Catalog

Gelation(I)

1. The Core essence of Gel Phenomenon

The core of gelation is the formation of a continuous three-dimensional network structure in the system.The components such as dispersion medium (solvent/carrier),resin and powder are locked through chemical bonds or strong physical forces,caursing the system to lose fluidity and present a jelly-like,elastic semi-solid state.In severe cases,it completely solidifies and becomes inactive.

In the industry,gels are generally classified into two major categories,which form the main foundation for the subsequent analysis,prevention and rescue:

① Irreversible chemically cross-linked gel:A stable network is formed through new chemical bonds.Once formed,its fluidity cannot be restored by conventional physical means.

② Reversible physically association type gel:No new chemical bonds are formed.Only temporary networks are formed through intermolecular forces.Fluidity can be restored after environmental/formula adjustments. It is also the most common type of gel in industrial production.(Figure 1 shows a microscopic comparison between irreversible chemically cross-linked gels and reversible physically associative gels)

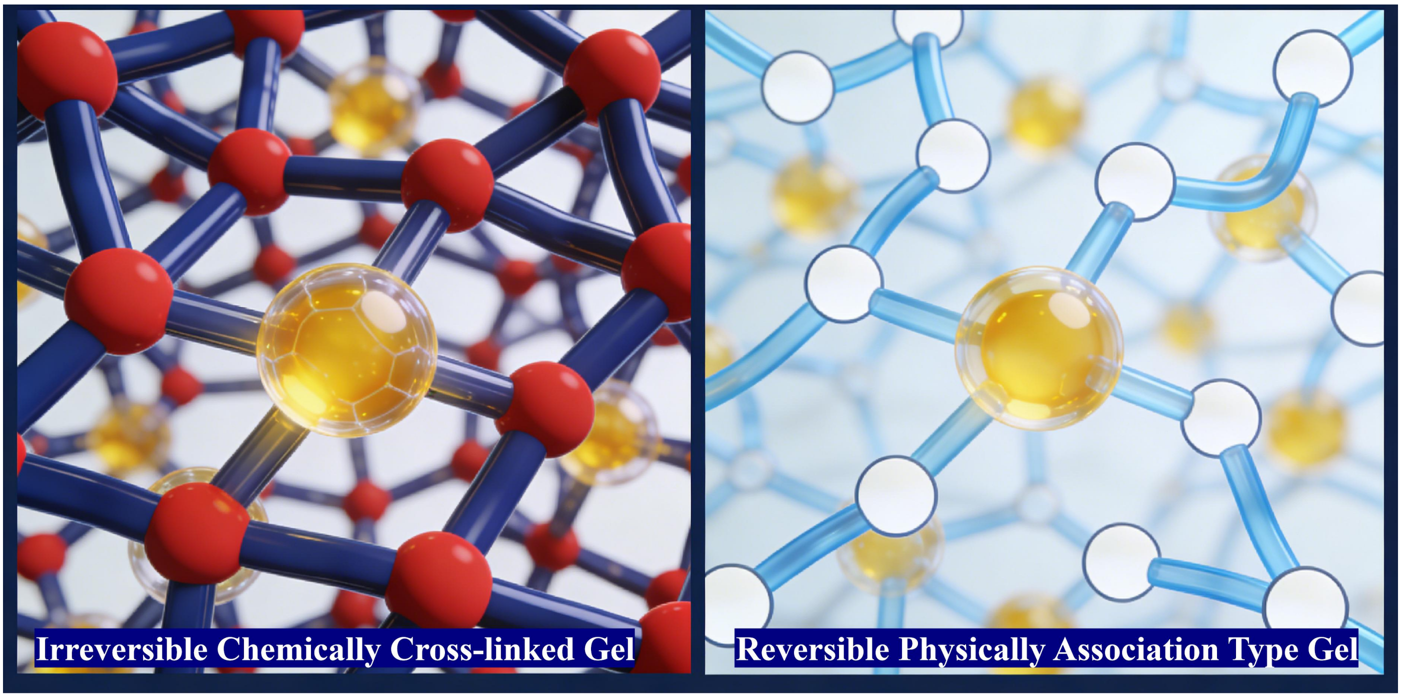
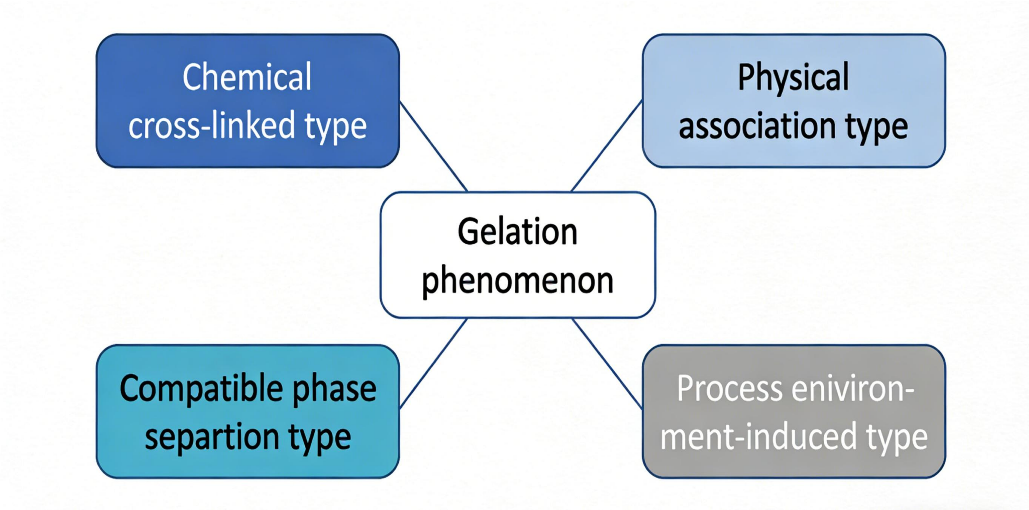


Figure 1

2. General Causes Of Gel Formation(Applicable to all system,covering the scenarios such as coatings,inks,adhesives,slurries and pastes)



1) Chemically Cross-linked Gel

The core mechanism:The core cause of the complete deactivation of the system is the formation of a three-dimensional network of cross-linked covalent bonds/strong ionic bonds through chemical reactions within the system.

Universal trigger scenario:

- The active functional groups are cross-linked in advance:Resin containing hydroxyl,carboxyl and amino groups will undergo pre-reactions with multifunctional curing agents (isocyanates,epoxies,multivalent metal ion crosslinking agents).Even if the slow reaction at room temperature accumulates to the critical value,it will trigger gelation.For instance,coordination and crosslinking of Zn^{2+} /Al^{3+} in stearate with hydroxyl resin,the early mixing of two-component systems,and early activation of latent curing agents.
- Oxidation/thermally initiated self-polymerization crosslinking:Resin containing unsaturated double bonds(such as acrylic acid,alkyd,unsaturated polyester,etc.)undergo free radical polymerization under the influence of heat,light ,and oxygen,causing a rapid increase in molecular weight and the formation of a crosslinked network.For an instance,resin self-polymerization gel caused by local overheating during grinding or excessively high storage temperature.
- The hydrolysis/polycondensation side reaction:siloxane,phenolic resin,amino resin and other systems undergo polycondensation reactions under the catalysis of water and acid-base impurities,rapidly forming cross-linked structure.For instance,gelation caused by the PH value being out of control in water-based systems or water ingress due to poor sealing.

- Impurity catalytic crosslinking:Heavy metal impurities mixed in the system,residues of strong acids and based,and catalytic sites on the surface of pigments/fillers can accelerate the crosslinking reaction.For instance,excessive drying agents or residual curing agents from equipment contaminating materials can cause gelation.

2) Physical Associative Gel(Reversible,The Most Common Soft Gel/Jelly-like In Industrial Production)

The core mechanism:No new chemical bonds are formed,and a reversible three-dimensional network is formed through intermolecular forces,which is the core reason for the jelly-like formation of the vast majority of pastes,slurries,and coating systems.

General trigger scenario:

- Large-scale hydrogen bond association:In the system,a large number of components containing hydroxyl,amino,and carboxyl groups(resins,thickeners,powder surface treatment agents)form hydrogen bond networks with each other,locking the carrier.For instance,hydrogen bond gels of cellulose/polyurethane thickeners in water-based systems,and association gels between hydroxyl groups of ketone resins/aldehyde-ketone resins.
- Ion/electrostatic complexation:Components with opposite charges adsorb each other,or multivalent metal ions form an ion cross-linked network with negatively charged resins.For instance,the aggregate gel of cationic dispersants and anionic resins,and the ionic association gel of zinc stearate and carboxyl/hydroxyl resins.
- Powder flocculation structuring: Poor dispersion of pigments/fillers, particles form a continuous flocculation network through van der Waals forces, encapsulating the solvent to form a gel; (Figure 2 shows the microscopic comparison between the well-dispersed state and the flocculated structured gel)

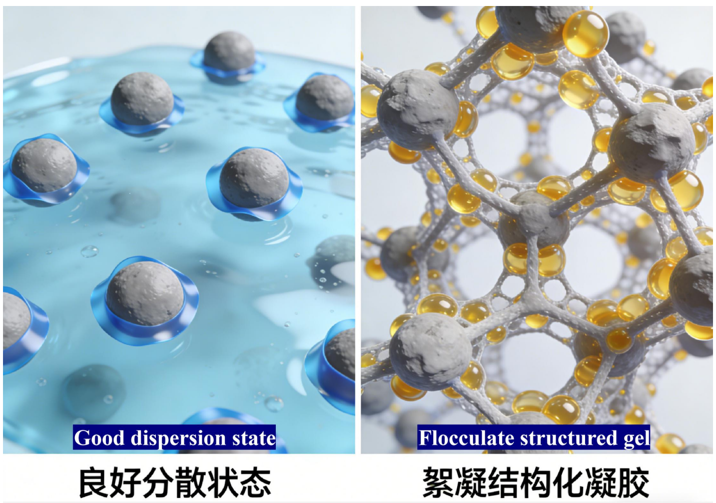


Figure 2

For instance, if large specific surface area powders such as nano-silica and nano-calcium carbonate are not properly dispersed, they are prone to form structured gels, which is also the core reason for the differences in the performance of various pigments.

- Thermosensitive association: Hydrophobic association occurs when nonionic resins/thickeners exceed their cloud point, or the solubility of the resin decreases at low temperatures, causing molecular chains to aggregate and form gels. For instance, the gelation of coatings at low temperatures during winter storage and the gelation of the system during high-temperature construction.

3) Gel induced by compatibility and phase separation

Core mechanism: The solubility parameters and polarities of each component in the system do not match, leading to phase separation. The enriched aggregated phases form a continuous network, ultimately presenting as gel. General trigger scenario：

- Poor compatibility between resin and solvent: The proportion of defective solvents is too high, causing the resin molecular chains to change from being stretched to curled and aggregated, forming a gel phase. For instance, the rapid evaporation of solvents can lead to local supersaturation of the resin, and excessive dilution of the resin with inferior solvents can cause precipitation and gelation.
- Compatibility mismatch between components: Excessive polarity difference of mixed resins, incompatibility between additives and the main system, resulting in phase separation and the formation of a continuous network; For instance, when the amount of dispersant exceeds the adsorption saturation of the powder, the free dispersants may associate with each other, causing gelation。

4) Gels induced by process and storage environment

The core mechanism: The formula itself has no essential problem, but external factors such as processing and storage trigger the above-mentioned cross-linking/association reaction, ultimately leading to gelation. General trigger scenario：

- Processing technology out of control: Excessively high grinding/stirring temperature causes resin cross-linking, insufficient dispersion leads to powder flocculation, excessive dispersion stripping the powder surface treatment agent causes secondary flocculation, and equipment wear introduces heavy metal impurities to catalyze the reaction。

- Storage environment out of control: High temperature accelerates crosslinking/association, low temperature causes resin precipitation, poor sealing leads to water/oxygen intake, triggering hydrolysis/oxidation, and ultraviolet radiation triggers free radical polymerization。
- System contamination: Residual curing agents, acids, bases, and incompatible materials in containers/equipment can contaminate the main system and cause gelation。

3. General prevention/avoidance methods for gel phenomena

1) Root cause control: Raw material selection and formula design

- Strictly control crosslinking risks: For single-component systems, latent/blocking curing agents should be given priority. The addition amount of multivalent metal ions and multifunctional group crosslinking agents should be strictly controlled to avoid exceeding the critical threshold. Strictly control the introduction of catalytic impurities such as strong acids, strong bases, and heavy metals within the system.
- Optimize compatibility design: Match resins, solvents, and additives through solubility parameters. Conduct small-scale compatibility tests on all new raw materials first. The dosage of additives should be precisely calculated based on theoretical values (for example, dispersants should be calculated based on the oil absorption value and specific surface area of the powder) to avoid overdosage.
- Powder selection and compatibility: Prioritize the selection of surface treatment powders that match the polarity of the main resin. For instance, for oil-based systems, choose stearic acid/silane treated powders; for water-based systems, select polyether/carboxyl treated powders to prevent powder flocculation and structuring from the source.
- Stability guarantee design: Add an appropriate amount of antioxidants and polymerization inhibitors according to the characteristics of the system to prevent oxidation and self-polymerization. A stable pH buffer zone should be set up in the water-based system to avoid acid-base catalytic side reactions. The temperature-sensitive system adds a co-solvent to broaden the dissolution temperature range of the resin.

2) Process control: Processing technology specifications

- Strictly control processing temperature: The grinding/stirring equipment is equipped with a temperature-controlled jacket to prevent local overheating. For heat-sensitive systems, low-temperature and low-speed dispersion processes are adopted to eliminate temperature-triggered cross-linking reactions
- Optimize the dispersion process: Set the dispersion speed, time and grinding medium according to the characteristics of the powder. First, complete the pre-dispersion of the powder and then enter high-speed grinding. This ensures that the powder is fully depolymerized without damaging the surface treatment agent of the powder.
- To prevent system contamination: Thoroughly clean processing equipment and containers to avoid residual curing agents and incompatible materials. The closed stirring and vacuum deaeration process are adopted to reduce the oxidation cross-linking caused by the introduction of air.

3) Long-term control: Storage and transportation norms

- Standardized storage environment: Store at normal temperature, away from light, and in a sealed container. For heat-sensitive systems, refrigerate at low temperatures. Avoid direct sunlight at high temperatures and freezing at low temperatures. Ensure that the container is well sealed to prevent moisture and oxygen from entering.
- Full-cycle quality monitoring: Set a reasonable shelf life, regularly test the viscosity and condition of the storage system, and detect abnormalities in advance. During transportation, proper temperature control and protection measures should be taken to avoid severe jolts that may cause phase separation and flocculation.

4) Pre-verification: Stability test

- Accelerated aging test: Before the formula is finalized, it undergoes a 7-14 day hot storage at 50℃ and a freeze-thaw cycle test to verify whether the system will gel during long-term storage.
- Critical value test: For crosslinking agents, additives, and powders, test the critical addition amount for initiating gel, and reserve a safety margin in production.
- Compatibility limit test: Simulate extreme conditions during production and storage to verify the anti-gel stability of the system.

4. Rescue plan for the gel phenomenon

Core premise

Irreversible chemically cross-linked gels are almost irreparable and can only be scrapped or downgraded for use. Only reversible physical association type, compatibility type and mild process-induced type gels can restore fluidity through corresponding methods. All rescue measures must first undergo small-scale laboratory tests to verify their effectiveness before being scaled up to the entire batch of materials to avoid secondary waste.

1) Treatment of irreversible chemically cross-linked gels

- The core judgment: If the gel fails to regain its fluidity after heating or adding good solvents, and even insoluble and infusible elastomers appear, it indicates that a stable covalent bond network has been formed
- process mode:

① Complete scrapping: Materials with a high degree of crosslinking and complete loss of fluidity, having no recycling value, are directly scrapped in compliance with regulations.

② Downgraded use: For slightly cross-linked materials, after being crushed, they can be used as fillers and added in extremely small amounts to the same type of system. Do not add in large quantities to avoid re-gelation.

③ Forced dilution is strictly prohibited: Forced addition of solvents will only lead to phase separation and caking of the system, making it impossible to restore fluidity, and will also result in solvent waste.

2) Targeted rescue methods for reversible gels

Scene 1: Hydrogen bond/ion association type soft gels (such as metal stearate + hydroxyl resin jelly, water-based hydrogen bond gels)

① Disrupt the associative network: Add strongly polar solvents (alcohols, alcohol ethers, etc.) to break hydrogen bonds; In an ion-associative system, a small amount of EDTA disodium, phosphate and other chelating agents are added to chelate multivalent metal ions and dismantle the ion cross-linked network.

② Regulate the system environment: The water-based system fine-tunes the pH value through organic acids/organic amines to break hydrogen bonds or ionic associations.

③ Heating deassociation: Within the temperature range that the resin can withstand, the system is heated to 40-80℃. The physical network is disrupted through molecular thermal motion. After stirring evenly, it is cooled slowly. Most systems can regain fluidity.

Scene 2: Gelation caused by powder flocculation/structuring

① Re-dispersion: The system is subjected to secondary high-speed dispersion or grinding to depolymerize the flocculated powder network and directly restore fluidity.

② Add a suitable dispersant: Conduct a small-scale test by adding a dispersant that matches the system, which adsorbs on the surface of the powder, reduces the intergranular force, and achieves deflocculation

③ Moderate dilution: Add an appropriate amount of good solvent to reduce the solid content of the system, minimize the collision and aggregation between powder particles, and break down the structured network.

Scene 3: Compatibility/phase separation, temperature-induced gels

① Add a good solvent: Add a good solvent that matches the main resin to enhance the resin's solubility, depolymerize the aggregated molecular chains, and restore the uniformity of the system;

② Temperature control: For gelation caused by low temperature, gradually increase the temperature to the optimal dissolution temperature of the resin, stir evenly, and then cool slowly. High-temperature phase separation gel, slowly cool to room temperature, add co-solvent, stir and homogenize;

③ Add compatibilizers: Add a small amount of coupling agent, leveling agent or compatible resin to improve the compatibility between components and eliminate phase separation.

Scene 4: Gel caused by mild oxidation/self-polymerization (not fully cross-linked)

① Terminate the reaction: Add an appropriate amount of polymerization inhibitor/antioxidant (BHT, hydroquinone monomethyl ether, etc.) to prevent the continuation of free radical polymerization.

② Dilution and cooling: Add a large amount of good solvent to reduce the system concentration, minimize intermolecular collisions, terminate the polymerization reaction, filter out the formed gel particles, and the remaining clear liquid can be downgraded for use

③ If a large number of insoluble gel particles have already appeared, it indicates that the crosslinking range is too high. It is not recommended to save them; they should be directly scrapped.