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Functions and molecular structure of organic binders for iron ore pelletization

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Abstract

Organic binders of iron ore pellets were widely investigated in past decades because they do not contaminate the product. This paper mainly involves the functions and molecular structure of ideal organic binders for iron ore pelletization based on fundamental principles of molecular design, interface chemistry, polymer science as well as failure model of a binding system. Investigation shows that good wettability, great adhesive and cohesive forces as well as fine thermal stability are essential functions of binders for iron ore pelletization. The molecular structure mold $[X–P–Y]_n$ of organic binders is proposed. Ionization potential, electron affinity, group electronegativity, bond ionicity and bond energy are calculated and/or applied in the selection and judgement of polar group (X) and hydrophilic group (Y). Organic chain skeleton (P) and polymerization degree (n) are investigated on the basis of the structure–property relationships of polymers. It is shown that $-COO^-$ and –OH are excellent polar group and hydrophilic group of organic binders of iron ore pellet, respectively, and organic skeletons with unsaturated hydrocarbon chain and ring aromatic structure are the best for organic binders of iron pellets. Two kinds of organic binders are synthesized and prepared on the basis of the investigations and they are found to be effective for pelletizing of iron ore concentrates. One of them has been used in commercial production of iron ore pellets in China.
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Keywords: Iron ore; Pelletization; Organic binder; Molecular structure

1. Introduction

Binders are widely used in agglomeration operations such as briquetting and pelletization to assure that the agglomerate possesses desired properties with regard to subsequent handling, transportation and processing. These properties depend on the requirements of a particular operation and installation. In certain instances, the binder may perform a chemical function as well as a physical one.

Bentonite is the most commonly used binder in iron ore pelletization. It controls the moisture in iron concentrate and significantly improves physi-

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cal properties of the pellets. However, there are some drawbacks with the use of bentonite. The most remarkable is the contamination of the product with gangue (silica). Addition of 1% bentonite to an iron ore concentrate results in a lowering of acid pellet iron content by 0.6% [1]. In the case of direct reduction pellets, every percent of acid gangue addition is associated with an increased energy consumption of 30 kWh [2].

In contrast to inorganic binders, organic binders have the inherent advantage of being eliminated during firing. They do not contaminate the product. This obvious advantage provided the incentive for the development of organic binders. A number of organic binders were reported in last decades [3–14]. Among them, Peridur was most extensively investigated [1,2,4,5,7]. Peridur is a natural polymer derived from cellulose. It is obtained by substitution of some of hydrogen atoms of the three-hydroxyl groups in each one of the anhydroglucose units. However, Peridur has not been widely used in production of iron ore pellets due to its high cost compared to bentonite [3] and potential environmental consequences with its use. In addition, mixing of raw materials bearing Peridur may be another problem because of its very low dose ($<0.2\%$) [4].

It should be noted that almost all organic binders reported so far were developed based on empirical selection of researchers followed by the verification of agglomerating tests. There have been few reports involving the molecular structure of agglomerating organic binders and people have not had a clear image on the molecular structure of an ideal organic binder so far, which limited the development of organic binders. This is partly why few organic binders have been used in industry although a number of them have been reported.

In this regard, the functions and molecular structure, an ideal iron ore pellet organic binder should possess, are investigated in this paper on the basis of the principles of molecular design, interfacial chemistry and polymer science as well as the failure model of binding systems. Two organic binders are synthesized and prepared based on the investigation and they are found to be effective to pelletizing of iron ore. Funa®, one of them, has been patented and used in the production of iron pellet in China.

2. Functions of organic binders for iron ore pelletization

2.1. Criteria for organic binders for iron ore pelletization

Experience of pellet production over past decades has led to the identification of a number of criteria that a binder must satisfy. They include:

1) *Mechanical properties*. Firstly, a good binder should maintain good mechanical properties of pellets, including green, dry, and fired pellets, e.g., deformation under load, resistance to fracture by impact and by compression, resistance to abrasion.
2) *Chemical composition*. A good binder should bring no environmentally and metallurgically harmful elements such as P, S, As, etc., into product pellets. It should not markedly reduce iron grade and increase impurities such as silica.
3) *Metallurgical performance*. A good binder should maintain pellet's excellent metallurgical properties, such as reducibility, swelling and pressure drop during reduction.
4) *Processing behavior*. Adding, mixing, dispersion of binder, green ball preparation, pellet drying, etc., should not be too complicated or essentially change conventional pellet production circuit.
5) *Cost factor*. Price of binder should be acceptable for iron pellets production.

2.2. Binding and failure model of particles-binder systems

Fig. 1 is a model of ore particles-binder system inside pellets. It can be found that there are two phases and one interface, which are binder B, ore particle P, and the interface BP between B and P. There are four kinds of interaction forces in this system:

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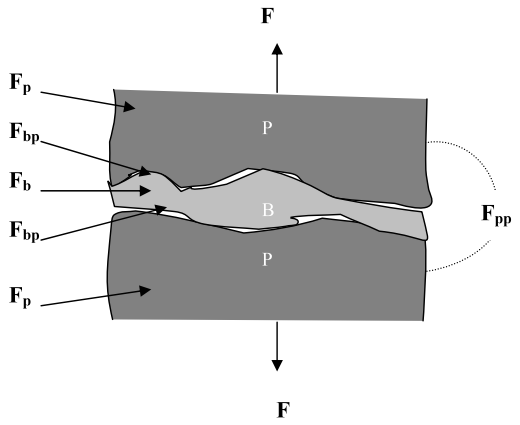


Fig. 1. Binding model and interaction forces inside particles-binder systems.

1) Binder cohesive force F_b: the sum of interaction forces between molecules, atoms inside binder and represents mechanical properties of the binder itself.
2) Ore cohesive force F_p: the sum of interaction forces between atoms, ions inside ore particle; it represents mechanical properties of ore particle itself.
3) Adhesive force at the interface F_{bp}: the sum of van der Waals, electrostatic, magnetic, hydrogen bonding, chemical bonding and viscous forces, etc., between binder and ore particle.
4) Interaction force between ore particles F_{pp}: the sum of van der Wall's forces, electrostatic forces, magnetic forces and mechanical interlocking forces and capillary forces (in the presence of water).

It has been shown that the capillary forces are very important to wet strength of pellets. A number of investigations have shown that the wet strength of pellets can be easily met in most cases if an organic binder is used. What people concern more is the dry strength of pellets. In the case of dry pellets, capillary forces are no longer present, while van der Wall's forces, electrostatic forces and magnetic forces are weak and negligible. Therefore, in dry pellets F_{PP} is mainly made up of mechanical interlocking forces, which are also weak and negligible compared to F_b, F_p or F_{bp}.

Failure of the binding system takes place if an exterior force (F) greater than either F_p, or F_b or F_{bp} is exerted to the system. There are following possible failures according to the relative magnitude of the three forces, as shown in Fig. 2 [15]:

1) If F_{bp} is less than F_p, F_b and F, the binder can debond from the adhered surface as shown in Fig. 2(b), which is called adhesive failure or interface failure.
2) If F_p is less than F_b, F_{bp} and F, the fracture takes place inside ore particle as shown in Fig. 2(c). This is cohesive failure of ore particles.
3) If F_b is less than F_p, F_{bp} and F, the fracture occurs inside binder layer as shown in Fig. 2(d). This is known as cohesive failure of the binder.

In addition to above three cases, cohesive failure of binder and adhesive failure may occur simultaneously because of uneven strain inside binding system or if F_b and F_{bp} are equivalent in magnitude.

In general, failure takes place always inside binder layer or at the binding interface in iron ore particles-binder system because of the inherent great cohesive strength inside iron ore particles. Therefore, binding intensity of iron ore particles-binder system depends on the binder cohesive force (F_b) and adhesive force (F_{bp}). Moreover, good wettability of binder solution to the surface of iron ore particles is precondition for achievement of great adhesive force. In addition, unlike other binding systems, iron ore pellets containing binder must be subject to further thermal treat-

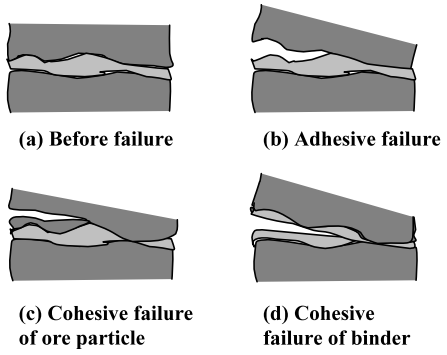


Fig. 2. Failure model of a binding system.

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ment, such as drying, preheating, induration or reduction, which require the binder to possess thermal stability. Therefore, good wettability, great adhesive force and cohesive forces as well as thermal stability constitute the essential functions of organic binder for iron ore pelletization.

2.3. Functions of organic binders for iron ore pelletization

2.3.1. Wettability

Based on the theory of adhesion, the adhesive must come into intimate contact with the adhered in order for maximum adhesion to occur. Maximum adhesion will occur when the work of adhesion, W_A, is a maximum. Contact angle, adhesion work, cohesion work and spreading coefficient are usually used in the identification of wettability [16].

When a liquid comes into contact with a solid surface, the liquid assumes characteristic drop shape; this is shown in Fig. 3. θ is defined as contact angle. γ_{lv}, γ_{sl} and γ_{sv} are known as interfacial tensions of liquid/vapor, solid/liquid and solid/vapor interfaces, respectively. The equation describing the balance among these forces and the contact angle is known as Young equation and it is stated in Eq. (1),

$$\gamma_{sl} + \gamma_{lv} \cos\theta = \gamma_{sv} \quad (1)$$

The work of adhesion W_a is the reversible work required to separate a unit area of liquid from a solid. It is defined by Eq. (2)

$$W_A = \gamma_{lv} + \gamma_{sv} - \gamma_{sl} \quad (2)$$

Substitution of Eq. (1) into Eq. (2) gives Eq. (3):

$$W_A = \gamma_{lv}(1 + \cos\theta) \quad (3)$$

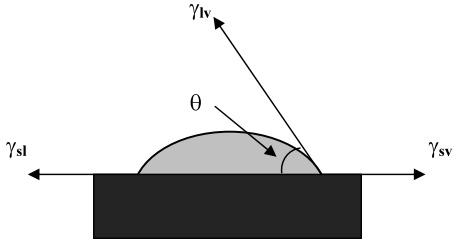


Fig. 3. The contact angle of a liquid on a solid surface.

Hence the work of adhesion is directly related to the surface tension of the liquid and the contact angle. This equation states that the maximum work of adhesion occurs when $\theta = 0^\circ$. Eq. (3) also shows that the work of adhesion can never be zero since all liquids display a surface tension under normal conditions.

In discussing wetting, spreading coefficient deserves mention. If a liquid is to spread on a solid, the work of cohesion of the liquid must be less than the work of adhesion of the liquid on the solid. Thus for spreading to occur, the spreading coefficient, S_H, defined by Eq. (4), must be greater than zero.

$$S_H = W_A - W_C \quad (4)$$

where W_C is the work of cohesion, which is the reversible work required to separate a column of liquid and create two liquid/vapor surfaces. It is a good measure of molecular interactions for symmetrical molecules. It is defined by Eq. (5)

$$W_C = 2\gamma_{lv} \quad (5)$$

Thus, we have

$$S_H = \gamma_{sv} - \gamma_{sl} - \gamma_{lv} \quad (6)$$

Hence γ_{sl} and γ_{lv} should be made as small as possible if spreading is to occur. From a practical viewpoint, it will be better if the binder behaves like a surfactant. It is adsorbed at both the solid/liquid and liquid/air interfaces and therefore lowers these interfacial tensions.

Substitution of Eq. (1) into Eq. (6) gives Eq. (7):

$$S_H = \gamma_{lv}(\cos\theta - 1) \quad (7)$$

It can be seen that the smaller the contact angle, the greater is the spreading coefficient if γ_{lv} is kept constant. Therefore, binder should be made to reduce the contact angle on iron ore surface as much as possible. Structurally, it is necessary to introduce hydrophilic functional groups into the binder molecules in order to reduce the contact angle.

As iron ore particles-binder system is concerned, wetting is also associated with capillary phenomenon since in this case the binder liquid is required to penetrate between particles.

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The driving force of penetration is that of the pressure difference across the curved surface of the meniscus. The relevant equation is [17]:

$$\Delta P = \frac{2\gamma_{lv}\cos\theta}{r} \quad (8)$$

where r is the radius of the capillary. It is helpful to write Eq. (8) in the following form according to Young equation if θ is not zero:

$$\Delta P = \frac{2(\gamma_{sv} - \gamma_{sl})}{r} \quad (9)$$

so that the principal requirement for a large ΔP is that γ_{sl} be made as small as possible, since for practical reasons it is not usually possible to choose γ_{sv}. On the other hand, if θ is zero, Eq. (8) takes the form

$$\Delta P = \frac{2\gamma_{lv}}{r} \quad (10)$$

and the requirement for a large ΔP is that γ_{lv} be large. The net goal is then to reduce γ_{sl} without at the same time reducing γ_{lv}.

In addition to ΔP being large, it is also desirable in promoting capillary penetration that the rate of entry be large. For the case of horizontal capillaries or, in general, where gravity can be neglected, Washburn [15,18] gives the following equation for the rate of entry of a liquid into a capillary:

$$\frac{dl}{dt} = \frac{r\gamma_{lv}\cos\theta}{4l\eta} \quad (11)$$

where γ_{lv} is the liquid/vapor interfacial tension, θ the contact angle, η the viscosity of solution, r the capillary radius and l the length filled by liquid.

It is clear that the rate of liquid penetration is directly proportional to the cosine of the contact angle, to the surface tension of the liquid and inversely proportional to the viscosity of the liquid. Therefore, reducing the viscosity of binder solution while reducing contact angle and increasing the surface tension of the liquid will be favor for full wetting of ore particles.

2.3.2. Adhesive force

Adhesive force refers to binding force at the interface between binder and ore particles. Table 1 lists the various attractive molecular forces that may operate across an interface along with the approximate range of the strength they cover [15]. It is clear that chemical bond forces, particularly of ionic bonds, are much greater than van der Waal's forces. Hydrogen bond force is also markedly greater than van der Waal's forces. The van der Waal's forces fall off rapidly with distance of separation by r^{-3} and for such forces to be effective the interacting surfaces must be as close as possible, typically 0.2–0.5 nm. Such an intimate contact is not typical inside iron ore pellets. In addition, the physical adsorption established by van der Wall's forces is easy to be stripped by water vapor. Therefore, it is essential to introduce as many as polar functional groups or hydrogen bond groups into binder molecules and establish chemical bonding between binder molecules and the ore particles.

2.3.3. Cohesive force

Cohesive force of an organic binder is a measure of mechanical strength of the binder itself [19]. It was once reported that, in failure tests of adhesive system, the observer did not see any obvious adhesive retained on the adhered surface, which seems to be an adhesive type failure, but higher resolution instrumentation showed more recently microscopic amounts of adhesive still present on

Table 1
Values of attractive molecular interaction at interfaces

Type of interaction	Approximate energy range (kcal mol^{-1})
van der Waals	
Dispersion	5
Dipole–dipole	0–10
Dipole-induced dipole	0–0.5
Hydrogen bonding	0–40
Chemical bonds	
Covalent bonds	15–170
Ionic bonds	140–250
Metallic bonds	27–83

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the adhered [20]. This indicates that the cohesive force may be a more important factor affecting binding strength than adhesive force.

The mechanical strength of an organic polymer depends on the chemical structure of the polymer, molecular weight, crystallinity and the extent of any crosslinking or branching.

2.3.4. Thermal stability

Usually, if an organic binder is composed of straight chain or less side chain polymers, its solution displays good viscoelasticity at room temperature and consequently green pellets display good mechanical properties. However, the binder will lose its viscoelasticity and become more fragile at elevated temperature (during drying, induration or reduction) and the strength of the pellets is hence reduced. Two kinds of changes will take place for polymer binders in heating: physical softening and melting, and chemical oxidation, degradation, decomposition, etc. [21,22]. These weaken mechanical strengths of binder and consequently of pellets. Improving the thermal stability of binders is very important to the selection and design of chain skeleton for organic binders of iron ore pellets. As a good binder for iron ore pellets, an organic polymer should have (a) an extremely high melting point (T_m) or glass transition temperature (T_g), (b) exceptional thermal and oxidative stability, and (c) properties of solubility, moldability or both at least in an intermediate form [22].

3. Structure of organic binders for iron ore pelletization

Based on the above discussions, the molecule of an ideal organic binder of iron ore pellet should possess the following characters in structure:

- Hydrophilic groups enforcing the wettability of ore particle surface,
- Polar groups bonding chemically on ore particle surface,
- Organic chain skeleton that is strong and heat-resistant.

Therefore, the structure mold of an ideal organic binder of iron ore pellets can be shown in Fig. 4.

3.1. Selection and design of polar functional groups (X)

Good adhesion requires that the binder molecules possess sufficient polar function groups. For iron ore, Fe^{3+} and Fe^{2+} are the main surface ions. The former belongs to hard acid and the latter may be categorized into intermediate acid based on Louis acid–base theory. In accordance with Pearson's hard–soft base–acid ruler, the polar groups that will react with iron ions include: $-COO^-$, $-OH$, $-CONH_2$, $-NH_2$, $-NO_2$, $=NH$, $-N^+R_3$, $-PO_3H$, $-SO_3H$, $-OSO_3H$, $-SH$, etc. Among them, the last four groups are hardly recommended because they contain elements of S and P harmful to iron and steel quality.

3.1.1. Calculation of HMO indices of polar groups

A series of characteristic parameters of polar groups can be figured out by using Hückel molecular orbit method. These parameters are hence called HMO indices. $-COO^-$, for example, is a hard base group and can be preliminarily selected as the polar group of the binder. Through establishing and solving orbit equations, the orbit energies of $-COO^-$ were attained. The ionization potential (E_P) and electron affinity (E_A) of $-COO^-$ were obtained as 12.1 and 4.0, respectively, according to the orbit energies. The great values of E_P and E_A indicate that $-COO^-$ group will easily react with iron ions.

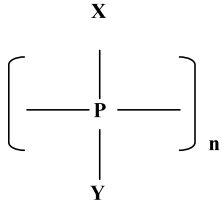


Fig. 4. The molecular structure mold of an organic binder for iron pellet (X, polar group; Y, hydrophilic group; P, organic chain skeleton; n, polymerization degree).

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3.1.2. Electronegativity of polar groups

Pauling has defined the electronegativity as the power of an atom in a molecular to attract electrons to itself. Recently, a modified definition stated that electronegativity is the ability of an atom or a group of atoms to attract or hold electrons to itself when combining with other atoms or groups [23]. There are at least seven different electronegativity scales and a number of calculating methods for electronegativity of group. The electronegativity values change widely with respect to different methods. Wang [24], one of this paper's authors, once investigated the group electronegativity and proposed a method to calculate electronegativity of group. The electronegativity values obtained by his method as well as those by other methods for several commonly used groups in mineral and metallurgical industry are listed in Table 2.

3.1.3. Bond ionicity

The electronegativity difference between two bonded atoms are often used to express bond ionicity. Several empirical relations have been proposed in order to evaluate bond ionicity for a B–A bond. Barbe proposed the following expression [25]:

$$f_i = \frac{X_A - X_B}{X_A} \tag{12}$$

where f_i is the bond ionicity, X_A and X_B are the electronegativities of two bonded atoms.

If $|f_i|$ is less than 0.5, the formed compound is said to be covalent, otherwise, the compound is ionic.

Pauling [26] proposed ionicity percentage to express bond ionicity:

$$\Phi\ (\%) = 100\left[1 - \exp\left[-\frac{1}{4(X_A - X_B)^2}\right]\right] \tag{13}$$

where Φ is the ionicity percentage and X_A and X_B are the electronegativities of two bonded atoms, respectively. It can be found that Φ is equal to 51% at $|\Delta X| = 1.7$. Correspondingly, a covalent compound is formed if $|\Delta X|$ is less than 1.7 and an ionic compound is formed if $|\Delta X|$ is greater than 1.7.

For the bonding of $-COO^-$ and Fe, it is known that the electronegativity of $-COO^-$ (X_A) is 3.9 based on Wang's method and that of iron (X_B) is 1.8. The bond ionicity (f_i) and ionicity percentage (Φ) to $-COO^-$/Fe bond are hence obtained from Eqs. (12) and (13) as follows:

$$f_i = 0.54 \tag{14}$$

$$\Phi = 67.0\% \tag{15}$$

The results indicate that $-COO^-$ will form ionic-bonded compound with iron.

Similarly, from Wang's electronegativity values, it can be obtained that –OH, $-NH_2$ and $-NO_2$ will form ionic compounds with iron, and –SH and –CN will form covalent compounds with iron.

It should be noted that the bond ionicity might be different for the same compound since the electronegativity of the same group varies very much with different calculation methods.

3.2. Type and position of hydrophilic groups (Y)

Typical hydrophilic group is –OH. Common hydrophilic groups include: –OH, –O–, $-SO_3H$,

Table 2
Electronegativities of some groups [24]

Groups	Wilmushurst's method	Hinze's method	Muller's method	Zhang's method	Yuan's method	Wang's method
–OH	3.89	3.82	3.46	3.84	3.58	3.8
–SH	2.61	2.38		2.24	2.60	2.6
–CN	3.17		3.20	3.2	2.90	3.0
$-NH_2$	3.40	2.96	3.00	3.01	3.09	3.7
$-COO^-$	2.84		2.85	2.9	3.13	3.9
$-NO_2$	3.45					3.8

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–COOH, –$CONH_2$, –PO_3H, etc. Actually, most of the polar groups function as hydrophilic groups. What is worth noting is that the type of hydrophilic groups will affect the affinity of polar groups to iron ore surface. If the hydrophilic group is an electron-withdrawing group (e.g., –SO_3H, NO_2, –COOH, etc.), it will reduce the affinity of polar groups. If the hydrophilic group is an electron-donating group (e.g., –NH_2, –OH, –SH, etc.), it will enforce the affinity of polar groups. Therefore, –OH and –NH_2 should be preferentially chosen as hydrophilic groups.

The relative position of hydrophilic group to polar group has also affect the function of the binder. If the polar group and hydrophilic group are kept apart from each other, the interactions between them will become weak. However, if X and Y are located at each end of the molecule while molecule is long enough, bending of the molecule may occur and both X and Y may take orientation toward ore surface and non-polar carbon chain is toward outside. In this case, ore surface will become hydrophobic.

3.3. Selection of organic chain skeleton (P)

3.3.1. Unsaturated hydrocarbon chain

Good mechanical strength and thermal stability of the pellets require increasing double, triple bonds and reducing single bonds in binder molecules as many as possible. Double and triple bonds have greater bond energies than single bonds as shown in Table 3 and make the molecule more rigid and hence resist greater stress force.

Table 3
Bond lengths and energies of part bonds [25]

Carbon bond	Bond length (Å)	Bond energy (kJ mol^{-1})
C–C	1.5	348
C=C	1.3	606
C≡C	1.2	828
C–H	1.1	412
C–O	1.4	333
C=O	1.2	705
C–N	1.4	292
C–F	1.4	441
C–Cl	1.8	328
C–Br	1.9	275
C–I	2.1	240

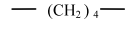
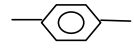
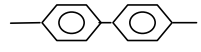
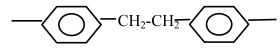
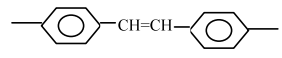
3.3.2. Ring structure and aromatic group

Extraordinary thermal stability has been achieved with a large variety of polymers containing aromatic and heterocyclic ring [22]. In general, both the crystalline melting temperature (T_m) and glass transition temperature (T_g) of polymer increase with decreasing flexibility of the polymer chain. Flexibility decreases with increasing aromatic composition of main chain or by incorporation of bulky substituent groups or nonrotational groups in the main chain. As shown in Table 4, for an analogous series of polyesters, replacement of the aliphatic sequence $(CH_2)_4$ of compound A with an aromatic ring (compound B) increases T_m by 220 °C. Replacement by two coupled aromatic rings (compound C) further increases T_m by 85 °C, but incorporation of a flexible $(CH_2)_2$ group between aromatic rings lowers T_m by 135 °C (compound D). By contrast, incorporation of a nonrotational, unsaturated –CH=CH– linkage between aromatic rings (compound E) results in the highest T_m polyester.

3.4. Selection of polymerization degree (n)

The polymerization degree of an organic polymer determines its molecular weight, while the

Table 4
Effects of backbone structure on T_m of polyesters derived from ethylene glycol

Compound	Main-Chain Unit	T_m (°C)
A		50
B		270
C		335
D		220
E		420

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molecular weight can have important effects on its cohesive force or mechanical strength and thermal stability.

For low-molecular-weight binders, there is a relatively weak interaction among adjacent chains; movement of one chain past another is easy and the tensile or shear strength is low. In a high-molecular-weight binder, chain interactions are greatly increased, they may become tangled, and the binder exhibits a much greater strength: stretching and "necking" as shear is applied, but resisting a much greater force before failing. Therefore, the so-called molecular entanglement, that is, as the binder molecules become longer, they become more "wrapped up" in their neighbors, serves as an excellent process for the dissipation of the stress forces, as shown in Fig. 5 [15].

This dissipation process depends directly on the amount of chain entanglement and the nature of the forces acting between chains. In a bulk binder, the degree of entanglement is a direct result of the nature of the binder (molecular weight, branching, etc.) and its method of preparation.

In addition, entanglement is also helpful to adhesion at an interface. In any case, if entanglement can be increased, the strength of the bond at the interface will be improved.

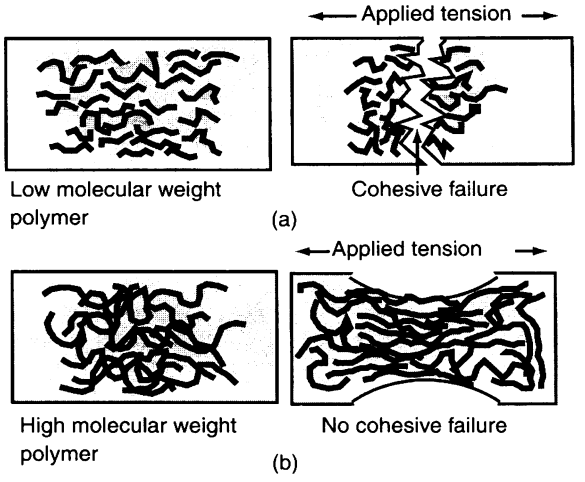


Fig. 5. Effects of molecular weight of a polymer on its cohesive strength; after Drew Myers [15].

The glass transition temperature, T_g, increases with molecular weight at low molecular weight but reaches a point at moderate molecular weight where further increase in molecular weight has very little effect on T_g. The dependence of T_g on molecular weight is approximated by the following equation [27]:

$$T_g = T_g^0 - \frac{K}{M_n} \quad (16)$$

where T_g^0 is the limiting value of T_g at high molecular weight, M_n the number-average molecular weight and K is a constant for a given polymer.

Therefore, it is clear that the higher the molecular weight of a binder, the greater is its mechanical strength and the better is its thermal stability. However, on the other hand, the viscosity of polymer solution increases rapidly with its molecular weight [27], which in turn causes the reduction in wettability in terms of Eq. (11). Moreover, the selection of appropriate polymerization degree of a binder is also associated with the nature of polar group and hydrophilic group, and structure of organic chain skeleton.

4. Preparation and applications of organic binders

Based on the above investigation on functions and molecular structure of organic binders, a new binder, named S-1, was synthesized [28]. It is a kind of modified starch and has the structure unit shown in Fig. 6. The presence of carboxylic and hydroxyl groups makes it an anionic and hydrophilic binder.

With S-1 as binder, pelletizing experiments were made on a magnetic concentrate with a particle size of 86.10% passing 0.074 mm (with a specific

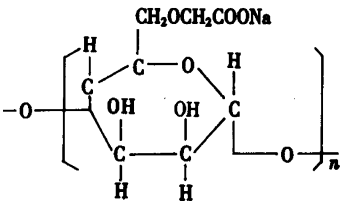


Fig. 6. The structure unit of organic binder S-1.

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surface area of 1820 $cm^2\ g^{-1}$) and total iron grade of 68.11%. The concentrate bearing the binder was pelletized 20 min with a total moisture content of 8.1% in a balling disc with a diameter of 800 mm, an edge height of 150 mm, a tilt angle of 49° and a revolution rate of 20 rpm. Results in Table 5 show that pellet strengths, especially dried pellet strengths are much greater than those of pellet with bentonite as binder. The pellets also display good heat stability.

Like other synthesized organic binders, S-1 binder is found expensive in cost compared to bentonite. In order to reduce the cost of organic binders, Funa® has been systematically developed as a cheap binder of iron ore pelletization. Funa is not a pure compound but a composite matter with humates as its major constitute. It is made from lignite or weathered coal by extraction of caustic solution. Eq. (17) represents the simplified chemical reaction of Funa preparation:

$$(OH)_mR(COOH)_n + nNaOH=(OH)_mR(COONa)_n + nH_2O \quad (17)$$

It has been found that the adhesive properties of Funa as a pellet binder are mostly determined by the nature of raw materials and the careful selection of the raw materials is important to make high-quality iron pellet binder. In addition, pH, temperature, and liquid/solid ratio, etc., are also affecting factors on the properties of Funa as a binder.

The molecular structure of humates is not well understood, however, it is widely accepted that humates are highly reactive, amorphous, predominantly aromatic complex anionic polyelectrolytes and a number of carboxylic, hydroxyl and phenolic groups present in the molecules, as demonstrated in Fig. 7. The carboxylic groups are the ideal polar and can chemically bond on the surface of iron ore particles. The hydroxyl groups are the typical hydrophilic and can markedly increase hydrophilic character and ballability of iron ore particles. And the chain skeleton characterized by phenolic groups enables the binder to possess the favorable thermal stability. The other characteristic of the structure is that it looks a net punctured by voids or holes of different dimensions, which can trap or fix organic and inorganic compounds such as iron ions and oxides. Measurement of contact angles has shown that Funa reduces the contact angle of magnetic concentrates from 46° to zero [29]. IRS (infrared spectroscope) investigation has shown that Funa is chemically adsorbed on the surface of iron ore concentrates [29]. Pelletizing tests show that the pellets prepared with Funa possess a shock temperature of 780 °C and much higher wet and dry strengths than do those prepared with bentonite [30]. The partial experimental results of pelletization with Funa as binder are also shown in Table 5. The concentrate and pelletizing conditions used here are same as above.

Although there are a few investigations on other organic binders in recent years, few of them involved the molecular structures of the binders. None of them mentioned that any of the binders has the similar structure to Funa. Peridur was intensively developed as a pellet binder in 1980s. It was obtained by substitution of a proportion of the hydroxyl groups in cellulose molecules with anionic groups, which suggests the presence of hydrophilic (hydroxyl) and polar (anionic) groups in Peridur. There was no report that mentioned that Peridur has a netty structure or phenolic-like groups as Funa does.

Table 5
Pelletizing results with S-1 and Funa as binders

Binder and dosage %	Wet pellet strength		Dry pellet strength		Shock temperature (°C)
	Compression N/P	Drop times/1.0 m	Compression N/P	Drop times/1.0 m	
S-1 (0.4%)	21.8	6.7	322.8	16.2	820
Funa (1.5%)	27.8	13.7	286.8	10.2	780

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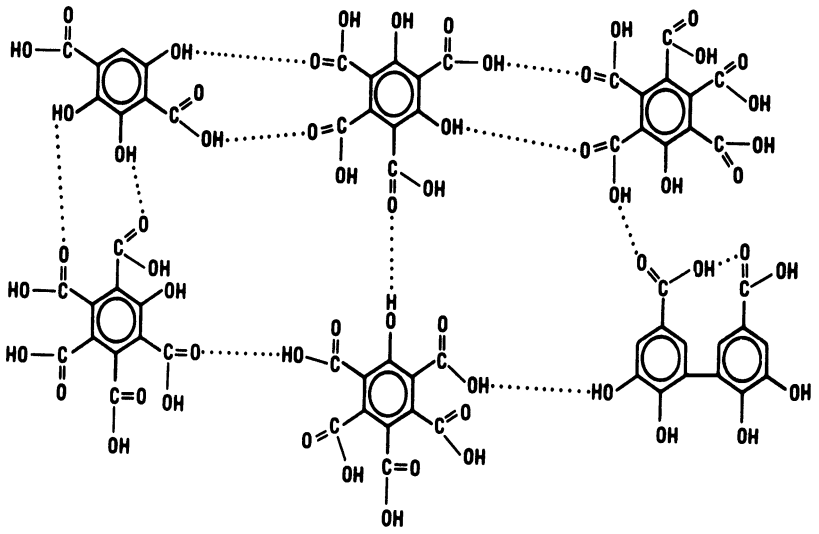


Fig. 7. The molecular structure of humates proposed by Schnitzer [31].

In addition, Funa is found less expensive than other organic binders reported before and much cheaper than cellulose-based binders, which allows it to be used at greater dosage and consequently reduce the mixing problem of raw materials bearing very low dose binder. Funa has been patented and put into commercial production of iron ore pellets for direct reduction and in agglomeration of coals and phosphate ores, etc., in China [30]. And the investigation into its application in pellets for iron-making of blast furnaces is in progress.

5. Conclusions

The functions and molecular structure of organic binders for iron ore pelletization have been investigated in this paper based on the basic principles of molecular design, interface chemistry and polymer science as well as failure model of binding systems. The following conclusions are achieved.

Functionally, good organic binders for iron ore pellets should improve the wettability of iron ore particles; possess great adhesive force to iron ore surface, great cohesive strength and good thermal stability. Structurally, good organic binders for iron ore pelletization should contain sufficient polar groups (X) and hydrophilic groups (Y) and possess the structure mold like $[X–P–Y]_n$. Ionization potential, electron affinity, group electronegativity, bond ionicity and bond energy are important parameters in the selection of polar groups and hydrophilic groups. Investigations show that $–COO^-$ and –OH are ideal polar and hydrophilic groups of organic binders, respectively. A chain skeleton of organic binders with aromatic ring or netty structure with unsaturated double or triple bonds is recommended in order to improve the thermal stability. The cohesive strength of binders is improved with the increase in polymerization or molecular weight. Two organic binders for iron ore pellets have been developed based on the investigation. Pelletizing experiments show that both of them are effective to iron ore pelletization. One of them, Funa, prepared from lignite or weathered coal and with humates as major constitutes, possesses a netty molecular structure and sufficient carboxylic, hydroxyl and phenolic groups in its molecules. Funa is found less expensive than other organic

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binders reported before and has been put into industrial production of iron ore pellets in China.

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