



PPS Newsletter

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November 2011 Information to Polymer Processing Society Members

PPS-2011 in Kish Island, Iran, another Solid Success

The PPS-2011 regional meeting for Asia-Australasia of the Polymer Processing Society (<http://www.pps-2011.com>) took place in Kish Island, Iran, in November 15-17, 2011. Kish Island is a special free-zone island, for which no visas are needed and frequent flights from Dubai were available. The meeting was held for the first time in Iran, which boasts a strong Polymer Processing Community with many PPS members. The Organizer, Prof. Nazockdast, and his superb team made sure that the Meeting was a solid success, both in scientific and organizational terms. Around 300 registered participants (mainly from Iran with some 30 people from abroad) made this meeting another happy occasion for our Society. The venue was the state-of-the-art Kish International Conference Center, a world-class congress facility. There were about 400 presentations, with plenary (5), keynote (16), and oral (235) lectures from leading scientists and engineers, while 150 of these presentations were posters. The subtropical site of Kish Island, with the sunny weather and warm waters of the Persian Gulf, made this an unforgettable trip for the PPS participants. The banquet featured local entertainment from southern Iran, including Kish Island. PPS-2011 was another manifestation of a truly international scientific society, which encompasses many different people and different cultures, which share a common goal, the advancement of polymer processing.



Prof. Nazockdast, PPS-2011 Organizer, during the Banquet where sincere appreciation and many thanks were extended to PPS for giving the opportunity to hold PPS-2011 in Iran for the first time.



The venue for PPS-2011 was the Kish International Convention Center, a state-of-the-art venue for International Conferences.



Prof. Saha (ex-president of PPS) introducing the Plenary Lecture on November 17, 2011.



Entrance to the Dariush Grand Hotel, where International delegates stayed during the PPS-2011 Regional Meeting in Kish Island, Iran.



Part of the banquet celebrations featured fishermen songs from the southern part of Iran including Kish Island.



International representatives from PPS enjoying midday lunch with Iranian delegates during the PPS-2011 meeting.

PPS prepares for its Americas Conference, PPS-2012, in May in Niagara Falls, Canada

The PPS-2012 Americas Conference will take place in Niagara Falls, Canada, in May 21-24, 2012. The venue of the meeting will be the superb Marriot Gateway on the Falls. The meeting is organized by the Department of Mechanical Engineering, University of Toronto, Toronto, Ontario, Canada, under the able direction of Prof. Chul Park. More information can be found at <http://www.pps2012.mie.utoronto.ca>. Prof. Park and his team are working hard in putting together an excellent and stimulating scientific program. All important sessions on polymer processing will be covered in the meeting, while several North American plastics companies will be represented for fruitful collaboration with the Conference attendees.

Niagara Falls is one of the seven natural wonders of the world. Come experience its breathtaking beauty while a fine mist from the falls refreshes you. There are a great number of amazing experiences nearby for you and the whole family. Niagara Falls has a tremendous amount of things to do. Whether it is fine dining, attractions, outlet shopping, taking in a show, or going to the casino, you will never be bored in Niagara Falls. Nearby, experience some of Ontario's award-winning wonderful wines and the quaint charm of Niagara-on-the-Lake. The Falls are part of the border between Canada and USA. The Buffalo-Niagara International Airport (about 40 km away from the venue) is known for cheap flights from several USA cities, which can be combined also with international travel.



Niagara Falls, one of the seven natural wonders of the world, is the site of PPS-2012. The falls are only 120 km away from the Canadian city of Toronto, capital of the province of Ontario.



The Marriot Gateway on the Falls Hotel, venue of the PPS-2012 Americas Conference in Niagara Falls, Ontario, Canada.



Another view of the Niagara Falls, from the Canadian side, where the horseshoe formation of the falls is in full display.

Future Meetings

In its continuing effort to be a truly international society, PPS strives to have meetings every year in different parts of the world. The following list of upcoming meetings is a good indication of these efforts.

2012 Meetings

International Conference (PPS-28), Pattaya, Thailand, December 11-15
Conference Chair: Prof. Suchiva

2013 Meetings

International Conference (PPS-29), Nuremberg, Germany, July 15-19
Conference Chair: Prof. Altstaedt

Asia/Australasia Conference PPS-2013, Bangalore/Kerala, India, December
Conference Chairs: Profs. Ghosh, Misra

2014 Meetings

International Conference (PPS-30), Cleveland/Akron, OH, USA, June
Conference Chairs: Profs. Jana, Maia

Europe/Africa Conference PPS-2014, Tel Aviv, Israel, mid-October
Conference Chair: Prof. Kenig

Other Meetings of Interest to PPS Members

2012

PLASTINDIA 2012

Feb. 2012 | Delhi, INDIA

For information visit: <http://www.plastindia.org>

NPE 2012

01 - 05 Apr 2012 | Orlando, FL, USA

For information visit: <http://www.npe.org>

ANTEC 2012, Society of Plastics Engineers

April 2-4, 2012, Orlando, FL, USA

For information visit: <http://www.4spe.org/conferences-and-events>

PLAST 2012

08 - 12 May 2012 | Milan

For information visit: <http://www.plast12.org>

The XVIth International Congress on Rheology

August 5-10, 2012, Lisbon, PORTUGAL

For information visit: <http://www.rheology-esr.org/ICR2012>

PPS Secretariat Change

Effective January 1, 2012 the PPS Secretariat will move from American Institute of Physics (AIP) to ALLEN PRESS. The new service providers will enable online membership fee payment. All PPS members in good standing will be informed individually about the change and the new enhanced services, in late December or early January. Access to IPP will remain unaffected.

PPS Membership Website

A complete list of all PPS members, their addresses, phone numbers and e-mails, is available at the PPS membership website: <http://pps.mcmaster.ca>.

The user ID is "ppsmember" and the password "ppsmember".

Next Newsletter – May 2012

If you have comments on how to improve this newsletter or want to share some information in the next one, please contact the Newsletter Editor Prof. Evan Mitsoulis at mitsouli@metal.ntua.gr. The next issue of the Newsletter is due in May 2012.

Polymeric Nanocomposites: An Overview from Science to Technology*

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1. Introduction

A decade of research has shown that nanostructured materials have the potential to significantly impact growth at every level of the world economy in the 21st century. This new class of materials is now being introduced in structural applications, such as gas barrier film, flame retardant product, and other load-bearing applications. Of particular interest is recently developed nanocomposites consisting of a polymer and layered silicate because they often exhibit remarkably improved mechanical and various other properties [1] when compared with pure polymer or conventional composites (both micro- and macro-composites).

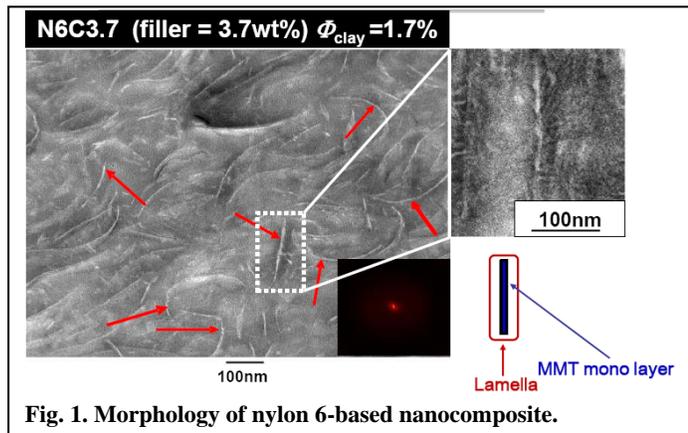
A primary progress in polymer/layered silicate nano-composites, a Nylon 6/layered silicate hybrid [2] reported by Toyota Central Research & Development Co. Inc. (TCRD), was successfully prepared by in-situ polymerization of ϵ -caprolactam in a dispersion of montmorillonite (MMT). The silicate can be dispersed in liquid monomer or a solution of monomer. It has also been possible to melt-mix polymers with layered silicates, avoiding the use of organic solvents. The latter method permits the use of conventional processing techniques such as injection moulding and extrusion. The extensive literatures in nano-composite research are covered in the recent reviews[3-6].

Continued progress in nanoscale controlling, as well as an improved understanding of the physicochemical phenomena at the nanometer scale, have contributed to the rapid development of novel nano-composites. In this news letter we presents current research on polymer/layered filler nanocomposites (PLFNCs) with the primary focus of recent advances from basic science to technology.

2. Morphological features and properties

Polymer/clay nanocomposites (PCNs) and their self-assembly behaviors have recently been approached to produce nanoscale polymeric materials. Additionally, these nanocomposites have been proposed as model systems to examine polymer structure and dynamics in confined environments [7]. In order to understand the processability of these materials (i.e., the final stage of any polymeric material), one must understand the detailed rheological behavior of these materials in the molten state. Understanding the rheological properties of PCN melts is not only important in gaining a fundamental knowledge of the processability but is also helpful in understanding the structure–property relationships in these materials. Although rheological measurement is an indirect probe, it is a well-established approach to probe the interaction between nanofiller and polymer matrix and the time-dependent structure development. In addition, more clear nanoscale and mesoscale structure development of the systems could be provided when combined with X-ray/light-scattering experiments and electron microscopy.

The original mesoscale structure in PCNs consists of randomly oriented exfoliated layers or tactoids of layers. The randomly distributed nanofiller forms a “organo-clay network” structure that is mediated by polymer chains and organo-clay–organo-clay interactions, responsible for the linear viscoelastic response



* Based on a plenary lecture given at the PPS-27 Annual Meeting in Marrakech, Morocco

observed in PCN melts. This mesostructure, which is intrinsically in a disordered metastable state and out of equilibrium, and offers an apt analogy to soft colloidal glasses and gels, was discussed in our lecture [8, 9].

Fig. 1 shows the results of TEM bright field images of nylon6-based nanocomposite (N6C3.7: clay loading = 3.7wt%), in which white entities are the cross section of the discrete lamella and the dark area is the nylon 6 matrix due to the staining with 12 tungstophosphoric acid at 80 °C for 2 h. The black strip inside the white part is an individual (exfoliated) MMT particle. The silicate layers are more homogeneously and finely dispersed. The figure shows larger view permitting the observation of discrete nanolayers. After a close look, a black clay particle inside the lamella is clearly observed. In other words, lamellar growth occurs on both sides of the clay particles, i.e. the clay particles are sandwiched by the formed lamellae. This is a unique observation of lamellar orientation on the clay layers. In the semicrystalline polymer generally the stacked lamellar orientation takes place. It is speculated that the nylon 6 chains are absorbed on the solid clay surface and the first few absorbed layers are immobilised. This loss of mobility translates in their model into a free volume loss (the reduction in free volume by 12–17%) [10].

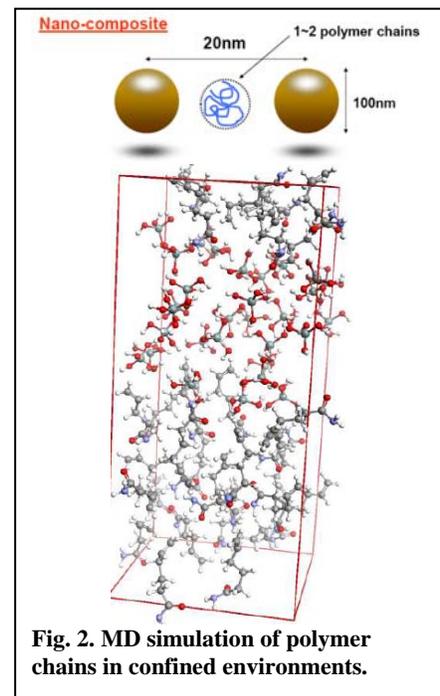
We estimated the form factors obtained from TEM images, i.e. average value of the particle length (L), thickness (D), of the dispersed particles and the correlation length (ξ) between the particles. For N6C3.7, D , L and ξ are in the range of 1–2 nm, 100±10 nm and are 20±5 nm, respectively. The ξ value ($\cong 20$ nm) corresponds to the random coil size of nylon 6 in N6C3.7. The root-mean-square radius of gyration $\langle s^2 \rangle^{1/2}$ is around 9 nm. The chain mobility of the nylon 6 presumably is decreased in translational motion. The study of the dynamics of polymer chains in confined environments by MD simulations (see Fig. 2) is underway in our laboratory. We take into account the quantitative understanding of the mechanical behavior of a single clay layer in a completely exfoliated state by 3D-FEM.

The curved nature of the sheet is also observed, for it is well known that smectite clay sheet have a large degree of flexibility [11]. In such curved state, the layer experiences an external stress of 0.5–0.7 GPa. When the microscopic structure of a curved clay layer is examined, it is concluded that the main origin of the flexibility lies in the change of Si–O–Si angle in the silicate tetrahedral sheets rather than in the change of bond lengths. These simulation results agree with the atomic force microscopy (AFM) observations [12].

3. Solid-state processing

The complete delamination of organically modified layered fillers (OMLFs) in continuous polymer matrix is still challenging issue because it could not be satisfactorily attained. Gardolinski and Lagaly [13] described a very distinctive definition of delamination and exfoliation in aim to avoid the controversial use of these terms.

Exfoliation is defined as the decomposition of large aggregates into smaller particles, whereas delamination denotes the process of separation of the individual layers of the particles at the nanoscale. To the best of our knowledge, so far, the complete delamination is not feasible after melt intercalation with appropriate shear. Only a few examples of this type can be found in the literature [2, 8], but many published photographs show very small regions in the melt compound where partially exfoliation occurred [3]. Delamination of stacked layered fillers in polymeric nanocomposite is the ultimate target for controlling better overall materials' properties. Thus, we are far from the goal of understanding the mechanisms of the nano-structure control and the preparation of the nanocomposite with discrete dispersion of the nanofillers. From this reason, a novel preparation method is currently in progress. Some methods for the delamination of OMLFs were conducted by using supercritical CO₂ (sc-CO₂) [14, 15] and in-situ ultra-sonication [16]. However, the compounding with an assist from sc-CO₂ fluids and ultra-sonication did not improve the state of the nano-filler dispersion once a critical morphology was established. That is, the dispersion of the nano-filler in the polymer matrix is governed by judicious choice of OMLF. In this regard, we have shown solid-state processing of poly(*p*-phenylenesulfide) (PPS)-based nano-composites to delaminate the stacked, layered filler in the polymer matrix [17]. The pressure drop (Δp) within the nano-



galleries, which makes the polymer penetration more difficult, has not yet been discussed fully. Okamoto reported the estimated value of Δp (~24 MPa), which is much larger than the shear stress (0.1 MPa) during melt compounding [17].

The mixture of PPS and OMLF (95/5 wt.) was subjected to the processing using a thermostatted hot-press at 150°C, below T_m of PPS (i.e., PPS is still in the solid-state), and applying pressures of 33 MPa for 30 s. The mixture exhibited disorder and delaminated layer structure with a thickness of 10–20 nm into the PPS matrix. On the contrary, nanocomposite prepared by melt compounding at 300°C for 3 min showed large stacked silicate layers in the PPS matrix. The processing led to delamination of the silicate layers and attained the discrete dispersion. This approach can be extended to prepare polymeric nanocomposites with fine dispersion of the nano-fillers in overcoming the pressure drop within the nano-galleries (see Fig. 3).

Furthermore, for the preparation of polypropylene (PP)-based nano-composites, we conducted solid-state processing by using internal mixer. For processing with a rotating speed of 50 rpm at 50 °C for 5 h, the dispersed morphology of the silicate layers exhibits same trend with applying pressure [18]. The disordered and delaminated silicate layer structure is observed in TEM image. LMMT and tMMT are in the range of (372±38) nm and (33.2±3.8) nm, respectively. From these facts, the solid-state processing is extremely effective method to collapse the stacked structure in overcoming the pressure drop ($\Delta p \sim 24$ MPa) within the nano-galleries.

To understand the kinetics of the solid-state processing, we explain to apply a phenomenological formulation for the breakup of mineral particles (Rittinger's law): $dE = -b(1/D^n)dD$, where E is the energy for breakup, D is the mean diameter of particles and the parameter b and n are the breakup coefficients, which depend on processing condition and materials [19]. The mixing torque T is constant throughout the processing so that the input energy E is proportional to residence time t , i.e., $E \propto T \cdot t$. Hence, the eq. can be rewritten as $T \cdot t \sim (1/D^{n-1})$. The effect of the different applying torque and residence time on the delamination behavior of the OMLF is clarified. We have shown a novel and feasible method for the nanoscale control of the dispersed layered fillers via solid-state processing by using common experimental tools. This processing led to delamination of the silicate layers and attained the discrete dispersion. This approach can be extended to prepare polymeric nanocomposites with delamination of the nano-fillers in overcoming the pressure drop within the nano-galleries.

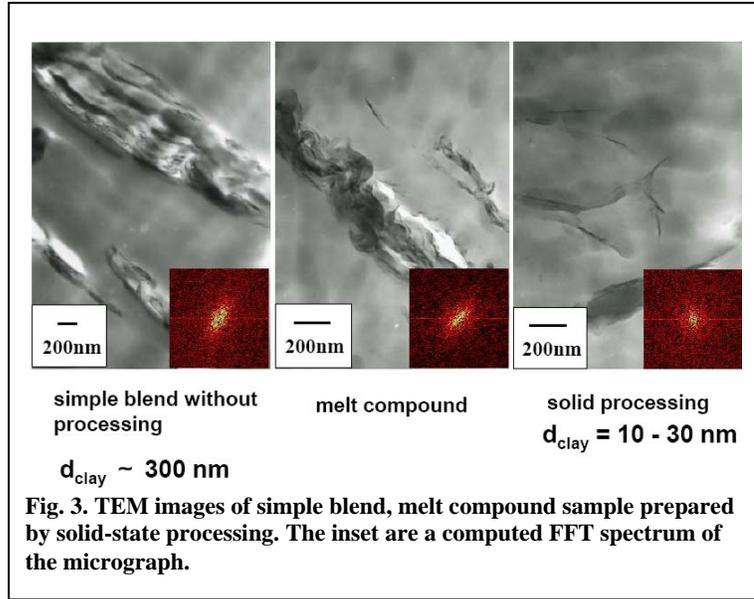


Fig. 3. TEM images of simple blend, melt compound sample prepared by solid-state processing. The inset are a computed FFT spectrum of the micrograph.

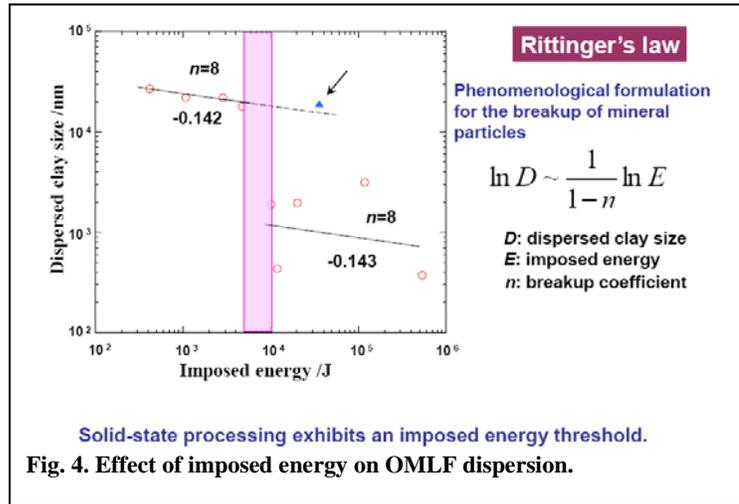


Fig. 4. Effect of imposed energy on OMLF dispersion.

4. Fabrication of porous 3D structure

The first successful nanocomposite foam, processed by *sc*-CO₂ as a physical foaming agent, appeared through a pioneering effort by Okamoto and his colleagues [20]. We have shown the preparation of the porous three-dimensional (3D) structure from a poly(*L*-lactide) (PLLA)-based nano-composite foam via enzymatic degradation. We specifically discussed the influence of the foam structure having high cell density (nanocellular) on the enzymatic degradation and porous structure development based on the results of the observation of SEM [21]. However, for a better understanding of the development of the porous 3D structure, one needs to pin down the morphological details of the enzymatic degradation of the foam structure having microcellular cell density. In this aspect, the main aim is to correlate the developed 3D morphology after degradation versus foam structure with microcellular level. Then we expect the effect of the foam structure having different cell density (microcellular and nanocellular) on the enzymatic degradation and porous structure development. Such a comparison will be worthwhile not only for assessing the fabrication of porous 3-D structure for tissue engineering scaffolds but also for studying the degradation performance in nano-composite foams.

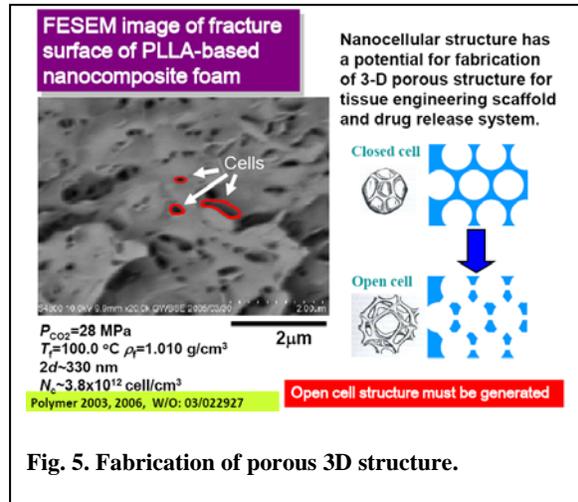


Fig. 5. Fabrication of porous 3D structure.

5. Perspective

The critical challenge in the development of polymer nanocomposites with remarkable improvements in the thermo-mechanical, electrical, and optical properties lies in the dispersion of nanoparticles in the polymer matrix. Despite various surface-modified technologies and processing of polymer nanocomposites, there are still opportunities and challenges to improve dispersion and interfacial properties of these materials. Thus, further research and development from these perspectives is required. More often than not, poor characterization of these materials and inadequate quantitative descriptions of observed phenomena have led to contradictions and misleading impressions of these nanocomposites. Thus, much more work is needed to develop analytical/modeling tools to predict and verify the behaviors of these nanocomposites.

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