand is increased.

The interface volume may be expressed as :

interface volume = (specific surface area)

x (thickness of interface)

We can simultaneously increase the specific surface area and decrease the interface volume by reducing the thickness of the interface. This can be done by means of manipulating the coupling agent. i.e. choosing the amount and the method of application of coupling agent.

As we can see, it is necessary to find an optimal specific surface area to get the maximum strength.

Finally, a good grading of the aggregate not only reduces the binder content in the polymer concrete, but also well-distributes the force loaded on the material. i.e. reduces the stress concentration. We tried to use experiment to find the best grading of the aggregate for certain polymer composition.

SECTION 2

LITERATURE REVIEW

In the nineteenth century and at the beginning of twentieth century portland cement concrete has been fulfilled almost in the excellent way requirements of construction including civil engineering, industrial, municipal and public builings. In fact, the cement concrete has been one of the older composite materials. It is well known however that cement concrete has some disadvantages, such as delayed hardening, low tensile strength, porous structure and in consequence poor chemical and freeze resistance.

Growing industrial activity has created a continual demand for materials that satisfy more stringent requirements. Reinforced concrete including prestressed concrete, ferrocement and fiber reinforced concrete have been made essential steps in development of concrete. After all in these cases the matrix has been the same (i.e. portland cement) and it has created a limit of modification effectivenes. The further advancement has been involved with improvement of cement paste (high quality cement) and

concrete consolidation method (e.g. pressing). In actual fact the top limit of this modifications we can evaluate as the 11,500 psi. of compressive strength. The inprovement of portland cement concrete is not just the problem of mechanical strength but also others performance features, especial durability, i.e., chemical, weather and abrasion resistance and so on. A rapid strength gain and good adhesion to the building materials are the technological features which have been also very often required.

The development of the polymer technology and combining it\$ with concrete technology has given the good answer for questions mentioned above. The concrete containing polymer so-called " polymer concretes " are generally categorized as : Polymer Cement Concrete (PCC), Polymer Impregnated Concrete (PIC) and Resin Concrete (PC) which are called Polymer concrete, abbreviated as PC.

Polymer concrete (PC) is an aggregate bound with a polymer binder. This material can be cast and formed in the field. It is called a concrete because by the general definition, concrete consists of any aggregate bound with a binder. The cheapest binder is portland cement. Polymer filled with aggregate , for example , powdered walnut shells in plastics for table tops and furniture products has been known for a long time. What is referred to with PC is an aggregate filled with a polymer. The polymer acts as a binder for the aggregate.

The typical procedure is : tread and mix the aggregate,

monomer is then diffused up through the mixed aggregate and the polymerzation is initiated by either radiation or There is also another reason for loosing chemical means. forward with interest to the development of this new class of PC materials. The problem with conventional concrete is the alkaline portland hydraulic cement which on curing, forms internal voids, water can be entrapped which on freezing can readily crack the concrete. Furthermore the alkaline cement can be chemically attacked by acidic materials and concrete rapidly deteriorates under this condition. With polymer as a binder, most of these difficulties are overcome. The polymer can be made compact with a minimum of open voids and most polymer are hydrophobic and resistant to chemical attack. PC compressive strengths can be obtained as high as 30,000 psi. A silane coupling agent is used to improve the bond strength between the polymer and the aggregate.

As we mentioned before, polymer concrete has been developed by combining the polymer technology with concrete technology. The concrete technology means the mixing design theory of concrete.

The proportioning of concrete mixtures, more commonly referred to as mixing design, is a process that consist of two interrelated steps: (1) selection of the suitable ingredients (cement, aggregate, water, and admixtures) of concrete, and (2) determining their relative quantities ("proportioning") to produce, as economically as

possible, concrete of the appropriate workability, strength, durability ... These proportions will depend on the particular ingredients used, which will themselves depend on the application. Other criteria, such as designing to minimize shrinkage and creep or for special chemical enviroments, insulation, may also be considered. And although many concrete properties are important, most design procedures are based primarily on achieving a specified compressive strefgth. It is assumed that if this is done, the other properties will also be satisfactory.

There have been two aspects of mixing design in which most of the theoretical work has been carried out: water content and aggregate grading.

The basic idea behind aggregate grading is the achievement of as high a packing factor as possible. The amount and size of the fines in the mixing should be such as to fill the spaces between the coarse aggregate. All of the properties of PC can be modified by controlling the partical size distribution of the aggregates.

For example, to obtain less than 20% by volume voids, a stone aggregate mix of 3/8 - 1/2 in. stone (60.7wt%), 20 - 30 mech sand (23%), 40 - 60 mech sand (10.2%) and 170 -270 sand (6.1%) are mixed and vibrated together in a form.

The main technique in producing PC are to explore the conditions of polymerzation and to use the mixing theory to minimize void volume in the aggregate mass so as to reduce the quantity of the relatively expensive polymer

needed for binding the aggregate. This is accomplished by grading and mixing the aggregate to minimize void volume.

According to the Abrams water to cement (w/c) ratio law for the strength of concrete, for given materials, the strength of σ in the form : [1][4]

$$\sigma_{c} = A / B^{1.5(w/c)}$$

where σ_{c} = compressive strength

A = empirical constant

B = constant that depends mostly on the cement properties.

w/c = water/cement ratio by weight.

The " ideal " grading curve (one giving minimum voids) could be represented closely by the expression [1][4]

 $P_{+} = (d / D)^{q}$

Where P_t = fraction of total solid finer size d.

D = maximum particle size

0 < q < 1

the voids content depends only on q, it is approaching zero as q approches zero. Thus, by choosing an arbitrarily low q, an arbitrarily dense grading could be obtained. The assumption was that denser grading (with the minimum value of voids requiring the minimum cement) would produce both more economical and better concrete. in practice, these grading simply do not work.

Based on the difference in the application and the availability of source of the aggregate, each country sets its own practical grading limites . ASTM C33 sets some grading limits are summarized in Table 1 for fine aggregates and coarse aggregates of various nominal maximum sizes.[7]

For the aggregates with size smaller than 150 m (No.100) because the specific surface area becomes more important, the grading limit will be different from above.

As we mentioned proviously, a good grading of aggregate will distribute the stress throughout the whole material as uniformly as possible. Figure 5 [14] shows the idealized stresses around single aggregate particle in polymer under compressive stress. A stress analysis indicates the following order of failure: (1) tensile bond failure, (2) shear bond failure, (3) shear and tensile matrix failure, and (4) occasional aggregate failure. Of course, the real suatuation is much more complicated than has been indcated. Polymer concrete is heterogeneous, and the aggregate particles are not only irregular in shape but also are imperfectly bonded to the polymer. Thus, highly localized stresses and strains may be quite different from the nominal applied stresses and strains. This is shown in Figure 6 .[15]

The localized strains may be as much as 4.5 times the average strains, and localized stresses may be more than

twice as high as the average stresses.

Theoretical analysis has been done for the particle reinforcement of the composite material.when the aggregate particle size decreases (i.e. increased specific surface area), the energy demand is increased. The particles have a crack arresting action, they help to arrest crack growth. The reinforce efficicy F may be repressed as :[6]

$$F = F / F$$

$$1 \quad 2$$

where F is the strength of material with particles 1 reinforcement and F is the strength of material without 2 particles reinforcement.

F is the function of the particle size, volume fraction, particle distribution and the distance between the particles. when the particale size is about 0.01 m, the F can attain to 4 - 15, for the particale size is about 0.1 - 10 m, the F is about 1 - 3. A good example is when carbon black is added to rubber. It improves the tensile strength about twenty per cent. The small size particles were used not only to fill the space between the coarse particles, but also to arrest crack growth.

The exist of particles also influence on distribution of catalyst in binder. And T of polymer also increases due to the effect of particles. A possible relationship for estimating of change of T is :[5]

> T = T + AT fge go

where T_{q} is temperature of glass transition of polymer, T_{qe} is T_q of composite material, T_{qo} is T_g of polymer, f is chain fraction in interface and T is maximum change of T_{q} . ΔT is depends on particular binder system.



The structure of interface is :[5][6]

The thickness of interface includes the thickness of layers in polymer phase and in aggregate phase, the coupling agent and the products of coupling reaction. The former is only depended on the surface energy of the material. A probable relationship for the thickness of layer is:[5]

$$d(r) = C e^{f(r)}$$

where d is thickness of layer. C is constant depends on the system. r is surface energy.

The latter is controlled by the method of using coupling agent.

As we see, the influence of aggregate grading on strength of polymer concrete is the sum of all the effects

mentioned above. They have been studied for many years. The mechanisms are not clear. In this research, we tried to study the influence of grading of aggregate on the strength of polymer concrete to find the best grading of the aggregate .

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SECTION 3

EXPERIMENT

3 - 1 <u>Materials</u>

1. Organic System and its composition

The organic component consist of monomer, catalyst, crosslinking agent and coupling agent, monomer styrene, methye methacrylate (MMA) and unsaturated polyesters resin are the main part of the organic component. It occupies about 90% by weight in the organic part. Benzoyl peroxide is used catalyst. as а Sartomer-350 (trimethylolpropane trimethacrylate) is used as a crosslinking agent. A-174 (Methacryloxypropyl trimethoxy siline) is used as coupling agent for binding the aggregates and organic parts together. N,N-Dimethyl-ptoluine as a accelerator were added into the resin for hardening.

The two organic systems used in this experiment were :

(1) Organic system-1 :

unsaturated polyester resin*	41.50 wt%
styrene	50.64 wt%
S - 350	3.93 wt%
A - 174	3.93 wt%
· · · · · · · · · · · · · · · · · · ·	

* supplied by Reichheld Chemicals, Inc.

(2) Organic system-2 :

MM	A		92.23	wt%
s -	350		3.88	wt%
A -	174	•	3.88	wt%

2. Aggregate

Commercil silica sand: Flintshet-3, Ottawa-70,#106silcosil and #37-silcosil, listed in the Table 2 are used in all the mixing proportions. It is supplied by U.S. Silca Co., Ottawa, IL..

Their grading curves are shown in Figure 6 .

In this case, each aggregate was pretreated and air - dried to remove the moisture.

3 - 2 Procedure

Appropriate mixing proportions of polymer resin concrete were obtained by the following procedure.

1. Determine the specific surface area of aggregate for the particular binder.

Some aggregate groups, as shown in Table 4 were mixed to prepare various continuously graded compositions and the specific surface area, bulk densities of these compositions were determined (Table 5).

The polymer concrete was prepared by mixing the binder with the aggregate compositions, and was tested for compressive and tensile strength. Two binder contents, i.e. 13% and 11.5% by weight were used for organic system-1. and 13.4% and 11.5% by weight were used for organic system-2.

All the polymer concrete specimen was cured at 75°C for 2.5 hrs.

The results were shown in the Tables 6 through 9 and

Figures 9 and 10.

The bulk densities, specific surface area of the aggregates and the densities of polymer concrete which was made of the aggregate were determined. The results are shown in Table 8 and the Figure 8.

2. To select the aggregate compositions having the desired specific surface area. (numerical methods to combine aggregates)

(1) Method 1. To combine aggregates to obtain desired specific surface area.

According to the results above, we can see that for a certain organic system , based on the application of work, a corresponding specific surface area of an aggregate will lead to a set of optimum properties of the polymer concrete. For the organic systems used in our experiment , the specific surface area requred is about 180 cm^2/g . and 190 cm^2/g for organic system-1 and organic system-2 respectively. The next problem is how to prepare the aggregate with the desired specific surface area by using the aggregates available .

Taking for simplicity a sphere of diameter D as representative of the shape of the aggregate. Based on the sieve analysis of the aggregates (see Table 2) we can calculate the specific surface area of each aggregate. See Table 3.

Let X_1 , X_2 , X_3 and X_4 represent the weight percent of the aggregate required to get the desired specific surface area S (cm^2/g). S is 180 cm^2/g for organic system 1. Therefore the total specific surface area is

 $42.64X_1 + 105.82X_2 + 401.93X_3 + 537.07X_4 = 180$ (1)

because $X_1 + X_2 + X_3 + X_4 = 1$

thus two of the four unknowns are independent. There is an infinite number of solutions. i.e, there is infinite number of groups of aggregates which have the desired surface area. Now let us first determine the relationship of x_1 , x_2 , x_3 and x_4 , and then based on these relations, using the computer to calculate all of the possible solutions. From equation (2)

 $x_4 = (1 - x_1) - x_2 - x_3$ (3)

substitute eq.(3) into eq.(1):

 $431.25x_2 + 135.14x_3 = 357.07 - 494.43x_1$

 $135.14x_3 = (357.07 - 494.43x_1) - 431.25x_2$

therefore

$$x_3 = (2.64 - 3.66x_1) - 3.19 x_2$$
 (4)

because

$$x_2 + x_3 + x_4 = (1 - x_1)$$

and $x_4 \ge 0$

we have
$$x_2 + x_3 \leq (1 - x_1)$$

or $x_3 \leq (1 - x_1) - x_2$ (5)

Substitute (4) into (5):

 $(2.64 - 3.66x_1) - 3.19 x_2 \le (1 - x_1) - x_2$ $2.19x_2 \ge 1.64 - 2.66x_1$

 $x_2 \ge 0.75 - 1.21x_1$

and because $x_3 \ge 0$ from eq.(4) $3.19x_2 \le 2.64 - 3.66 x_1$ or $x_2 \le 0.83 - 1.15x_1$

finaly we get the relationship between x_2 and x_1

$$0.75 - 1.21x_1 \leq x_2 \leq 0.83 - 1.15x_1$$
 (6)

the range of x_1 can be determined by following because $x_4 = 1 - (x_1 + x_2 + x_3)$ Substitute into Eq.(1):

 $494.43x_1 + 431.25x_2 + 135.14x_3 = 357.07$

Obviously x1 will get it's maximum value

when $x_2 = 0$ and $x_3 = 0$

that is

or

 $494.43x_1 = 357.07$

 $x_1(max.) = 0.72$

therefore the range of the x₁ is

$$0 \leq x_1 \leq 0.72$$

Because the coarse aggregate is the cheapest, in most cases we want to increase x_1 as much as possibble.

Once x_1 is chosen we can determine the range of the x_2 from Eq.(6). then x_3 and x_4 will be calculated from Eqs.(4) and (3) respectively.

Notice that when x_1 is chosen as it's maximum valune, 0.72, the range of x_2 is

$$-0.12 \le x_2 \le 0$$

That is $x_2 = 0$

The corresponding grading curves with specific surface area of 180 $\rm cm^2/g$ are shown in Figure 11.

From the three extreme cases , We can fit the data to the equation

Y = A [1 - exp(X - D) / B]

where X is the ASTM sieve number of the mesh and Y

is the corresponding cumulative percentage retained. D is the ASTM sieve number on which the maximum particle size is retained and A and B are the constants to be determined.

The grading curve corresponding to the given formula is shown in Figure 1 and the grading limits of specific surface area between about $170 - 200 \text{ cm}^2/\text{g}$. This range, according to the results of the experiment, is satistactory for the compresive srtength. Which is shown in Figure 2.

These curves are used to combine aggregates in the following method.

Similarly, we can determine the X_1 , X_2 , X_3 and X_4 for specific surface area of 190 cm²/g for organic system-2 :

 X_1 (max.) = 0.70

the range of the X_1 is

 $0 \leq X_1 \leq 0.70$

and

 $0.71 - 1.21 X_1 \leq X_2 \leq 0.8 - 1.15 X_1$ $X_3 = (2.56 - 3.66X_1) - 3.19X_2$

the computer program and all the possible solutions for organic system 2 was shown in Appendix 2.

(2) Method 2. To combine aggregates to obtain the desired grading and specific surface area.

This method is based on this principle : a grading curve corresponds to a specific surface area. From Figure

7 we can see that the upper curves represent coarse

particles with specific surface area less than that of the lower curves.

The procedures of calculation are illustrated by means of an example.

The gradings of the four aggregates size fractions are listed in Table 2, and we can combine the materials to the approximation of the grading of Figure 1. From Figure 1, the cumulative percentage retained on sieve 60 is 26, on sieve 120 is 59 and on sieve 325 is 91.

 x_1 , x_2 , x_3 and x_4 are the fractions of the four aggregates, We have

 $0.98x_1 + 0.21x_2 = 0.26 (x_1 + x_2 + x_3 + x_4)$ $x_1 + 0.73x_2 + 0.12x_3 = 0.59 (x_1 + x_2 + x_3 + x_4)$ $x_1 + x_2 + 0.68x_3 + 0.17x_4 = 0.91 (x_1 + x_2 + x_3 + x_4)$

make rearaggment

 $0.72x_1 - 0.05x_2 - 0.26x_3 - 0.26x_4 = 0$ $0.41x_1 + 0.14x_2 - 0.47x_3 - 0.59x_4 = 0$ $0.09x_1 + 0.09x_2 - 0.23x_3 - 0.74x_4 = 0$

let $x_1 = 1$ we get

 $0.05x_2 + 0.26x_3 + 0.26x_4 = 0.72$ $0.14x_2 - 0.47x_3 - 0.59x_4 = -0.41$ $0.09x_2 - 0.23x_3 - 0.74x_4 = -0.09$

and we can calculate the value of x_2 , x_3 and x_4

· · · ·			ana ing sa	
	0.05	0.26	0.26	
	0.14	-0.47	-0.59	= 0.026
	0.09	-0.23	-0.74	
	0.72	0.26	0.26	
	-0.41	-0.47	-0.59	= 0.101
	-0.09	-0.23	-0.74	
	0.05	0.72	0.26	
	0.14	-0.41	-0.59	= 0.056
	0.09	-0.09	-0.74	
	1			·
	0.05	0.26	0.72	
	0.14	-0.47	-0.41	= -0.0015
	0.09	-0.23	-0.09	

therefore $x_2 = 0.21 / 0.027 = 3.88$ $x_3 = 0.055 / 0.027 = 2.15$ $x_4 = -0.0015 / 0.027 = -0.05$

we find

 $x_1 : x_2 : x_3 : x_4 = 1 : 3.88 : 2.15 : -0.05$ because X_4 is very small, let $X_4 = 0$

i.e. the four aggregates are combined in the proportions

1 : 3.88 : 2.15 : 0
the results are shown in the Table 11.

Figure 12 shows the grading of the combined aggregate, the specific surface area of the combined aggregate is about 188.7 cm^2/g , The compressive strength of the polymer concrete prepared by using the gradings given in Table 10 are shown in Table 12 and 13.

The results show that the compressive strength of polymer concrete made with aggregates having same specific surface area are almost the same.

TABLE 1 ASTM C33 Grading Limits for Concrete Aggreggates

Fine Ago	gregate		Coars	e Aggreg	ate	
Sieve %Passing Sieve Size Size			% (Nomin	Passing al Maxim	um Size)
			1.5	1.0	0.75	0.5
3/8 in.	100	1.5 in.	95-100	100		-
No.4	95-100	1.0 in.		95-100	100	
No.8	80-100	3/4 in.	35-70	-	90-100	100
No.16	50-85	1/2 in.		25-60	-	90-100
No.30	25-60	3/8 in.	10-30	-	20-55	40-70
No.50	10-30	No.4	0-5	0-10	0-10	0-15
No.100	2-10	No.8		0-5	0-5	0-5

TABLE 2 Size distribution of sand used in the experiment

	Cumulative Percentage Retained									
				Sieve	Size	(ASTM	No.)			
	40	50	60	80	120	140	170	325	400	<400
A	85.7	97.	7 98.3	2 98.9	9 100					4
в	0	14.3	21.3	59.8	72.9	79.0	81.8	100		
С	0	0	0	0	11.5	24.2	27.5	68.4	82.6	5 -
D	0	0	0	0	0	0	0.8	17.3	62.0) –

TABLE 3Specific surface area of aggregatesused in the experiment

	-			
	A	В	С	D
Specific Surface Area (cm ² /g)	42.61	105.82	401.93	537.07

A	:	Flir	ntshet-3
в	:	Otta	awa-70
С	:	106	Silcosil

D : 37 Silcosil

TABLE 4Size Distribution of Aggregate Groupsused in the experiment

		Cumulative Percentage Retained								
			Si	eve Si	ze (A	STM No	··)			
	40	50	60	80	120	140	170	325	400 <	400
#1	78.5	90.1	92.2	95.6	97.7	98.3	98.5	100		
#2	64.2	74.8	76.6	81.6	85.6	88.0	88.7	96.1	97.8	
#3	60.5	71.1	73.2	75.1	83.5	84.7	85.2	90.3	92.7	taine
#4	45.8	54.7	56.6	64.8	71.0	75.9	77.1	91.6	95.4	
#5	49.8	57.9	59.2	67.7	68.1	71.5	72.6	84.8	92.4	-
#6	52.8	61.9	62.1	68.6	69.1	71.6	72.2	84.7	94.2	-
#7	47.1	55.5	57.2	63.3	67.2	69.5	70.3	80.3	90.7	
#8	49.9	56.3	57.2	59.4	62.9	65.6	66.5	78.2	91.5	-
#9	25.7	32.4	34.4	43.6	50.4	55.8	57.5	73.9	87.1	
#10	34.2	41.0	48.6	52.7	55.6	56.6	68.2	83.7	97.5	-
#11	34.2	38.8	39.2	39.5	41.5	44.4	57.9	80.1	99.5	-

Grading (No.)	Specific Surface (cm ² /g)	Bulk Density (g/cm ³)	
# 1	47.49	1.4757	
# 2	84.08	1.4578	
# 3	111.20	1.4143	
# 4	127.15	1.3615	
# 5	158.54	1.2893	
# 6	165.20	1.2565	
# 7	177.60	1.2622	
# 8	192.20	1.2104	
# 9	234.80	1.2571	
#10	254.30	1.2758	
#11	314.01	1.2422	

TABLE	5	Bulk Density, Specific Surface	of	aggregate
		groups used in the experiment		

TABLE 6 Mechanical strength of polymer concrete made with aggregate of different specific surface (Organic system-1 binder content 13%)

Grading (No)	Specific surface (cm ² /g)	Compresion (psi)	Tension (psi)
44			
# 1	47.49	11.600	1,200
# 2	84.08	19,800	2,400
# 3	111.20	22,600	2,600
# 4	127.15	23,500	2,100
# 5	158.54	22,000	3,600
# 6	165.20	22,500	3,650
# 7	177.60	23,900	3,400
# 8	192.20	23,125	3,200
# 9	234.80	17,000	****

TABLE 7Compressive strength of polymer concrete
made with aggregate of various specific
surface
(Organic system-1, binder content 11.5%)

Grad	ding(No.)	Specific Surface (cm ² /g)	Compresion (psi)
#	1	47.49	8,400
#	2	84.08	18,000
#	4	127.15	20,250
#	6	165.20	20,500
#	7	177.60	19,000
#	8	192.20	17,500

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TABLE	8	Specific grading a of polyme	Surface and the er concre	of corr te	aggregate esponding	with densi	various ty

	Specific	Density of polymer concrete (g/cm ³)			
Grading (No.) (ng area) (cm ² /g)	Organic system-1 (binder 13%)	Organic system-2 (binder 13.4%)		
# 1	47.49	1.9100			
# 2	84.08	2.2468	2.0162		
# 3	111.20	2.2426	-		
#4	127.15	2.2627	-		
# 5	158.54	2.2511	2.1659		
# 6	165.20	2.2432	-		
# 7	177.60	2.2456	. –		
# 8	192.20	2.2418	2.1923		
# 9	234.80	2.1912	-		
# 10	254.30	-	2.2044		
# 11	314.01	_	2.0972		

sur	face (Organic syste	m 2)
Grading (No)	Specific surface (cm ² /g)	Compressive Strength (psi)
		Binder Content (13.4%) (11.5%)
# 2	84.08	9,000 10,000
# 5	158.54	25,500 15,000
# 8	192.20	27,500 13,750
#10	254.33	26,000 -
#11	314.01	21,750 -

TABLE 9 Mechanical strength of polymer concrete made with aggregate of different specific surface (Organic system 2)

No. of Groups	We	Weight Percent			Specific Surface _ area (cm²/g)		
	x ₁	x ₂	x ₃	x ₄			
1	72	0	0	28	180		
2	62	0	38	0	180		
3	0	74.9	25.1	0	180		
4	70	0	0	30	190		
5	60	0	36.4	3.6	190		
б	0	71	3.99	17.01	190		

TABLE 10 Some Extreme Gradings with Specific surface area of 180 cm^2/g and 190 cm^2/g

C Sieve r No		Cumulative percentage retained for			Total	Graing of combined aggregate	
	×1	×2 ×	² 3	×4			
	(1)	(2)	(3)	(4)	(5)	(6)	
40	85.7	0	0	0	85.7	12.19	
50	97.7	14.3	0	0	153.18	21.79	
60	98.2	21.3	0	0	180.84	25.72	
80	98.9	59.8	0	0	330.92	47.07	
120	100	72.9	11.5	0	407.58	57.98	
140	100	79.0	24.2	0	458.55	65.23	
170	100	81.8	27.5	0.8	476.51	67.78	
325	100	100	68.4	17.3	635.06	90.34	
400	100	100	82.6	62.0	665.59	94.68	

TABLE	11	Example of Combining Aggregates to Obtain
		a Desired Grading Curve

 $(5) = (1) \times 1 + (2) \times 3.88 + (3) \times 2.15 + (4) \times 0$

(6) = (5) / (1 + 3.88 + 2.15 + 0)

TABLE 12	The compresive strength of polymer conrete with accregate mixed by using				
	method 1 and 2 (organic system 1	.,			
	binder concent 13%)				

No. of Groups of aggregate	1	2	3	7
Workability	medium	medium	low	medium
Compresive strength (psi)	23,500	23,000	22,500	23,750

TABLE 13 The Compressive Strength of Polymer Concretewith Aggregate Mixed by Using Method 1 and 2(Organic System 2, Binder content 13.4%)

No.of Groups of aggregate	4	5	6	
Workability	medium	medium	medium	
Compressive Strength(psi)	24,000	26,250	24,500	

Aggregate groups 1,2,3,4,5,6 are the extreme aggregate compositions (from Table 10) and group 7 is the aggregate composition based on method 2 (Table 11).



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Figure 4. Idealization of stresses around a single aggregate particle at the discontinuity point under uniaxial compressive.





Stress (kg em²)

Figure 5. Distributions of strain and stress in the mortar and aggregate phases of a concrete specimen under uniaxial compression. Dashed lines represent the average values Broken outlines represent aggregate particals.



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SECTION

RESULTS AND DISCUSSION

The mixing proportion of polymer concrete as well as properties of the polymer concrete were investigated in this experiment. The results show that the specific surface area of the aggregate is the major factor which influences the amount of the binder reguired for fine aggregate. The specific surface area can be used as an important parameter for mixing design and quality control of polymer concrete.

From Figure 9 we can see that the compressive and tensile strength of polymer concrete made with organic system 1 increase as specific surface area increases at first, and reach their maximum values at specific surface area of 180 cm^2/g . It is easy to understand that when the specific surface area is further increased, because the amount of the binder is not enough to wet all surfaces of the aggregate, the strength decreases as the results have shown. But in the case of small specific surface area the effect of the void in the aggregate becomes important. More

binder will be needed. If the specific surface area is too

small (for example in the case of specific surface area of $47 \text{ cm}^2/\text{g}$), the aggregate will not be able to hold enough binder to fill all the voids in the aggregate, and the void will be filled with air or vapor of the binder. Because the Young's modulus of air is zero, its presence as a phase in the composite material will reduce the strength.

This result can also be justified by means of the relationship between the strength and the density of the polymer concrete. From Table 8 we can notice that the density of the polymer concrete becomes very low when the specific surface area is small. On the other hand, When the specific surface area is large, more binder will be needed to wet the increased surface, the density of the polymer concrete will also decrease. A high density of the polymer concrete means a high loading of aggregate.

The interesting thing is that the highest density appeared at about 130 cm²/g of specific surface area. But the highest compressive strength and tensile strength occurs at about 180 cm²/g of specific surface area. That is because two factors, i.e. (1) loading of aggregate and (2) size of particles, which influence on the strength in opposite ways. As the specific surface area is lower than $180 \text{ cm}^2/\text{g}$. the size of the particles playes the main factor, but when the specific surface area is larger than $180 \text{ cm}^2/\text{g}$. the effect of size becomes less significant.

It is indicated in Figure 8 that the high bulk density of aggregate occures at low specific surface area of aggregate. Therefore instead of seeking high bulk density of aggregate (e.g.to minimized void volume in aggregate), we have to explore the suitable specific surface in order to make the highest strength polymer concrete.

The compressive strength of polymer concrete made with aggregate having same specific surface area but different grading for organic system-1 are summerized in Table 12. The result shows that their compressive workbilities and strength are almost the same. The No.3 group has a little lower volume in workbility and strength. This indcats that the grading of aggregate has shown same effects on the strength.

Obviously, for different kinds of binder, the optimal binder amount required are different and so are the optimal specific surface area. They can be determined only by means of experiment.

For organic system-2, the strength of polymer concrete reaches its maximun value at specific surface area of 190 cm^2/g . For binder content of 13.4%, the compressive strength reaches as high as 27,500 psi.

In order to combine aggregates to obtain the desired specific surface area and grading, two methods have been developed. One of them based only on the consideration of the specific surface area gives a wide spectrum of

possible compositions, i.e. grading, as listed in the computer program output. The other one provides only one composition which is satisfactory not only for the desired specific surface area but also for the desired grading curve.

Also, the curing conditions, the modified polymer and the coupling agent were investigated.

In the case of room tempreture cure, the compressive and tensile strengths of the polymer concrete increase proportionally with curing time, become nearly constant at the age of 7 days, regardless of the curing conditions.(Figrue 15)

In the case of heigh temperature curing, the compressive and tensile strengths of the polymer concrete various upon the temperature and the heating time. At the heating time of 2.5 hrs and the 75 C, the polymer concrete shows the highest strength. (Figure 13,14)

SECTION 5

CONCLUSION

The conclusions obtained from the aforementioned results are summarized as follows:

1. The influence of grading of aggregates on the mixing design and the strength of the polymer concrete is in the range of this study.

2. For the fine aggregate, the main factor which affects the content of the bider is the specific surface area of the aggregate. The bulk density in the aggregate can be negligible.

3. For a given binder system there is an optimal specific surface area and a range of grading which leads to the highest strength of polymer concrete. In stead of seeking high bulk density of aggregate, we have to explore the specific surface area and the grading limit by means of experiment.

4. For organic system-1 and organic system-2, the both binder contents required were about 13%, the specific

surface area were $180 \text{ cm}^2/\text{g}$ and $190 \text{ cm}^2/\text{g}$ and their compressive strength were 25,000 and 27,500 psi.respectively

5. Once the suitable specific surface area and grading is determined, the method 1 or method 2 can be used to combine available aggregates to obtain the desired specific surface area and the grading.

6. Method 2 also can be used for cemment concrete for combining any number of aggregates to obtain the desired specific surface area and the desired grading curve.

7. It should be noted that the strength of polymer concrete primarily depends on the properties of polymer, the constituent material, the methods of preparation and the cure conditions and so on. The effect of grading of aggregate is relative. A wide range of aggregate grading is satisfactory for using. However, for the grading which was out of the range, the strength of polymer concrete decrease considerably.

8. In the case of room temperature cure, the compressive and tensile strength of the polymer concrete become nearly constant at the age of 7 days .

9. The heat cured polymer concrete gives a considerably higher srength than that of the room temperature cured one and the 2.5 hrs 75°C the polymer concrete shows the highest srength.

APPENDIX 1.

Computer program and aggregate composition for organic system-1

20 FOR I = 1 TO 8 40 READ X1(I) 60 NEXT I 30 DATA 0.0,0.1,0.2,0.3,0.4,0.5,0.6,0.7 100 FOR I = 1 TO 8120 UPLI(I) = .83 - 1.15 * X1(I) 140 DOLI(I) = .75- 1.21 * X1(I) 180 P(I) = UPLI(I) - DOLI(I) 200 J(I) = P(I) / .01 $202 \ A_{\%}^{\%}(I) = J(I)$ 203 $B(I) = A_{3}^{(I)} / 2$ 204 NEXT I 205 LPRINT" " 206 LPRINT" " 207 LPRINT" " 208 LPRINT" The aggregates composition having specific " 209 LPRINT" ** surface area of 180 Sq cm/g 210 LPRINT " for organic system-1 " 211 LPRINT" " 212 LPRINT^H x1 $\mathbf{x2}$ xЗ х 4 14 213 LPRINT" " 215 FOR I = 1 TO 8 217 A = DOLI(I)220 FOR K = 1 TO B(I) STEP .5 225 Y2(K) = A + .01226 IF A < 0 THEN Y2(K) = 0 226 IF A < G InEM 12(K) = 0 240 Y3(K) = 2.64 - 3.66 * X1(I) - 3.19 * Y2(K) 245 IF Y3(K) < 0 THEN Y3(K) = 0 260 Y4(K) = 1 - X1(I) - Y2(K) - Y3(K) 265 X1 = 100 * X1(I) 267 X2 = Y2(K) *100 269 X3 = Y3(K) * 100 271 Y4 = Y4(K) * 100 271 X4 = Y4(K) * 100272 X = X1 + X2 + X3 + X4340 LPRINT USING" 350 A = Y2(K)##.##";X1,X2,X3,X4 360 NEXT K 380 NEXT I 800 END

The aggregates composition having specific surface area of 180 Sq cm/g for organic system-1

xl	x2	x3	x4 /
0.00	76.00	21,56	2.44
0.00	77.00	18.37	4.63
0.00	78.00	15.18	6.82
0.00	79.00	11.99	9.01
0.00	80.00	8.80	11.20
0.00	81.00	5.61	13.39
0.00	82.00	2.42	15.58
10.00	63,90	23.56	2.54
10.00	64,90	20.37	4.73
10.00	65,90	17.18	6.92
10.00	66.90	13.99	9.11

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$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	· .			· · · · · · · ·	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		10.00	67.90	10.80	11.30
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		10,00	68.90	7.61	13.49
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		10.00	70.90	1.23	17.87
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	х.	20.00	51.80	25.56	2.64
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		20,00	52.80	22.37	4.83
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		20.00	53.80	19.18	7.02
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		20.00	54.80	15.99	9.21
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		20.00	56.80	9.61	13.59
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		20.00	57.80	6.42	15.78
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		20.00	58.80	3.23	17.97
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		30.00	39.70	27.56	2.74
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		30.00	40.70	24.37	4.93
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		30.00	41.70	21.18	7.12
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		30.00	43.70	14.80	11.50
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		30.00	44.70	11.61	13.69
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		30.00	45.70	8.42	15.88
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		30.00	46.70	5.23	18.07
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		30.00	47.70	2.04	20.26
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		40.00	28.60	29.56	5.03
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		40.00	29.60	23.18	7.22
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		40.00	30.60	19.99	9.41
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		40.00	31.60	16.80	11.60
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		40.00	32.60	10 42	13.79
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		40.00	34.60	7.23	13.93
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		40.00	35.60	4.04	20,36
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		50.00	15.50	31.56	2.94
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		50.00	16.50	28.37	5.13
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		50.00	18.50	25.18	7.34
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		50.00	19.50	18.80	11.70
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		50.00	20.50	15.61	13.89
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		50.00	21.50	12.41	16.08
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		50.00	22.50	9.22	18.27
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		50.00	23.50	6.U3 2.94	20.47
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		60.00	3.40	33.55	3.05
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		60,00	4.40	30.36	5.24
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		60.00	5.40	27.17	7.43
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		60,00	6.40	23.98	9.62
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		60.00	7.40	20.79	11.81
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		60.00	9-40	14.41	16.19
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		60.00	10.40	11.22	18,38
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		60.00	11.40	8.03	20.57
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		60.00	12.40	4.84	22.76
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		60.00	13.40	1.65	24.95
70.00 2.00 1.42 26.58 70.00 3.00 0.00 27.00 70.00 4.00 0.00 26.00 70.00 5.00 0.00 25.00 70.00 6.00 0.00 24.00 70.00 5.00 0.00 25.00 70.00 6.00 0.00 24.00 70.00 8.00 0.00 23.00		70.00	1.00	4.61	22.20
70.003.000.0027.0070.004.000.0026.0070.005.000.0025.0070.006.000.0024.0070.007.000.0023.0070.008.000.0022.00		70.00	2.00	1.42	26.58
70.004.000.0026.0070.005.000.0025.0070.006.000.0024.0070.007.000.0023.0070.008.000.0022.00		70.00	3.00	0.00	27.00
70.00 5.00 0.00 25.00 70.00 6.00 0.00 24.00 70.00 7.00 0.00 23.00 70.00 8.00 0.00 22.00		70.00	4.00	0.00	26.00
70.00 8.00 0.00 24.00 70.00 7.00 0.00 23.00 70.00 8.00 0.00 22.00		70.00	5.00	0.00	25.00
70.00 8.00 0.00 22.00		70.00	5.00 7.00	0.00	24.00
		70.00	8.00	0.00	22.00

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70.00	9.00 10.00	0.00	21.00 20.00

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APPENDIX 2.

Computer program and aggregate composition

for organic system-2

20 FOR I = 1 TO 8 40 READ X1(I) 60 NEXT I 80 DATA 0.0,0.1,0.2,0.3,0.4,0.5,0.6,0.7 100 FOR I = 1 TO 3 100 POR I = 1000 120 UPLI(I) = .8 - 1.15 * X1(I) 140 DOLI(I) = .71 - 1.21 * X1(I) 180 P(I) = UPLI(I) - DOLI(I) 200 J(I) = P(I) / .01 202 J(I) = .7(I)202 $A_{*}^{*}(I) = J(I)$ 203 $B(I) = A_{*}^{*}(I)/2$ 204 NEXT I 205 LPRINT" " 206 LPRINT" " 207 LPRINT" " The aggregates composition having specific " surface area of 190 Sq cm/g " 208 LPRINT" 209 LPRINT" 210 LPRINT" for organic system-2" 211 LPRINT" " 212 LPRINT" $\times 1$ $\times 2$ х3 х 4 " 213 LPRINT" " 215 FOR I = 1 TO 8 217 A = DOLI(I)220 FOR K = 1 TO B(I) STEP .5 225 Y2(K) = A + .01 226 IF A < 0 THEN Y2(K) = 0 226 IF A < 0 THEN $Y_2(K) = 0$ 240 Y3(K) = 2.56 - 3.66 * X1(I) - 3.19 * Y2(K) 245 IF Y3(K) < 0 THEN Y3(K) = 0 260 Y4(K) = 1 - X1(I) - Y2(K) - Y3(K) 265 X1 = 100 * X1(I) 267 X2 = Y2(K) *100 269 X3 = Y3(K) * 100 271 X4 = Y4(K) * 100 272 Y = Y1 + Y2 + Y2 + Y4 272 X = X1 + X2 + X3 + X4340 LPRINT USING" ##.##";X1,X2,X3,X4 350 A = Y2(K)360 NEXT K 3SO NEXT I 800 END

The aggregates composition having specific surface area of 190 Sq cm/g for organic system-2

×l	×2	×3	x4
0.00	72.00	26.32	1.68
0.00	73.00	23.13	3.87
0.00	74.00	19.94	6.06
0.00	75.00	16.75	8.25
0.00	76.00	13.56	10.44
0.00	77.00	10.37	12.63
0.00	78.00	7.18	14.82
0.00	79.00	3.99	17.01
10.00	59.90	28.32	1.78
10.00	60.90	25.13	3.97
10.00	61.90	21.94	6.16

14

		11 12	
10.00	62.90	18.75	8.35
10.00	63.90	15,56	10.54
10.00	64.90	12.37	12.73
10 00	65 90	0 19	14 01
10.00	03.90	9,10	14.92
10.00	66.90	5,99	17.11
10.00	67.90	2.80	19.30
20-00	47.80	30 32	201
20,00	40.00	27.12	1.00
20.00	48.00	21.13	4.07
20.00	49.80	23.94	6.26
20.00	50.80	20.75	8.45
20.00	51.80	17.56	10.64
20.00	52 80	14 37	17 97
20.00	52.00	74.21	12.03
20.00	53.80	11.18	15.02
20.00	54.80	7,99	17 .21
20.00	55.80	4.80	19.40
30.00	35 70	72 72	1 99
20.00	33.70	20 12	1.70
30.00	36.70	29.13	4.1/
30.00	37.70	25.94	6.36
30.00	38.70	22.75	8.55
30.00	39 70	19 56	10 74
20.00	10.70	10.00	10.74
50.00	40.70	16.37	12.93
30.00	41.70	13.18	15.12
30.00	42.70	9,99	17.3 1
30.00	43.70	6 80	19 50
20.00	44 70	0.00	19.50
30.00	44.70	3.61	21.69
40.00	23.60	34.32	2.08
40.00	24.60	31.13	4.27
40.00	25.60	27.94	646
40.00	26 60	24 75	0 65
40.00	20.00	24.75	0.00
40.00	27.60	21.56	10.84
40.00	28.60	18.37	13.03
40.00	29.60	15,18	15.22
40.00	30 60	11 99	17 41
40.00	33.60	11.00	20.00
40.00	21.60	8.80	19.60
40.00	32.60	5.61	21.79
50.00	11.50	36.32	2.19
50.00	12 50	33 13	4 38
50.00	12,50	20.04	4.50
50.00	13.50	29.94	6.57
50.00	14,50	26.75	8.76
50.00	15.50	23.55	10.95
50.00	16.50	20.37	13.14
50.00	17 50	17 17	1 - 1 - 1
50.00	17.00	1/ • 1/	10.00
50.00	18.50	13.98	17.52
50.00	19.50	10.79	19.71
50.00	20.50	7.60	21.90
50.00	21 50	4 41	24 00
50.00	22.50	7.74	24.09
60.00	0.00	36.40	3.60
60.00	1.00	33.21	5.79
60.00	2.00	30.02	7.98
60.00	2 00	26 23	10 17
00100	5.00	20.05	10.17
60.00	4.00	23.64	15-30
60.00	5.00	20.45	14.55
60.00	6.00	17.26	16.74
60.00	7 00	14 07	1 2 0 7
CO 00		10 00	10.73 NA 10
8U.UU	8.00	10.88	21.12 -
60.00	9.00	7.69	23.31
60.00	10.00	4.50	25,50
60.00	11.00	1.31	27.69
70.00	10.00	0.00	20.00
70.00	0.00	0.00	50.00
70.00	1.00	0.00	29.00

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1	70.00	2.00	0.00	28.00
	70.00	3.00	0.00	27.00
	70.00	4.00	0.00	26.00
	70.00	5.00	0.00	25.00
	70.00	6.00	0.00	24.00
	70.00	7,00	0.00	23.00
	70.00	8.00	0.00	22.00
	70.00	9.00	0.00	21.00
	70.00	10.00	0.00	20.00
	70.00	11.00	0.00	19.00

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