Orclever Proceedings of Research and Development
https://doi.org/10.56038/oprd.v5i1.577
OR CLEVER Science & Research Group

Conference Article

Enhancement of Oil-Resistance in Acrylic Dispersions

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Received 28 October 2024
Received in revised form 14 December 2024
In final form 24 December 2024

4th International Conference on Design, Research and Development
(RDCONF 2024)
December 19 - 20, 2024

Reference: Berksun, E., Alptoğa, Öz., Önen, A., & Akarsu Dülgar, C. (2024). Enhancement of oil-resistance in acrylic dispersions. Orclever Proceedings of Research and Development, 5(1), 451-458.

Abstract

Acrylic dispersions are favoured due to their cost-effectiveness, environmental friendliness, and versatile chemical properties. Given the inherent advantages of acrylic dispersions, their application as packaging lamination adhesives necessitates improved chemical resistance, especially oil resistance. To address this need, we systematically explored the incorporation of oil repellent additives into acrylic formulations. By analysing the compatibility of these additives and their impact on oil resistance performance, our research aims to provide insights into optimizing acrylic adhesives for more effective use in packaging applications.

Keywords: *Acrylic, packaging adhesive, oil- resistance, delamination*

1. Introduction

Packaging adhesives used in various applications require water resistance, oil resistance, heat resistance, flexibility, low migration, and a good adhesion-cohesion balance on

https://doi.org/10.56038/oprd.v5i1.577

different substrates such as PE, kraft paper, aluminium, PP, OPP, CP, CPP, polyamide, and others [1]. The oil resistance of packaging adhesives is a critical property for ensuring the durability and functionality of high-performance materials used in food, consumer goods, and industrial packaging. Moreover, the structure of oil can be found in different forms, such as grease, fuels or food-grade oils. Therefore, they play a vital role in enhancing the longevity and reliability of products, from food packaging, consumable products, automotive gaskets to industrial seals and protective coatings [2], [3].

In resin materials, oil-resistant dispersions like latex are used in various applications due to their ability to form flexible, durable films with excellent resistance to oils and greases. Some of the most referred dispersions are nitrile butadiene rubber (NBR), styrene butadiene rubber (SBR), chloroprene rubber (CR), polyurethane and acrylics [4].

While traditional oil-resistant dispersions such as nitrile and chloroprene latexes have been widely used for their proven performance, the evolving needs of industries call for more versatile and environmentally friendly solutions. Acrylic dispersions have emerged as a compelling alternative, combining excellent oil resistance with the added advantages of customization, durability, and eco-friendly formulation potential. Their compatibility with various substrates and ability to be formulated for specific applications make them highly adaptable for modern manufacturing processes.

The key parameters behind a successful oil-resistance mechanism relieve two principles. Oil resistance is primarily influenced by the polymer's ability to repel non-polar oil molecules, and the presence of polar groups significantly enhances this property through the incompatible chemical structures with the non-polar molecules. This intrinsic incompatibility between the polar and non-polar groups minimizes the penetration and swelling caused by oils, thereby it improves the oil resistance. Moreover, polar groups such as hydroxyl (-OH), carboxyl (-COOH), and nitrile (-CN) form hydrogen bonds or ionic interactions within the polymer matrix [5], [6].

Based on this approach, we conducted a study based on the aforementioned mechanism and designed systems using additives containing polar groups. To enhance oil resistance in these systems, we incorporated materials containing ZnO, isocyanate, fluorine [7], and silicon groups [8], [9] and analyzed the resulting dispersions to observe their effects.

Zinc oxide (ZnO) is widely used as an additive in oil-resistant formulations due to its unique properties that enhance the performance of polymeric materials in oil-exposed environments. Its role extends beyond simple reinforcement to include contributions to the chemical and physical properties of the material. As an additive, ZnO particles enhance the density of the polymer matrix, reducing the free volume available for oil

https://doi.org/10.56038/oprd.v5i1.577

molecules to penetrate. On the other hand, ZnO interacts with carboxyl or hydroxyl groups in polymers, forming ionic bonds that reinforce the matrix [10], [11].

Isocyanates are reactive chemical compounds that play a potential role in enhancing oil resistance. Their high reactivity with hydroxyl groups and other active hydrogens enables the formation of highly crosslinked, dense polymer networks that provide exceptional resistance to oils and hydrocarbons. High crosslink density minimizes the free volume in the polymer matrix, making it difficult for oil molecules to penetrate or diffuse [12], [13].

Advances in the development of oil-resistant polymers continue to expand their potential applications, improving efficiency and sustainability in various sectors.

In this study, we made systematic research focusing on the incorporation of most abundant oil-repellent additives into acrylic dispersion to observe their application performance as laminated surfaces.

2. Materials and Methods

Acrylic dispersion is provided by Organik Kimya. Isocyanate, ZnO, fluorine and silicone additives were all commercial grades. Chemical compositions cannot be revealed for proprietary reasons.

Solid content was measured by drying the polymer films at 150 °C for 20 min after filtered from 60-micron filter. Viscosity was measured by Brookfield viscosimeter under room conditions by LVT 3/60 (ISO 3219). pH of polymers was measured at room temperature according to ISO 976, by calibrated pH meter. Wet tack and viscosity-shear rate profiles were measured with TA Rheometer. The contact angle and SFE Polar energy values were measured by using a sessile drop method with Krüss Drop Shape Analyzer . The volume of drops was 1 μl, and the images of the droplet were taken with a CCD camera.

3. Results

In this study, five samples were evaluated for their oil resistance efficiency as lamination adhesives as detailly shown in Table 1. All samples exhibited solid content in a narrow range of 45-46%, pH levels were stable around 7.0-9.0, and final viscosities of the samples were suitable for application.

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Table 1: Sample formulations and principal properties

Sample	Polymer + Additive	Polymer (wt%)	Additive (wt%)	pH	Solid (%)	Viscosity(cps)
Sample 1	Neat Acrylic Resin	100	0	7.9	45.0%	500
Sample 2	Acrylic Resin + Isocyanate	98	2	7.5	46.0%	750
Sample 3	Acrylic Resin + Fluorine Moiety	98	2	7.9	45.3%	690
Sample 4	Acrylic Resin + Silicone Moiety	98	2	7.9	45.5%	370
Sample 5	Acrylic Resin + Zinc Oxide	98	2	8	Unstable Dispersion	

Isocyanates are highly active compounds capable to bond via their -NCO end groups. Upon addition of isocyanate into acrylic dispersion, a spontaneous viscosity increment was observed. This thickening behavior is possibly due to the formation of crosslinking points as it was desired for enhancement of oil resistance. Fluorine has a strong hydrophobic and oleophobic nature arises from its high electronegativity and polarity. On the other hand, C-F bonds are so strong that they form very stable networks and chemicals like non-polar oil structures face a barrier and cannot penetrate the network. Silicone moiety decreased the viscosity mainly due to its low surface tension and reducing effect of internal friction between the particles[14]. ZnO is an inorganic additive, originally insoluble in water. Nevertheless, ZnO nanoparticles can be dispersed in organic systems and water with specific modifications [10]. Despite surface modifications, ZnO nanoparticles couldn't form a stable and homogenous medium in our system, agglomerations couldn't be completely avoided. Therefore, Sample 5 is not chosen for further characterizations and application tests.

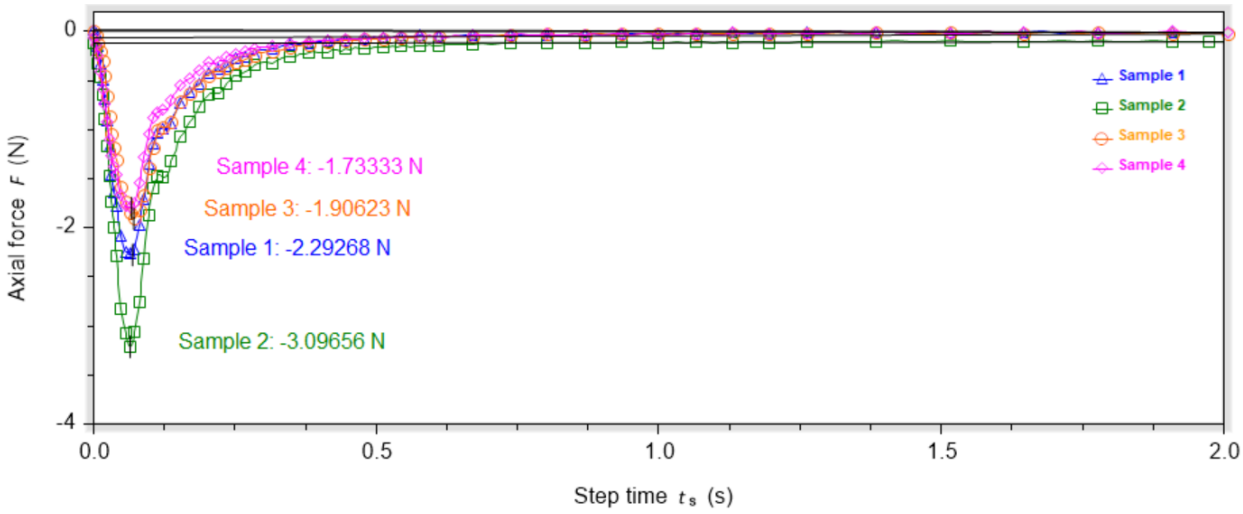

Figure 1: Wet-Tack performances of the dispersions.

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Wet-tacks properties have been evaluated to predict the first tack efficiencies and lamination performance of the present samples. The highest wet tack was obtained in Sample 2, containing isocyanate moiety. Since isocyanate are intrinsically show high adhesion profile, this result is expected. Sample 2 and Sample 3 exhibited lower wet tack compared to Sample 1, our neat acrylic dispersion.

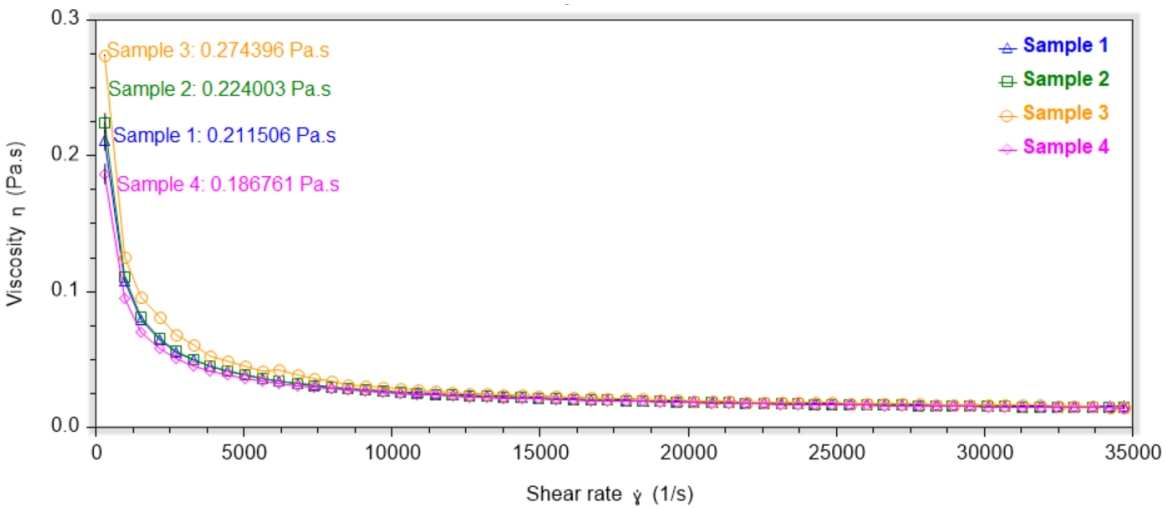

Figure 2: Viscosity-Shear Rate profiles of dispersions.

The viscosity-shear rate graphs are presented in the Figure 2. Sample 2 and Sample 3 showed initially higher viscosity than other samples, in accordance with the viscosity data presented in Table 1. All the samples exhibited shear-thinning properties and they were stable up to 35000 1/s shear rate, which means that they are easy-to apply materials over different machine speeds.

Table 2: Contact Angle and Polar Surface Free Energies

Sample	CA ([º] /Diiodo Methane)	CA ([º] /Water)	SFE Polar (mN/m)
Sample 1	52(±2.86)	80(±6.93)	4.87 ±2.71
Sample 2	55(±7.75)	72(±1.41)	8.67 ±1.68
Sample 3	60 (±2.29)	81(±4.31)	5.73 ±1.86
Sample 4	56 (±4.66)	78(±2.73)	6.03 ±1.41

In packaging applications, oil resistance property should be accompanied with an optimum level of water repellency. Dominance of only of them is not sufficient for a complete performance.

https://doi.org/10.56038/oprd.v5i1.577

Therefore, hydrophobicity should be continuously checked. Surface free polar energy give more information about the accumulation of polar groups on the surface; therefore, it gives idea of oil repellency of a surface. As it is reported in Table 2, while the highest SFE polar energy is observed in Sample 1, with isocyanate; the highest contact angle against diiodo methane solution was obtained in Sample 3, with fluorine moieties.

Subsequently, in order to observe the efficiency of oil resistance, hard-to bond surfaces with different surface energies were laminated using our samples. The thickness of the laminates were 0.5 gsm. The laminated samples were left in an oil environment for an extended period to simulate their delamination behavior as packaging adhesive.

Table 3: Oil performance of laminated surfaces

Sample		Comparison Of Delamination Force
Sample 1	Neat Acrylic Resin	+
Sample 2	Acrylic Resin + Isocyanate	++
Sample 3	Acrylic Resin + Fluorine Moiety	++++
Sample 4	Acrylic Resin + Silicone Moiety	+++

**Poor: +; Low: ++; Medium: +++; High: ++++*

Table 3 shows the delamination force comparison after aging test in oil. Although isocyanate has showed higher values in terms of wet-tack and high polar surface energy, it couldn't show the expected oil performance on the laminated surfaces. The reason of this weak lamination oil performance is probably due to the isocyanate reaction with water, producing side products such as amines. This side reactions form a non-uniform spreading over the laminated surface and decrease the delamination force. In the Sample 3, fluorine moiety addition showed the higher contact angle, and the best oil performance is achieved via this strategy. Silicone moiety addition also improved the oil resistance, yet it is lower than fluorine moiety.

4. Discussion and Conclusion

Acrylic dispersions are highly versatile materials that can be modified with additives to enhance specific properties, including oil resistance. The incorporation of polar groups significantly influences the oil resistance behavior of the films and laminated surfaces. Among these, the flour moiety exhibited the highest contact angle against diiodomethane and demonstrated the best oil resistance performance on laminated surfaces. However, due to restrictions on PFAS (per- and polyfluoroalkyl substances), this approach may not

https://doi.org/10.56038/oprd.v5i1.577

be viable for future packaging applications. Consequently, the development of alternative strategies to enhance oil resistance, without relying on such additives, will be crucial for advancing acrylic dispersions in packaging applications.

5. Acknowledge

The authors would like to express their gratitude to Organik Kimya San. ve Tic. A.Ş. and technical teams for their technical and financial support.

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