

DEVELOPMENT OF A COARSE-GRAINED FORCEFIELD FOR POLYMER CLAY NANOCOMPOSITES

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DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI

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by

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Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy

to



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*Dedicated to
my Parents*

Certificate

This is to certify that the thesis entitled, “**Development of a coarse-grained forcefield for polymer clay**”, being submitted by **Mr. Parvez Khan** to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy** in Chemical engineering, is a record of bonafide research work carried out by him. Mr. Parvez Khan has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard. The results contained in this dissertation have not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

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Abstract

Polymer nanocomposites consisting of highly anisotropic layered-silicate (clay) nanoparticles are an important class of materials with tunable properties. These anisotropic nanoparticles provide a large polymer-particle interfacial area, and therefore, show significant impact on mechanical, structural, and barrier properties of polymer-clay nanocomposites (PCNC) even at low loadings. A large number of material and process parameters, and non-monotonic dependence of target properties on these parameters makes the development of PCNCs for specific applications a challenging task. Molecular simulations provide a means to quickly sample a large parameter space to probe dependence of nanoscale structure of the composite material on parameters such as polymer – clay interfacial interactions and clay polarity. However, two key issues that limit the application of atomistic simulation to this system are long relaxation times associated with polymer dynamics and the requirement of large system size for anisotropic particles. To this end, we have developed an accurate, self-consistent coarsegrained (CG) model of a polymer-clay system consisting of organically modified montmorillonite nanoclay as the nanoparticle. The CG model is developed in accordance with the MARTINI forcefield for polymers and lipids that has been shown to accurately capture the polar-apolar character of individual sub-units. We have used mechanical properties and cleavage free energy of clay particle to respectively parameterize bonded and nonbonded interaction parameters for an organically modified montmorillonite (oMMT) clay particle where intergallery Na^+ ions are replaced by tetramethylammonium (TMA) ions. The mechanical properties were determined from the slope of stress-strain curve and cleavage free energy was determined by allowing for full surface reconstruction corresponding to a slow equilibrium cleavage process. Individual dispersive and polar contributions to oMMT cleavage energy were used for determination of appropriate MARTINI bead types for CG oMMT sheet.

The self-consistency of developed MARTINI FF parameters for TMA-MMT – polymer system was verified by comparing estimates for select structural, thermodynamic, and dynamic properties obtained in all-atomistic simulations with that obtained in coarsegrained simulations. We have calculated all properties separately in near-clay and far-clay regions, as the former is expected to provide a stringent check for suitability of developed CG parameters for modeling the clay-polymer system. We have determined the influence of clay particle on properties of three polymer melts (polyethylene, polypropylene, and polystyrene) at two temperatures to establish transferability of the developed parameters. Overall, we have shown that developed CG parameters give approximately 90 times speed-up in simulations and provide a good quantitative agreement for structural, thermodynamic, and dynamic properties calculated from the atomistic approach. We also report some interesting insights into the role of clay-polymer interactions on structure-property relationships in polymer-clay nanocomposite systems. Finally, we have used long timescale CG-Martini simulations to determine partitioning and clustering of PE-b-PEO compatibilizer in a TMA-MMT – polyethylene nanocomposite. We have also determined the effect of compatibilizer and clay exfoliation on matrix polymer's structural, thermodynamic, and dynamic properties.

सारांश

अत्यधिक अनीसोट्रोपिक स्तरित-सिलिकेट (मिट्टी) नैनोपार्टिकल्स से युक्त पॉलिमर नैनोकम्पोजिट ट्यून करने योग्य गुणों वाली सामग्री का एक महत्वपूर्ण वर्ग है। ये अनिसोट्रोपिक नैनोपार्टिकल्स एक बड़े बहुलक-कण इंटरफेशियल क्षेत्र प्रदान करते हैं, और इसलिए, कम लोडिंग पर भी पॉलिमर-मिट्टी नैनोकंपोजिट (पीसीएनसी) के यांत्रिक, संरचनात्मक और बाधा गुणों पर महत्वपूर्ण प्रभाव दिखाते हैं। बड़ी संख्या में सामग्री और प्रक्रिया पैरामीटर और इन मापदंडों पर लक्ष्य गुणों की गैर-मोनोटोनिक निर्भरता विशिष्ट अनुप्रयोगों के लिए पीसीएनसी के विकास को एक चुनौतीपूर्ण कार्य बनाती है। आणविक सिमुलेशन, बहुलक-मिट्टी इंटरफ़ेसअल इंटरैक्शन और क्ले पोलरिटी जैसे मापदंडों पर समग्र सामग्री की नैनो-स्तर संरचना की निर्भरता की जांच करने के लिए एक बड़े पैरामीटर स्थान को जल्दी से नमूना करने का साधन प्रदान करता है। हालांकि, दो प्रमुख मुद्दे जो इस प्रणाली में परमाणु सिमुलेशन के आवेदन को सीमित करते हैं, बहुलक डायनामिक्स से जुड़े लंबे विश्राम समय और अनिसोट्रोपिक कणों के लिए बड़े सिस्टम आकार की आवश्यकता है। यह अंत करने के लिए, हमने एक बहुलक-मिट्टी प्रणाली का एक सटीक, आत्म-सुसंगत मोटे तौर पर (सीजी) मॉडल विकसित किया है जिसमें नैनोकण के रूप में व्यवस्थित रूप से संशोधित मॉन्टमोरोलाइट नैनोकल शामिल है। सीजी मॉडल को पॉलिमर और लिपिड के लिए मार्टिनी फोर्सफील्ड के अनुसार विकसित किया गया है जिसे व्यक्तिगत उप-इकाइयों के ध्रुवीय-एपोलर चरित्र को सटीक रूप से पकड़ने के लिए दिखाया गया है। हमने मिट्टी के कण के यांत्रिक गुणों और दरार मुक्त ऊर्जा का उपयोग क्रमशः एक व्यवस्थित रूप से संशोधित मॉन्टमोरोलाइट (ओएमएमटी) मिट्टी के कण के लिए बंधुआ और गैर-अंतर्क्रिया इंटरैक्शन मापदंडों को निर्धारित करने के लिए किया है, जहां अंतरग्रहीय Na^+ आयनों को टेट्रामिथाइल अमोनियम (TMA) आयनों से बदल दिया जाता है। यांत्रिक गुणों को तनाव-तनाव वक्र के ढलान से निर्धारित किया गया था और एक धीमी गति से संतुलन प्रक्रिया के अनुरूप पूर्ण सतह पुनर्निर्माण की अनुमति देकर मुक्त ऊर्जा का निर्धारण किया गया था। ओएमएमटी दरार ऊर्जा के लिए व्यक्तिगत फैलाव और ध्रुवीय योगदान सीजी ओएमएमटी शीट के लिए उपयुक्त मार्टिनी मनका प्रकार के निर्धारण के लिए उपयोग किया गया था। टीएमए-एमएमटी के लिए विकसित मार्टिफ़ मापदंडों की स्व-संगति - बहुलक प्रणाली को चुनिंदा संरचनात्मक, थर्मोडायनामिक और गतिशील गुणों के लिए अनुमानों की तुलना करके सत्यापित किया गया था, जो सभी परमाणु-परमाणुओं में सह-संयोजी सिमुलेशन में प्राप्त किए गए थे। हमने निकट-मिट्टी और दूर-मिट्टी क्षेत्रों में अलग-अलग सभी गुणों की गणना की है, क्योंकि पूर्व में मिट्टी-बहुलक प्रणाली के मॉडलिंग के लिए विकसित सीजी मापदंडों की

उपयुक्तता के लिए एक कड़े चेक प्रदान करने की उम्मीद है। हमने विकसित मापदंडों की हस्तांतरणीयता स्थापित करने के लिए दो तापमान पर तीन बहुलक मेल्ट्स (पॉलीइथाइलीन, पॉलीप्रोपाइलीन और पॉलीस्टायरीन) के गुणों पर मिट्टी के कण के प्रभाव को निर्धारित किया है। कुल मिलाकर, हमने दिखाया है कि विकसित सीजी पैरामीटर सिमुलेशन में लगभग 90 गुना गति प्रदान करते हैं और परमाणु, दृष्टिकोण से गणना किए गए संरचनात्मक, थर्मोडायनामिक और गतिशील गुणों के लिए एक अच्छा मात्रात्मक समझौता प्रदान करते हैं। हम बहुलक-मिट्टी के नैनोकम्पोसाइट सिस्टम में संरचना-संपत्ति संबंधों पर मिट्टी-बहुलक बातचीत की भूमिका में कुछ दिलचस्प अंतर्दृष्टि की रिपोर्ट करते हैं। अंत में, हमने टीएमए-एमएमटी - पॉलीइथिलीन नैनोकम्पोसिट में पीई-बी-पीईओ कॉम्पिटिबलाइजर के विभाजन और क्लस्टरिंग को निर्धारित करने के लिए लंबे समय के सीजी-मार्टिनी सिमुलेशन का उपयोग किया है। हमने मैट्रिक्स पॉलीमर के संरचनात्मक, थर्मोडायनामिक और डायनेमिक गुणों पर कंपेटिबिल और क्ले एक्सफोलिएशन के प्रभाव को भी निर्धारित किया है।

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