# Effects of Internal Emulsifier Structure and Concentration on Dispersion Properties and Film Performance of Anionic Waterborne Polyurethanes

*Ingi Hong[1], Md Morshedur Rahman[1], Jinwon Cho[2], Sung Hyun Kwon[1], Hyunwoo Byun[1], Seung Soon Jang[2], Joonseok Koh[1]*

*[1] Department of Materials Science and Engineering, Konkuk University, Seoul 05029, Republic of Korea*
*[2] School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245, United States*

*dlsrl3760@konkuk.ac.kr*

Anionic waterborne polyurethanes (WPUs) are amphiphilic polyelectrolyte dispersions in which charged ionic moieties, introduced via internal emulsifiers, drive the formation of colloidal particles with core-shell architectures. The hydrophobic polyurethane segments form the particle core, while ionized carboxylate groups at the particle surface generate electrical double layers that stabilize the dispersion electrosterically. This study investigates the effects of two widely used anionic internal emulsifiers, dimethylolpropionic acid (DMPA) and dimethylolbutanoic acid (DMBA), on the dispersibility and physicochemical properties of WPUs designed for breathable membrane applications, through a combination of experimental characterization and computational simulation. DMPA and DMBA differ in alkyl chain length and hydrophilicity, with log P values of −0.5 and −0.09, respectively. Their concentrations were varied from 0.065 to 0.105 mol. Dynamic light scattering and zeta potential measurements show that increasing emulsifier concentration reduces particle size from 1547 to 174 nm for DMBA and from 3949 to 242 nm for DMPA, accompanied by enhanced electrostatic stabilization. DMBA yields smaller, more narrowly distributed particles at lower ionic content, attributed to its greater miscibility with the isocyanate component and more efficient ion distribution at the particle interface. Dissipative particle dynamics (DPD) simulations were performed using Flory–Huggins χ-parameters derived from DFT-based molecular dynamics calculations. Pair correlation function analysis shows that DMPA, with a lower χ-parameter with water (0.34 vs. 0.40 for DMBA), promotes more uniform polymer–water interfacial mixing, whereas DMBA induces larger water cluster formation consistent with its hydrophobic character. The experimental and simulation results are in good agreement, providing a consistent picture of how emulsifier molecular structure influences polyelectrolyte interfacial organization and colloidal stability in WPU dispersions.

**Keywords:**
waterborne polyurethanes, internal emulsifiers, breathable membranes, dissipative particle dynamics simulation

**References:**

[1] Yin, L.; Zhang, B.; Tian, M.; Ning, N.; Wang, W., Prog. Org. Coat. 2024, 186, No. 108095.
[2] Oh, S.; Oh, N.; Rahman, M. M.; Youm, K.; Kim, M.; Kumar, S.; Koh, J. Fibers Polym. 2023, 24, 1741–1758.

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