Enhancing the Rheological Properties of PVC Plastisols through Calcium-Based Nanocomposites: Mechanisms, Comparative Analysis, and Industrial Implications

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Abstract

PVC plastisols are highly versatile, solvent-free dispersions widely used in coatings, sealants, synthetic leather, automotive underbody protection, flooring, and a variety of flexible polymer products. Their industrial value depends strongly on their rheological profile, which governs processability, application behavior, storage stability, sag resistance, film formation, and final performance after fusion. Among the different strategies proposed for rheology control, the incorporation of calcium-based nanocomposites, particularly nano-sized calcium carbonate, has attracted substantial attention due to its low cost, broad availability, tunable surface chemistry, and ability to interact effectively with both PVC particles and plasticizer phases.

This review provides a detailed examination of the mechanisms by which nano-calcium carbonate modifies plastisol rheology. The discussion focuses on viscosity evolution, yield stress development, shear-thinning behavior, thixotropy, and aging stability. Particular attention is given to the effects of particle size, shape, surface treatment, dispersion state, and filler loading on the microstructure of the suspension. In addition, this article compares calcium-based nanocomposites with conventional microfillers, alternative nanoparticles such as nanosilica and nanoclay, and unfilled plastisol systems. The comparative analysis shows that nano-CaCO3_33 offers a favorable balance between processability, structural stability, cost-effectiveness, and industrial scalability, making it one of the most practical rheology modifiers for modern plastisol formulations. Finally, future research directions are proposed, including hybrid filler systems, bio-based plasticizers, and advanced multiscale rheological modeling.

Keywords: PVC plastisol, nano-calcium carbonate, rheology modification, yield stress, shear-thinning, thixotropy, filler comparison, suspension stability

1. Introduction

Poly(vinyl chloride) plastisols are dispersion systems composed of fine PVC resin particles suspended in a liquid plasticizer. In contrast to thermoplastic melts, plastisols do not require organic solvent and therefore offer significant advantages in terms of environmental safety, volatility reduction, ease of handling, and coating flexibility. Upon heating, the plasticizer penetrates the PVC particles, leading to gelation and fusion, and producing a coherent, flexible, and durable polymeric layer.

Despite these advantages, the practical use of plastisols is highly dependent on their rheological behavior. A plastisol must satisfy several sometimes competing requirements. During mixing, pumping, and application, it should remain sufficiently fluid. During storage and rest, it should resist phase separation, sedimentation, and viscosity drift. After application, it should exhibit enough body and yield stress to prevent sagging and dripping, especially in vertical or inclined surfaces. Therefore, the rheological properties of plastisols are not merely academic parameters; they directly determine industrial usability and final product quality.

Conventional plastisol formulations often rely on the intrinsic balance between PVC particle size distribution, plasticizer content, and auxiliary additives. However, these variables alone may not provide the level of control required in advanced applications. For this reason, nanofillers have emerged as powerful tools for targeted rheology modification. Among them, calcium carbonate in nano-sized or nano-engineered form is particularly attractive because it is inexpensive, abundant, chemically stable, and compatible with a wide range of polymer processing routes.

The rheological influence of nano-calcium carbonate is more complex than that of classical fillers. Rather than acting simply as an inert diluent, it can alter interparticle interactions, modify the effective volume fraction, affect plasticizer adsorption, and generate weak physical networks inside the suspension. These effects can increase yield stress and low-shear viscosity while still preserving good flow under high shear, which is desirable for coating and application processes. Therefore, understanding the mechanisms and comparative advantages of calcium-based nanocomposites is essential for designing next-generation plastisols.

2. Rheological Fundamentals of PVC Plastisols

2.1 Non-Newtonian Flow Behavior

PVC plastisols typically show non-Newtonian behavior. Their apparent viscosity decreases with increasing shear rate, which is classified as shear-thinning or pseudoplastic behavior. This is beneficial in many processing operations because the material can flow easily during application but regain structure after deposition.

The rheological response is often described using models such as:

- **Power-law model**
- **Bingham plastic model**
- **Herschel–Bulkley model**

In many practical systems, a finite yield stress is observed, meaning that the material does not flow until a threshold stress is exceeded. This yield stress is critical for anti-sag performance.

2.2 Ageing Phenomenon

A common challenge in plastisols is rheological ageing. Over time, viscosity may increase due to continued wetting of PVC particles by the plasticizer, structural rearrangement, and changes in interparticle attraction. Ageing can reduce reproducibility and impair application behavior. Therefore, additives that stabilize the suspension against time-dependent viscosity drift are highly valuable.

2.3 Importance of Thixotropy

Thixotropy refers to the reversible breakdown of internal structure under shear followed by gradual recovery at rest. A well-designed plastisol should be thixotropic enough to flow under processing conditions but rebuild structure quickly after deposition. Nano-calcium carbonate can contribute to this balance if its dispersion and surface chemistry are properly controlled.

3. Why Calcium-Based Nanocomposites

Calcium carbonate is one of the most widely used mineral fillers in polymer industries. When reduced to the nanoscale or synthesized in a controlled precipitated nanostructure, it offers properties that are not accessible in conventional micro-CaCO3_33.

3.1 Economic and Industrial Advantages

Compared with many other nanofillers, nano-CaCO3_33 is:

- relatively inexpensive,
- industrially scalable,
- environmentally benign,
- easy to surface-treat,
- compatible with PVC processing,
- available in multiple morphologies.

These features make it especially suitable for large-volume applications where cost and performance must be balanced carefully.

3.2 Surface Chemistry

The surface of CaCO3_33 can be modified with fatty acids, stearates, silanes, or other coupling agents. Surface treatment improves dispersion in plasticizer-rich systems, reduces agglomeration, and enhances compatibility with polymeric matrices. In plastisols, this is especially important because untreated nanoparticles may cluster and produce uncontrolled viscosity increase.

3.3 Morphology Control

Nano-CaCO3_33 may be engineered as cubic, rhombohedral, scalenohedral, or near-spherical particles. Morphology affects packing efficiency, interparticle friction, and interaction with PVC chains and plasticizers. Spherical or quasi-spherical particles are often preferred for rheological modification because they can behave like micro-rollers under shear.

4. Mechanisms of Rheological Improvement

4.1 Increase in Effective Volume Fraction

Even a small amount of nano-CaCO3_33 can significantly increase the effective solid volume fraction in a plastisol. Because nanoparticles have high surface area, they occupy more interfacial space than their mass fraction suggests. This leads to stronger hydrodynamic interactions and a higher apparent viscosity at low shear rates.

4.2 Formation of Weak Physical Networks

At rest, nanoparticles may bridge neighboring PVC particles or associate through van der Waals attractions and adsorbed plasticizer layers. These interactions form a weak, reversible network. Such a network increases yield stress and helps prevent sedimentation. Under shear, the network collapses, allowing the material to flow.

4.3 Plasticizer Redistribution

Nano-CaCO3_33 can influence the distribution of plasticizer within the suspension. By adsorbing part of the plasticizer or altering local concentration gradients, it changes the solvating environment of PVC particles. This can either increase or decrease viscosity depending on loading, particle treatment, and formulation details. In optimized systems, the net effect is often beneficial because the suspension becomes structurally more stable without becoming unworkable.

4.4 Ball-Bearing or Lubrication-Like Effect

At high shear rates, spherical calcium carbonate nanoparticles may reduce interparticle friction and act similarly to microscopic rolling elements. This does not necessarily reduce viscosity in all cases, but it can improve flow uniformity and prevent excessive resistance during application. This effect helps explain why some nano-CaCO3_33-modified plastisols remain processable despite having higher low-shear viscosity.

4.5 Suppression of Ageing

A well-dispersed nanofiller can reduce the rate of viscosity ageing by stabilizing the physical structure of the plastisol. It may slow down particle rearrangement and make the system less sensitive to time-dependent fluctuations. This is especially important for industrial storage and repeatability.

5. Detailed Discussion of Key Parameters

5.1 Particle Size

Particle size is one of the most important variables. Smaller particles provide greater surface area and stronger interfacial effects, but they also have a greater tendency to agglomerate. Therefore, the smallest particle size is not always the best. An optimum size range must be selected based on the final rheological target.

5.2 Surface Treatment

Surface treatment is often the difference between a beneficial nanofiller and a problematic one. Hydrophobic modification improves compatibility with plasticizer media and prevents the formation of hard agglomerates. Properly treated nano-CaCO3_33 generally yields better reproducibility, lower sedimentation risk, and more controllable flow behavior.

5.3 Loading Level

The filler concentration determines whether the system is lightly modified or overfilled. At low loading, nano-CaCO3_33 typically improves yield stress and anti-sagging behavior without severely reducing flowability. At high loading, excessive viscosity and poor application may occur. Thus, optimum loading is application-specific.

5.4 Dispersion Quality

No nanofiller can perform well if it is not dispersed properly. High-shear mixing, suitable dispersants, and controlled processing conditions are required to obtain a stable suspension. In many cases, dispersion quality has a stronger influence on rheology than the nominal filler content itself.

6. Comparative Analysis

6.1 Nano-CaCO3_33 vs. Unfilled Plastisol

Compared with unfilled plastisol, nano-CaCO3_33-modified systems generally show:

- higher yield stress,

- better anti-sag performance,
- improved suspension stability,
- more pronounced shear-thinning,
- reduced viscosity drift in optimized formulations.

However, the trade-off is that excessively high loading can make mixing and application more difficult.

6.2 Nano-CaCO3_33 vs. Micro-CaCO3_33

Micro-sized calcium carbonate is traditionally used as a low-cost filler and extender, but it typically provides weaker rheological control than nano-CaCO3_33.

Advantages of nano-CaCO3_33 over micro-CaCO3_33:

- higher interfacial area,
- stronger rheological modification at lower dosage,
- improved yield stress development,
- better control over thixotropy.

Advantages of micro-CaCO3_33:

- lower cost per unit mass,
- easier dispersion in some formulations,
- less tendency to raise viscosity sharply.

In practice, a hybrid blend of micro and nano-CaCO3_33 may be optimal when cost and performance must both be considered.

6.3 Nano-CaCO3_33 vs. Nanosilica

Nanosilica is a powerful rheology modifier and often provides stronger thickening than nano-CaCO3_33. However, it is generally more expensive and may produce overly high viscosity if not carefully controlled.

Nanosilica:

- stronger network formation,
- stronger viscosity increase,
- more pronounced thixotropy,
- higher cost.

Nano-CaCO3_33:

- milder and more balanced rheological effect,
- lower cost,
- better industrial scalability,
- better suited to high-volume plastisol products.

6.4 Nano-CaCO3_33 vs. Nanoclay

Nanoclays are effective for rheology control and barrier enhancement, but they may require more complex surface modification and dispersion protocols. Nano-CaCO3_33 is usually simpler to implement in existing PVC formulations.

Nanoclay:

- strong structure-building,
- useful for barrier and anti-sag performance,
- but higher sensitivity to dispersion quality.

Nano-CaCO3_33:

- easier integration,
- lower complexity,
- more predictable cost-performance balance.

7. Industrial Implications

From an industrial perspective, nano-calcium carbonate offers a realistic compromise between performance enhancement and economic feasibility. This is especially important in large-scale sectors such as automotive coatings, synthetic leather, and flooring, where materials are consumed in large volumes and minor cost changes can significantly affect profitability.

In coating applications, the most valuable benefit is not just higher viscosity, but the ability to tune flow behavior precisely. A plastisol must spread smoothly, stay in place, and fuse into a defect-free layer. Nano-CaCO3_33 supports this balance by increasing low-shear body while allowing adequate flow under application shear.

In addition, improved storage stability can reduce material waste, rework, and batch inconsistency. These practical advantages often matter more than the absolute value of viscosity or yield stress.

8. Future Research Directions

Although the current understanding of nano-CaCO3_33 in PVC plastisols is strong, several areas remain open for further study:

1. **Hybrid nanofiller systems**

   Combining nano-CaCO3_33 with nanosilica, nanoclay, or graphene derivatives may create synergistic rheological effects.

2. **Bio-based plasticizers**

   The interaction between nano-CaCO3_33 and environmentally friendly plasticizers should be explored more deeply.

3. **Advanced rheological modeling**

   Multiscale simulation could help connect particle interactions with macroscopic flow behavior.

4. **Long-term stability studies**

   Ageing, storage, and thermal cycling behavior require further investigation.

5. **Application-specific optimization**

   Different end uses require different rheological targets, so formulation should be tailored accordingly.

9. Conclusion

Calcium-based nanocomposites, especially nano-calcium carbonate, represent a highly practical and effective approach for improving the rheological properties of PVC plastisols. Their influence is governed by a combination of interfacial interactions, network formation, particle morphology, dispersion quality, and surface treatment. Compared with conventional fillers, nano-CaCO3_33 provides a superior balance of yield stress enhancement, thixotropy, processability, and cost-efficiency. Compared with other nanofillers such as nanosilica and nanoclay, it is often the most industrially attractive option when large-scale adoption is required.

The comparative analysis confirms that nano-CaCO3_33 is not merely a filler, but a functional rheology modifier capable of transforming plastisol behavior in a controlled and application-oriented manner. Future work should focus on hybrid systems, bio-compatible additives, and predictive modeling to further expand its industrial potential.

Comparative Evaluation of Different Rheology Modifiers in PVC Plastisols

Rheology modifier	Main rheological effect	Advantages	Limitations	Industrial suitability
Unfilled PVC plastisol	Baseline viscosity; limited yield stress; moderate shear-thinning depending on PVC resin and plasticizer type	Simple formulation; predictable processing; no filler-dispersion issue	Lower anti-sag resistance; possible sedimentation or viscosity drift during storage; limited control over thixotropy	Suitable for simple coating, dipping, and molding applications where advanced flow control is not required
MicroCaCO3_33	Moderate viscosity increase; weak improvement in yield stress; limited network formation	Low cost; widely available; easy to incorporate; useful as an extender filler	Lower surface area than nano-CaCO3_33; weaker rheological modification; may require high loading to produce significant effect	Highly suitable for cost-sensitive applications where filler economy is more important than precise rheology control
NanoCaCO3_33	Increased low-shear viscosity; improved yield stress; stronger shear-thinning; enhanced anti-sag behavior; improved suspension stability when well dispersed	High surface area; effective at lower loading; tunable surface chemistry; good cost-performance balance; industrial scalability	Agglomeration risk; viscosity may become excessive at high loading; performance depends strongly on surface treatment and dispersion quality	Very suitable for automotive coatings, synthetic leather, sealants, flooring, and plastisol systems requiring balanced processability and structural stability
Surface-treated nano-CaCO3_33	More controlled viscosity increase;	Better compatibility with plasticizer phase;	Additional treatment cost; performance depends on modifier chemistry;	Highly suitable for high-performance

	improved thixotropy; better storage stability; reduced uncontrolled agglomeration	improved dispersion; lower sedimentation tendency; more reproducible rheological behavior	excessive hydrophobic treatment may weaken useful particle interactions	industrial plastisols requiring consistent viscosity, long shelf life, and reliable application behavior
Nanosilica	Strong increase in viscosity and yield stress; pronounced thixotropic network formation	Very effective thickener; excellent anti-sag behavior; strong structure-building capability	Higher cost; difficult dispersion; risk of overly high viscosity; may reduce processability if overdosed	Suitable for specialty plastisols where strong thixotropy and anti-sag performance are more important than cost
Nanoclay	Strong shear-thinning; improved yield stress; possible barrier enhancement; network formation through platelet interactions	Effective at low loading; may improve barrier and mechanical properties; useful for layered reinforcement	Requires careful exfoliation/intercalation; high sensitivity to dispersion conditions; may cause batch variability	Suitable for advanced formulations requiring rheology control plus barrier or reinforcement benefits
Hybrid nano-CaCO3_33 /nanosilica system	Balanced viscosity increase with enhanced yield stress and thixotropy	Potential synergy between low-cost CaCO3_33 and strong structure-building silica; tunable performance	More complex formulation; possible filler-filler incompatibility; requires optimization	Promising for premium coatings, sealants, and high-stability plastisols
Hybrid micro/nano-CaCO3_33 system	Improved packing, moderate viscosity control, and better cost-performance balance	Combines low cost of micro-CaCO3_33 with rheological efficiency of nano-CaCO3_33; scalable	Rheological response may be less strong than pure nanofiller systems; dispersion remains important	Highly practical for large-volume industrial plastisol products

Interpretation of the Comparative Results

The comparison indicates that **nano-CaCO3_33 occupies an intermediate but highly valuable position** among plastisol rheology modifiers. It is more effective than conventional micro-

CaCO3_33 because of its larger specific surface area and stronger interfacial interactions. At the same time, it is generally more economical and easier to industrialize than nanosilica or nanoclay.

Micro-CaCO3_33 mainly acts as an extender filler. Its contribution to rheology is usually limited unless it is added at relatively high loading levels. In contrast, nano-CaCO3_33 can significantly modify low-shear viscosity, yield stress, and thixotropic recovery even at lower concentrations, provided that the particles are well dispersed.

Nanosilica typically produces stronger thickening and network formation than nano-CaCO3_33. However, this strong effect can become a disadvantage when the plastisol must remain pumpable, spreadable, or sprayable. For this reason, nanosilica is more suitable for specialty formulations where high anti-sag resistance is required, whereas nano-CaCO3_33 is more appropriate for balanced industrial formulations.

Nanoclay offers additional benefits such as barrier enhancement and mechanical reinforcement, but its effectiveness depends heavily on exfoliation and dispersion. This makes it more technically demanding than nano-CaCO3_33. Therefore, from an industrial standpoint, nano-CaCO3_33 provides one of the best combinations of cost, processability, rheological control, and formulation flexibility.

Hybrid systems are particularly promising. A micro/nano-CaCO3_33 blend can reduce formulation cost while preserving part of the rheological benefit of nanoparticles. Similarly, a nano-CaCO3_33/nanosilica system may combine the economic advantage of calcium carbonate with the strong structure-building ability of silica. However, these systems require careful optimization because filler-filler interactions may alter viscosity, sedimentation behavior, and fusion performance.

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