POSTER PRESENTATIONS

INTEGRATED ENGINEERING OF HIGH-PERFORMANCE CARTILAGE/BONE PROSTHESIS FOR JOINT REPLACEMENT

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Introduction: Cartilage injury is a common disease in clinic. It is well known that articular cartilage lacks self-repair ability due to its non-vascular distribution, and some reports have shown that the damaged cartilage for adults was hard to self-repair if its diameter was larger than 3 mm. The design and industrial manufacturing of an artificial joint prosthesis that needs to just cut off the damaged part and can be inserted into the subchondral bone are of important significance to the bio-fixation, bringing a bright future for the joint replacement caused by cartilage damage. Combining the excellent mechanical properties and biocompatibility of ethylene-vinyl acetate copolymer (EVA) and hydroxyapatite/polyamide66 (HA/PA66), an integrated approached to cartilage/bone prosthesis was proposed and designed by a two-step injection molding method, in which the upper layer was made of EVA acting as the cartilage and the underlying layer was HA/PA66 composite as the artificial bone. The proposed methodology opens new possibilities to high-performance joint replacement materials.

Methods: A two-step injection molding was adopted to prepare the integrated cartilage/bone prosthesis. Specifically, the two-cavity mold was customized according to the actual size of an adult New Zealand white rabbit shoulder joint without and with the part of articular cartilage. Firstly, HA/PA66 was injected into the cavity without cartilage layer and cooled for 15 min, then taken out and drilled some holes on the linking surface, and then put into another cavity as the underlying bone. Secondly, EVA was injected into the cavity with the HA/PA66 part under 100 °C and 40 MPa and cooled for 20 min, then taken out to obtain an integrated cartilage/bone prosthesis.

Results: A two-step injection molding strategy is developed to structure an integrated cartilage/bone artificial joint, in which the outer layer composed of ethylene-vinyl acetate copolymer serve as the flexible and wear-resistant upper cartilage layer, and strong and biocompatible hydroxyapatite/polyamide66 composites as the underlying bone layer. The artificial joint has demonstrated good mechanical properties, excellent biocompatibility and impressive bioactivity, meeting the requirements to accelerate bone regeneration and early-stage bio-fixation. The artificial joint materials we have devised are of tremendous promise in the fields of joint replacement.

Discussion: The integrated EVA-HA/PA66 joint prosthesis prepared in the study showed excellent mechanical and bio-tribological properties, and the mechanical bonding between upper and underlying layer was improved greatly by the adoption of hole-structure. Furthermore, the underlying bone could well integrate with the surrounding bone after being implanted for 12 weeks. The integrated cartilage/ bone joint prosthesis shows a great potential for applications in joint replacement.

Keywords: Joint prosthesis, Integrated engineering, EV6, PA66, Joint replacement

METAL-POLYMER DIRECT JOINING: EFFECT OF INJECTED POLYMER TEMPERATURE NEAR JOINT AREA

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Metal-polymer direct joining has been receiving attentions because of its advantages such as light weight and high productivity. However, direct joining has not been applied to industries so much because the reliability is not sufficient. We need to elucidate the joining mechanism and to optimize the joining conditions for proper applications. We focus on one of the direct joining methods called Injection Molded Direct Joining (IMDJ). IMDJ consists of two elemental techniques, metal surface roughening and insert injection molding. In IMDJ process, melted polymer flows into metal surface structures, and then metal and polymer are joined directly and hardly. In our previous study, it is suggested that the polymer temperature (PT) considerably affects the replication ratio, which has relation to the joint strength. Therefore, in this work, we measured the polymer state during molding process and evaluated the joint strength in order to reveal the PT dependence on the joint strength.

We first roughened aluminum alloy (A5052) surface with a chemical etching method (NMT process, Taiseiplas). The surface structure sizes were around 20 nm. Secondly we produced metal/polymer (PBT) lap joints. In this molding process, we changed some conditions; polymer flow path, injection speed, and cylinder temperature, in order to control the PT in the cavity. In terms of the flow path, we changed the flow direction by using two different gate position. The flow path affects the PT in the timing when the cavity is filled, that is, we can change the time difference between the timing when polymer passes the joint area (t_{pass}) and when the cavity is filled (t_{fill}). Finally we carried out the tensile test with the original tester.

The tensile test results show several suggestions about the relation between the PT and the joint strength. First, the result about the flow path shows that the joint becomes stronger when the time difference between t_{pass} and t_{fill} is short. When the time difference is short, the PT at t_{fill} is high enough, which means polymer liquidity is high; therefore, the replication ratio becomes high. Secondly, the injection speed has negative effect to the joint strength although the positive correlation between the speed and the replication is well known in general transfer molding like emboss processing. This result suggests that other factors than PT affect the replication in our study, where the metal surface structure sizes are much smaller than general transfer molding. Finally, the cylinder temperature does not affect the strength. We discuss this result from the viewpoint of the injection speed. Since injected polymer gets cold as soon as flowing into the cavity, the PT on the joint area at t_{fill} should be low when the injection speed is low (t_{pass} and t_{fill} are not close). When the injection speed is high (t_{pass} and t_{fill} are close), pack pressure is applied to still hot polymer, and then the cylinder temperature dependence with high injection speed for future work.

Keywords: Direct joining, insert molding, joint shear strength, polymer temperature.

A STUDY ON OPTICAL AND MECHANICAL PROPERTIES BY REPROCESSING FOR INJECTION-MOLDED OPTICAL GRADE POLYCARBONATE

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The reprocessing of optical grade polycarbonate(PC) was studied to estimate the feasibility of recycled optical products. Injection molding and shredding processes were selected as reprocessing methods. Virgin resin was injection-molded to samples and those were shredded and molded under the same conditions again. Then, the effects of reprocessing on optical and mechanical properties of PC after up to two reprocessing cycles were evaluated and discussed.

As optical properties total and direct transmittance were measured using spectrometer for visible range for 3.5 inch light guide plate(LGP). Because LGP is one of the important components of back light unit(BLU) in liquid crystal display(LCD) acting as a light source, the present study focused on LGP's optical properties. Mechanical properties, i.e., tensile strength, flexural strength, and impact strength and rheological property of viscosity were measured, too.

The results showed that the mechanical and rheological properties were changed slightly as reprocessing. However, optical properties were changed with significant tendency as reprocessing. As the number of reprocessing increased, the total transmittance was decreased at low wavelength range and its color shift was changed systematically to yellow as shown in Figure 1. On the other hand, direct transmittance did not decline significantly(Fig.2), but higher color shift to yellow direction was found than total transmittance data(Fig.3).



Fig. 1 Total transmittance

Fig. 2 Direct transmittance

Fig. 3 Yellow index

Keywords: Polycarbonate, Injection molding, Reprocess, Optical properties, Mechanical properties

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PRECISE MEASUREMENT OF SHEAR STRESS DISTRIBUTION ON CAVITY SURFACE OF INJECTION MOLD DURING FILLING PROCESS

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Introduction: There has been no method for precisely measuring shear stress distribution on the cavity surface. The authors successfully developed a mold with a structure capable of step-change adjustment for conducting high precision measurement experiments on shear stress (Fig.1).

Measuring Method: A 3-component force transducer was directly connected to the bottom of block A, and shear force F acting on A was measured. To enable the height between A and B to be adjusted freely, block B was installed after assembling A and S. This allows step-change to be set below 5μ m. Front speed v was measured using two pressure sensors installed before and after block A. Shear stress distribution was calculated by the equation in Fig.1 using v and F. Experiments were conducted using PP and PS, and at different injection rates, with and without step-changes.

Results and discussion: Shear stress distribution without step-change (Fig.2) consists generally of these four patterns: ①stepped start, ②constant transition, ③slight rise, and ④slight decrease. At ①, stress at start is greater the higher is the injection rate. At ②, stress transitions constantly the higher is the injection rate, and stress is more conspicuous with PP than PS. Fig.3 shows the generation models of shear stress distributions. The shear stress of a certain area ②corresponding to the shear viscosity of the molten state in which no solidified area has formed, ③increases with the growth of the solidified area, then ④decreases due to the effects of shear heating and shear-thinning around the wall. If there is step-change, flow speed suddenly increases due to peeling flow at the step-change side (Fig.4). This indicates the effect of asymmetric fountain flow along the cavity thickness.



Fig.1 Calculation method of shear stress distribution based on shear force curve measured

Fig.2 Shear stress distributions measured under different injection rates (without step-change)

Fig.4 Shear stress distributions near flow front area with and without step-change

A STUDY ON THE FABRICATION OF 8 INCH LIGHT GUIDE PLATE BY ROLL STAMPING PROCESS

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LCD (Liquid Crystal Display) is one of the most widely used display types in these days. LCD has BLU (Back Light Unit) because of its non self luminous properties, which serves as a light source to TFT (Thin Film Transistor) LCD panel. BLU is composed of LED, LGP (Light Guide Plate), diffuser sheet and prism sheets. Among those LGP has an important role to convert point light to plane light source. It is gradually becoming thinner and larger in these days. Presently, there are three methods for fabricating LGP, i.e., injection molding, extrusion and roll to roll. In the present study, roll stamping process was tried for fabricating micro patterns directly on transparent plastic sheet. The transcription ratio on the sample and luminance level of finally assembled BLU were measured and compared with commercially available injection-molded LGP.

For roll stamping process PC sheet, width of 110.65 mm, length of 180 mm and thickness of 0.6 mm, was used. Micro patterned stamper was fabricated by laser ablation method. Roll surface temperature of 80°C and linear velocity of roll surface of 3.5 m/min were found as the best conditions for repeatability of final product through preliminary experiments. By applying uniform stamping force of 400 kgf, 800 kgf, 1,000 kgf, 1,600 kgf and 3,200 kgf to the sample surface the transcription ratio and luminance level were measured under the same roll surface temperature and linear velocity.

As a result, luminance level of light admitting area was increased as transcription ratio increases and that of light facing area was decreased. Also, luminance uniformity was increased as transcription ratio increased. However, when the transcription ratio was increased in a certain level, luminance uniformity reached the maximum of 80% as shown in Figure 1. Interestingly, luminance level made by roll stamping was even higher than commercially available injection-molded LGP for the cases when rather high stamping forces were applied to the roll as shown in Figure 2.



Fig. 1 Luminance uniformity and transcription ratio vs stamping force



Fig. 2 Luminance level (stamping force 1,000 kgf)

Keywords : Roll stamping, micro pattern, transcription ratio, luminance uniformity, LGP

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DOUBLE POROUS GEL-SLIPS FILMS WITH LONG-TERM ANTI-CORROSION PROPERTY

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Introduction: Innovative anti-fouling coating of slippery liquid-infused porous surface (SLIPS), immobilizing omniphobic lubricant on micro porous structure, was reported for multi-functional anti-fouling surface in 2011 by T. S. Wang *et al.* Although the development of SLIPS for wide range of application, the crucial challenges of preventing a loss of lubricant (in charge of anti-fouling) from evaporation or other liquid contact remain. Herein, we designed lubricant stability improved SLIPS, that gradually feed lubricant on surface from lubricant pool sandwiched by double porous films inspired GEL-SLIPS. As a result, a double porous GEL-SLIPS performed hydrophobicity over a longer duration than that of conventional SLIPS.

Methods: Double porous GEL-SLIPS films is composed of 3 layers of porous polymer film/ lubricant / porous polymer film. Porous polymer film was fabricated by non-solvent induced phase separation technique of Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP). A Fe plate were coated with porous polymer film, Perfluoropolyether (PFPE) lubricant, and porous polymer film, in this order. Lubricant retaining property was visually observed by corrosion of samples. Samples were immersed into pure water to observe corrosion area.

Results: Figure shows the elapsed time images of Fe plate corrosion for 6 weeks. We prepared 3 type samples of bare, SLIPS coated, and Double porous GEL-SLIPS coated Fe plate. Bare Fe plate was rotted within a day whereas, corrosion time was prolonged to 5 days on SLIPS-coated Fe plate. Double porous GEL-SLIPS coated Fe plate kept anti-corrosion at least for 6 weeks.

Discussion: Corrosion on metal plate occurs when a surface comes into contact with corrosion medium such as water. PFPE lubricant have a good barrier to corrosion medium because of its hydrophobicity. That means double porous GEL-SLIPS prevent a corrosion longer than SLIPS. Comparing the double porous GEL-SLIPS with SLIPS, top of the porous polymer controlled feeding of lubricant to prevent a loss of lubricant.

Keywords: Slippery Liquid Infused Porous Surface, long-term stability, anti-corrosion



Figure. Time-elapsed images of corrosion test on coated Fe plates conducted for 6 weeks.

SLIPPERY SMOOTH SURFACE WITH HOT WATER REPELLENCY FABRICATED ON EPOXY SUBSTRATE

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Introduction: In recent years, surfaces repellent to hot liquids have attracted much attention and they will have a lot of applications, such as repellent coating of hot fluidic food. Only a few reports have achieved hot liquids repellency which require fluorine materials and specific rough structure. Depending on fluorine compounds with low surface tension and complicated structure hampers development of biocompatible coating and usage in practical field. Here, we fabricated smooth slippery surface which holds biocompatible lubricant layer by OH- π interaction. This surface showed not only hot water repellency but also durability against boiling in hot water.

Methods: First, we fabricated a base layer by spin-coating phenyltriethoxysilane via sol-gel method on a hydrophilic substrate (glass or commercial aluminum can). After drying, oleic acid was casted on the base layer as a lubricant. Hot water repellency was analysed by measuring contact angles and sliding angles of water droplets with various temperatures. In addition, we conducted the boiling test, in which the film was immersed in hot water at 90°C for 30 minutes.

Results: The result of sliding angle of water droplets with various temperature (Fig. (a)) demonstrates that this slippery surface repelled hot water droplet of 80°C at very low sliding angle (\approx 1°). As shown in Fig. (b), this coating maintained its low sliding angle after the boiling and even the retort test (boiling test with closed vessels leading to high pressure).

Discussion: The smooth base layer made it possible to fabricate hot water repellent coating without any fluorine materials. The fact that the sliding property was maintained after both boiling tests shows that $OH-\pi$ interaction between the base layer and oleic acid functions under hot water. This film will be applicable to coatings for food containers and drink cans.

Keywords: Slippery surface, hot water repellency, biocompatibility, low sliding angle



Fig. (a) Variations of contact angles and sliding angles of water droplet with various temperatures. (b) Sliding angles both before tests and after the boiling test or the retort test.

PREPARATION AND CHARACTERISATION OF PLA BASED NANOCOMPOSITES WITH STARCH NANOCRYSTALS AS REINFORCEMENTS

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The demand for the generation of environmentally friendly material is increasing due to the problems posed by extensive use of petroleum based products. One of the "green" materials emerging in the market nowadays is biodegradable nanocomposites. Among the biopolymer matrices being used for the making of bio plastics, starch and PLA are extensively used materials, due to numerous advantages such as low cost, abundant availability, biodegradability, biocompatibility, nontoxicity and renewability.

Starch is a polysaccharide which accommodates energy in plants. It is the second most abundant biomass material in nature. The applications of bio plastics at present are limited due to various reasons such as higher cost compared to conventional petroleum based plastics, lack of sophisticated methods developed for large scale production and other major limitations on the functionality.

Nanocomposites prepared from polysaccharide nanocrystals of starch and biodegradable polymer like PLA can be examined to have superior properties. This study will involve the preparation of starch nanocrystals (SNC) from waxy maize starch and incorporation of the SNC, with concentration in the range of 1-5 wt%, in PLA matrix using melt processing as well as a solvent casting and evaporation technique with dichloromethane (DCM) as the solvent to form a homogeneous dispersion. The prime focus of this research will be to investigate the mechanical, barrier, thermal, morphological and rheological responses of the PLA-SNC nanocomposite.

Keywords: Starch nanocrystals, Nanocomposites, PLA

EFFECTS OF PROCESSING CONDITIONS ON TiO₂ NANOFILLER LOCI, MORPHOLOGY, MECHANICAL PROPERTIES AND DEGRADABILITY OF TIO₂-PLA/LDPE NANOCOMPOSITE FILMS

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TiO₂ photocatalyst played an important role in enhancing degradation of plastic film. It could also act as solid compatibilizer for immiscible blends such as in PLA/LDPE system. This work aimed to investigate effects of processing parameters i.e. mixing temperature, time, and order on TiO₂ nanofiller loci, morphology, mechanical properties, and degradability of (10:90) PLA/LDPE nanocomposite films. TiO₂ nanoparticle showed a preferential localization at the interface when introduced into the internal mixer after LDPE and PLA had been thoroughly mixed at 150 °C. The optimum mixing time for TiO₂ nanofiller incorporation was about 3-6 minutes to obtain a well-dispersed and uniform composite. Compressed film of this TiO₂-PLA/LDPE nanocomposite possessed significant improvements in morphology and mechanical properties including elastic modulus, yield strength, and elongation at break. However, the degradability of the film was lower than that of the film with TiO₂ photocatalyst located within LDPE matrix. This was found to be due to TiO₂ nanofiller induced photodegradation in LDPE but, at the same time, inhibited microbial growth in PLA which was necessary for biodegradation.

Keywords: polymer blend film, PLA, LDPE, photodegradation, biodegradability, solid compatibilizer, TiO₂ nanoparticle

COMPRESSIONMOLDINGPROCESSPOLYBENZIMIDAZOLE MATERIALS

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Introduction: Polybenzimidazole is well known for having a superior heat resistance and has good mechanical properties as good as heat resistance. PBI parts which is produced by using a compression molding process are promising materials in extreme environments. In this study, we synthesized PBI using a popular method and various equipment are utilized to confirm whether synthesis is succeeded. After cleaning and drying, hot press was used for compression molding process with a lot of comparisons. Modified carbon nano tubes, graphene and graphene oxide introduced imidazole group are compared and presented which filler has a better dispersion and a higher flexural strength and modulus. The dispersion was carried out using an ultrasonic processor and flexural test was performed 3-point bending test method.

Methods: Basic synthetic method is used. (3,3-diaminobenzidine, isophthalic acid and polyphosphoric acid) In case of pure PBI sintered body, after some preprocessing, compression molding process was conducted to use fine PBI powder. Operation temperature is 560°C and working pressure is 73MPa (12ton).

Results: Specially fixed size (126mm x 12.6mm x 4mm) was prepared to measure a flexural strength and modulus. A lot of variables such as temperature, pressure, size of powders, ratio of materbatch also were considered during a compression molding process. Furthermore, Fillers like CNT, Graphene also used in order to find out its correlation.

Discussion In case of temperature, the best result was 430° C (nearby the Tg) and 73MPa (12ton) was the best pressure. If the high pressure was applied, over-sintering was occurred. The other hand, when the low pressure is applied, material have a lot of pores. Modified CNT-PBI has a higher flexural modulus than pure PBI but flexural strength show the tendency to decrease. In case of Im-GO, both properties were increased slightly.

Keywords: Compression molding, Polybenzimidazole, Flexural modulus, Im-GO, Modified MWCNT

MANIPULATEDORIENTATIONCONTROLOFPOLYPROPYLENE CONTAINING RUBBER DISPERSION

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Introduction: The nucleating agent, *N*, *N*²–dicyclohexyl–2, 6-naphthalenedicarboxamide, was found to be dissolved into a molten polypropylene (PP). It appears as needle-shape crystals during cooling process and shows a nucleating ability for PP. PP molecules show epitaxial crystallization on the surface of the needle crystals of the nucleating agent. Because of this phenomenon, PP molecules orient perpendicular to the flow direction at extrusion. In this research, the orientation of PP molecules as well as the deformation of rubber particles were investigated.

Methods: Polypropylene (PP), ethylene-butene-1 rubber (EBR), and N,N'-dicyclohexyl-2,6-naphthalenedicarboxamide (NA) were employed in this study. PP with NA and EBR (PP/EBR = 70/30 wt%, NA = 1000ppm for PP) were fed into an extruder with a ribbon-shaped die at 200°C and cooled at 100°C by a chill roll. PP/EBR without NA was prepared in the same method.

Results and Discussion: The cut surface was observed by scanning electron microscope (SEM) after the etching treatment by xylene. Fig. 1 shows SEM photographs of the (PP+NA)/EBR blend. The rubber particles are deformed to the machine direction. Furthermore, X-ray diffraction patterns demonstrate that PP chains orient perpendicular to the flow direction, which is attributed to the epitaxial crystallization of PP chains on the surface of the needle-shape nucleating agents. As a result, the deformation direction of rubber particles is perpendicular to the molecular orientation of PP matrix.



Fig. 1 SEM photograph of (PP+NA)/EBR

Keywords : molecular orientation, polypropylene, ethylene-butene rubber

POLYHIPES FROM IONOMER STABILIZED HIGH INTERNAL PHASE EMULSIONS FOR OIL SPILL RECOVERY

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PolyHIPEs are promising as an absorbent for oil spill recovery due to their interconnected macro-porous structures. Recently, we have investigated high internal phase emulsions (HIPEs) and their application for efficient reclamation of spilled oils [1-6]. Herein, we present a continuous method to produce polyHIPEs for oil spill reclamation. The polyHIPEs were prepared from light induced polymerization of sulfonated polystyrene stabilized high internal phase emulsions (SPS-HIPEs). The SPS-HIPEs contains seawater as the dispersed aqueous phase and commercial monomers such as tetraethyl orthosilicate and butyl acrylate as the continuous phase. Sulfonated polystyrene was obtained from used polystyrene foams, realizing a green transformation of waste polystyrene. PolyHIPEs from SPS-HIPEs (SPS-polyHIPEs) obtained a high gel fraction of 93 % under UV irradiation for only 5 minutes, showing possibility to produce the polyHIPE monoliths continuously. SPS-polyHIPEs can be much greener in comparison to polyHIPEs from particlesor surfactant-stabilized HIPEs, and no purification is required before use. SPS-polyHIPEs exhibit interconnected macro-pores, and the sizes of pores as well as pore throats are controlled simply with the volume fraction of the internal phase. These monoliths are hydrophobic with water contact angle over 140°. SPS-polyHIPEs show excellent performances for oil spill reclamation, including high absorption rate of reaching saturated absorption in 3 to 5 minutes, high absorption capacity to a series of oils and organic solvents, a high recovery rate at about 85% and a high reusability for 20 times. A continuous process is illustrated using SPS-polyHIPEs as an absorbent for oil spill reclamation.

Keywords: PolyHIPEs, sulfonated polystyrene, high internal phase emulsion, spill recovery

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MODULUS ENHANCEMENT OF POLYCARBONATE BY ADDITION OF METAL SALT

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Introduction: Polycarbonate (PC) is widely employed in industrial fields because of its excellent transparency and mechanical toughness. However, Young's modulus is low as compared with other plastic glasses. Therefore, the modulus enhancement is required to widen applications.

In this study, we propose a new method to enhance the Young's modulus of PC without losing its transparency and mechanical toughness by the addition of a specific metal salt.

Methods: The blend films of PC with 5 wt% of lithium perchlorate (LiClO₄) were prepared by the solution casting method using tetrahydrofrane (THF). Pure PC films were also prepared by the same method to compare properties.

The temperature dependence of oscillatory tensile moduli, such as storage modulus E' and loss modulus E'', were measured by a dynamic mechanical analyzer. Tensile properties were examined by a uniaxial tensile machine at room temperature.

Results: Table 1 shows E' at room temperature and glass transition temperature (T_g) measured by the dynamic mechanical measurement. As shown in this table, E' at room temperature increases by the addition of LiClO₄. However, the glass transition temperature (T_g) is not affected.

Tensile properties of the films are summarized in Table 2. The strain at break, indicating the mechanical toughness, is not affected by the addition of LiClO₄. Furthermore, higher yield stress and Young's modulus are detected for $PC/LiClO_4$ (5%). Moreover, it is mentioned that the transparency is not affected by the LiClO₄ addition.

Table 2 Tensile properties

Table 1	E' at 25 °C	and T				
Table T		and I g		Yield stress	Strain at break	Modulus
				[MPa]	[-]	[GPa]
	<i>E</i> ' [GPa]	<i>T</i> _g [°C]	Pure PC	49.3	0.626	1.82
Pure PC	1.94	152	PC/LiClO ₄ 5%	58.3	0.616	1.97
PC/LiClO ₄ 5%	2.19	153				

Discussion: The effect of the addition of $LiClO_4$ on the mechanical properties of PC is discussed in this research. It is found that the addition of $LiClO_4$ enhances the Young's modulus of PC without losing the mechanical toughness, heat resistance, and transparency.

Keywords: Polycarbonate, Modulus enhancement, Antiplasticization

INTERPHASE TRANSFER OF LIQUID IN IMMISCIBLE POLYMER BLENDS AND ITS APPLICATION

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Introduction: Because of the light scattering at interface between phases, immiscible polymer blends are opaque in general. When the refractive index difference between phases is minimal, however, even an immiscible blend with phase separation is transparent. Therefore, the light transmittance of an immiscible polymer blend can be controlled by adjusting the difference in the refractive index.

In this study, the difference in the refractive index is controlled by the transfer phenomenon of a lowmolecular-weight compound with high refractive index in an immiscibe polymer blend.

Methods: Commercially available poly(ethylene-co-vinyl acetate) (EVA) and poly(vinyl butyral) (PVB) were employed. The refractive indices of EVA or PVB are 1.486 and 1.488, respectively. Tricresyl phosphate (TCP), as a low-molecular-weight liquid, was added to the blend. The refractive index of TCP is 1.554. The blend was compressed into a flat sheet using a compression-molding machine. Temperature dependence of light transmittance of these sheets was measured by a UV-Vis spectrophotometer.

Results: Temperature dependences of light transmittance of EVA/PVB/TCP (50/50/10) are shown in the figure. The light transmittance of the blend decreases with the ambient temperature. As a result, the blend is fairly transparent at low temperature, while it becomes opaque at high temperature.



Light transmittance of EVA/PVB/TCP

Discussion: The temperature dependence of the light transmittance, i.e., light scattering, is originated from interphase transfer of TCP. Becauce TCP has high refractive index, its transfer phenomenon affects the refractive index of each phase in the blend strongly.

Keywords: immiscible polymer blend, plasticizer, light transmittance, the refractive index

THE INFLUENCE OF MICRO-NANO LAMINATED TECHNOLOGY ON DIELECTRIC PROPERTERTIES OF CNTs+HIPS/HIPS MULTILAYERED COMPOSITES

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In order to study the influence of multilayered composites containing alternating layers on the dielectric properties of polymer composites, in this paper, various alternated microlayers of high impact polystyrene with carbon nanotube (CNTs+HIPS)/high impact polystyrene (HIPS) multilayered composites were prepared by using self-made micro-nano lamination extrusion device, and the contents of CNTs in the CNTs+HIPS layer was 6%. The experimental results show that the thickness of alternating micro-layers is uniform, the electrical resistivity of CNTs+HIPS/HIPS multilayered composites present significantly anisotropy between extrusion direction and thickness direction. The multilayered composites reflect highly conductive properties in the extrusion direction and insulating properties in the thickness direction, due to the HIPS layers blocking the conductive network formation in the thickness direction of composites system. The dielectric constant increases obviously with the increase in the number of layers, for example, the dielectric constant of the 128 layers is increased by 4.9 times than that of the 2 layers when the frequency is 100Hz. This because of that the interfaces between CNTs+HIPS layers and HIPS layers are increased, which is useful to accelerate the effect of interfacial polarization so that more electrical charges will accumulate at interfaces, and the effect of interfacial polarization is improved. The alternating layers structure of CNTs+HIPS/HIPS multilayered composites can not only increase the dielectric constant, but also keep the low dielectric loss at low frequency $(<10^{4}Hz)$. The results show that the micro-nano lamination extrusion technique provides a simple and easy method for preparing multilayered polymer composites with high dielectric constant and low dielectric loss. Figure 1 shows that the schematic diagram of micro-nano lamination extrusion device.



A, B: extruder C: confluence segment D: laminated elements E: die

Fig. 1 The schematic diagram of micro-nano lamination extrusion device

Keywords: Micro-nano lamination extrusion, Alternating layers, Dielectric properties, high impact polystyrene composites, carbon nanotube

GRAPHENE BASED POLYURETHANE NANOCOMPOSITES: A NOVEL MATERIAL FOR EMI SHIELDING COATINGS

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The Increasing uses of several electronic systems produce a lot of electromagnetic radiation pollution in current state. Thus there is a rapid rise in interest of scientific community to research for suitable absorbing materials for EMI shielding. Graphene has been explored to improvise better microwave absorption in a wide range of frequency. Graphene, a flat monolayer of carbon atoms tightly packed into a 2D honeycomb lattice, has acquired tremendous consideration owing to its unique properties such as superior electrical conductivity, thermal stability and extraordinary mechanical properties.

In our research group, chemically reduced graphene oxide (CRG) sheets, thermally reduced graphene sheets (TRG) and PVP-stabilized silver nanoparticle decorated graphene nanohybrid (Ag-PVP-CRG) were synthesized and studied for microwave absorption so that they can be used as potential RAM materials for stealth and electromagnetic interference (EMI) shielding coatings. CRG and Ag-PVP-CRG were prepared through chemical route and TRG through thermal exfoliation and annealing process. The microwave shielding and dielectric properties of the graphene sheets in the form of pellets were studied in the Ku band region (12.4–18 GHz). It was observed that the presence of Ag nanoparticle, residual functional groups and conductivity significantly changes the contribution of graphene sheets towards the microwave absorbing performance and dielectric losses. Absorption loss is found to be the dominant mechanism for EMI shielding. EMI shielding effectiveness (SE) values for CRG, TRG and Ag-PVP-CRG at 2mm thickness in the Ku-band region were found to be 80 dB, 45 dB and 58 dB respectively and electrical conductivity value obtained for CRG, TRG and Ag-PVP-CRG are 124.9 Scm⁻¹, 62.7 Scm⁻¹ and 0.25 Scm⁻¹ respectively. Further, the graphene sheets based polyurethane coating and nanocomposites were prepared and studied for shielding performance. The SE was found to be affected by the dispersion of graphene sheets inside the polyurethane matrix, as agglomeration of sheets restrict the electrical network formation of graphene sheets inside the TPU matrix. The electrical conduction and dielectric losses are important parameters to attain effective EMI attenuation. Thus, the present work showed great potential of graphene sheets and its polyurethane based nanocomposites as an effective candidate as a microwave absorbing material along with superior dielectric behaviour.

Keywords: Graphene, EMI Shielding, Microwave frequency, Silver nanoparticles.

SELECTIVE LOCALIZATION BEHAVIOUR OF CARBON NANOFILLERS IN IMMISCIBLE POLYMER PAIRS

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Introduction:

Due to their excellent properties, carbon nanofillers are good candidates to improve mechanical properties of polymeric materials. In this study, the transfer behaviour of carbon nanofillers, i.e, multi-walled carbon nanotube (MWCNT) and graphene nanoplatelet (GnP), between immiscible polymer pairs during meltmixing or laminating is investigated.

Methods:

For melt-mixing, a composite of polycarbonate (PC) and GnP (80/20) was mixed with polyethylene (PE) at 300 °C for 20 min using an internal-batch mixer. The blend ratio of PC/GnP to PE was 50/50 (w/w), i.e, PC/GnP/PE = 40/10/50. In the case of laminating, a pure PC sheet was annealed with a PE composite sheet, i.e, PE/MWCNT (97/3) or PE/GnP (97/3), at 300 °C for 20 min. Then, the laminated sheets were quenched and separated. In addition, the laminating test was also performed for the laminated sheets comprising of pure PE and PC composite.

Results:

It is found that GnPs move from PC to PE phase during melt mixing, even if GnP is first dispersed into PC. On the contrary, the transfer of GnPs from PC to PE cannot be detected during annealing treatment.

Furthermore, it is found that both MWCNTs and GnPs move from PE to PC during annealing. The amount of MWCNTs on the surface of the separated PC sheet is larger than that of GnPs.

Discussion:

The transfer phenomenon of GnPs from PC to PE during melt-mixing process is attributed to the adsorption of PE molecules on the GnP surface at high-temperature-mixing with the aid of oxygen. In the laminated sheet system, the transfer behaviour is attributed to the difference in the interfacial tension between filler and polymer with an aid of Brownian motion. In addition, the results indicate that MWCNTs can transfer faster than GnPs, demonstrating that the size and shape of nanofillers play a important role on the transfer.

Graphene nanoplatelets, Carbon nanotube, Interphase transfer, Brownian motion

FABRICATIONOFELECTRICALLYCONDUCTIVEGRAPHENE/POLYSTYRENECOMPOSITESVIAACOMBINATION OF LATEX AND LAYER-BY-LAYER ASSEMBLYAPPROACHES

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Introduction: Due to its excellent physical properties, graphene acting as reinforcing fillers has attracted intense interests. To achieve a controlled distribution, the formation of a conductive network composed of graphene sheets within polymer matrix is of critical importance. In this work, polystyrene (PS) microspheres wrapped by graphene oxide (GO) sheets were prepared via layer-by-layer assembly of oppositely charged GO sheets onto PS microspheres. The deposited GO was then reduced and the composite films with a graphene conductive network were prepared by hot-pressing. The morphology of graphene conductive network was studied and the thermal and electrical properties of the composite films were measured. The as-prepared composites showed an improved thermal stability as well as electrical conductivity with a percolation threshold as low as 0.2 vol%. The combination of latex technology and layer-by-layer self-assembly method thus demonstrated an efficient and facile approach to fabricate electrically conductive graphene/polymer composites.

Methods: The PS microspheres were prepared by a dispersion polymerization method. Graphite oxide was synthesized by Hummers method and exfoliated to give a brown dispersion of GO under ultrasonication. The resulting GO suspension is negatively charged over a wide pH condition. Positively charged GO was synthesized by formation of an amide bond between PEI and GO in the presence of EDC and NHS. The obtained GO-g-PEI was dispersed in water to form a stable and positively charged solution. The GO wrapped PS microspheres were prepared by alternating deposition of GO and GO-g-PEI on the PS microsphere template via LBL assembly, and then reduced by hydrazine at 90 °C for 4 h. Finally, conductive (RGO)_n/PS composite films were obtained by a hot-pressing processs.

Results: The RGO/PS composites exhibit a conductivity percolation threshold when the number of bilayer is between 0.5 and 1. The electrical conductivity increases dramatically from $7*10^{-7}$ to 0.02 S/m as the number of bilayer increases to two (i.e., n = 2) with slight increase to 0.05 S/m when n = 3. In addition, the thermal stability of $(\text{RGO})_n/\text{PS}$ composites is significantly enhanced, as compared with neat PS. The temperature at 5% weight loss is 402 °C for the $(\text{RGO})_3/\text{PS}$ composites, which is almost 25°C higher than the neat PS. The morphology of the hot-pressed composite films was observed by TEM. The distribution of RGO sheets is rather uniform and only very few agglomerations can be observed. When the bilayer number n = 1, some ribbon-like features (i.e., RGO sheets) are clearly seen in the PS matrix. These RGO sheets are non-continuously distributed in the matrix. With the increase of the bilayer number, the non-continuous ribbon-like features become longer and tend to intertwine together. As the bilayer number increases to 3, oval-shaped PS microspheres can still be discerned with a clear outline or "shell" of the wrapped graphene deposited on them. This graphene network will form conductive pathways in the insulating PS matrix, leading to an improved electrical conductivity.

Discussion: The conductive graphene networks or pathways thus formed in the polymer matrix can greatly improve the electrically conductive properties of the composites. More significantly, the use of organic solvents are avoided throughout the whole experiments, including the preparation of the graphene wrapped PS microspheres and construction of the graphene/PS composite films. Through the combination of latex technology and LBL assembly, a facile, efficient and environmentally friendly method has been developed to fabricate electrically conductive graphene/PS composites with improved dispersion uniformity and controllable filler contents. This strategy can be anticipated to provide a platform for the preparation of graphene-based polymer composites with high performance and multifunctionality for potential applications in various areas.

Keywords: Graphene, Nanocomposites, Electrical properties

BIODEGRADABILITY STUDIES OF NANOCRYSTALLINE CELLULOSE NANOCOMPOSITES

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Introduction:

Most petrochemical polymers being used widely cause environmental pollution as they are not easily degradable and remain in landfills for many years. Renewable, bio-compatible, bio-polymers such as polylactic acid (PLA), nanocrystalline cellulose (NCC), are expected to degrade easily in a waste stream into carbon dioxide (CO₂), water vapour (H₂O) and in some cases (aerobic degradation) methane (CH₄) gas. This work aims to establish a simple screening tool method to determine the exact rate of degradation of these polymers especially the nanocomposite systems

Methods:

The approach used here is abiotic and involves the use of hydrolysis and photo-degradation.

In hydrolysis method, among the 2 pathways i.e. acidic and alkaline; the latter was preferred since literature showed it being at least 100 times faster. The hydrolytic medium was 1M NaOH where the polymer samples PLA, PLA-NCC (1% to 5% w/w) and HDPE were immersed (23°C/50-60% relative humidity) away from light. The control solution was plain deionised water. The weight loss in comparison to initial was recorded over time. Simultaneously accelerated weathering testing was done using QUV and SUN methods, observing for visual changes.

Results:

It was evident from changes in physical appearance between H_2O and NaOH samples, that whilst the samples of PLA and PLA/NCC underwent significant degradation due to hydrolysis, the HDPE control samples were relatively unchanged. The surface of PLA and PLA/NCC samples exposed to NaOH for the duration of the test were etched, appearing textured and dull rather than smooth and shiny when compared to their appearance before exposure. This work explains the disintegration of samples in solution. The degradation was found to follow general integrated second order reaction rate equation. This is used to explain the possible mechanism of degradation under such conditions simultaneously comparing with some reported results.

Discussion and conclusion:

From the literature found, there are 2 broad approaches to study degradation of such bio-polymers and their composites with NCC, viz. biotic (microbial process) and abiotic (non-microbial). In the biotic process, composting is the most commonly used method wherein the polymer sample is buried in the inoculated soil. In another method the polymer is submerged in activated sludge sourced from municipal sewage treatment facilities. In the abiotic process, degradation is non-microbial and uses acid/base hydrolysis, photolysis / weathering methods. The main action is cleavage of key linkages in the polymer chain into smaller fragments. However the biotic process is usually time-consuming and involves use of bio-hazard substances. The abiotic process is relatively simple saving time. The method developed here is a simple, easy laboratory screening tool. Among others, the main types of monitoring are weight loss in solid testing, concentration changes when using liquids, yellowness index in case of photolysis / weathering studies and tensile properties.

The rate of hydrolysis of PLA/NCC and PLA samples in an alkaline solution with pH=14 was determined experimentally. It was found that the addition of 1 wt% NCC to PLA resulted in a rate of hydrolysis approximately double the rate of neat PLA. This is concurrent with expectations mirrored in literature.

Thus it appears that abiotic methods of simulating degradation on biopolymers like PLA, PCL, etc are a viable avenue to investigate further as against the biotic method. Additional research into the rate of degradation of PLA/NCC in acid could be performed, to compare hydrolysis rates.

Keywords: Polylactic acid (PLA), nanocrystalline cellulose (NCC), hydrolysis, biodegradation.

EFFECT OF GRAPHENE NANOPLATELET EMBEDDING ON PHYSICAL PROPERTIES OF POLY LACTIDE AND POLY (BUTYLENE ADIPATE-CO-TEREPHTHALATE)

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Biodegradable poly lactide (PLA) and poly (butylene adipate-co-terephthalate) (PBAT) were used in preparation of two series of bio-nanocomposites with 0-15 wt% graphene nanoplatelets (GNPs). Effect of GNP embedding on various properties of PLA/GNP and PBAT/GNP nanocomposites was determined via different techniques and the two systems were systematically compared. It was observed that addition of GNPs enhances thermal stability of both polymers effectively. In particular, degradation of PLA was significantly reduced due to the presence of GNPs. Differential scanning calorimetry measurements revealed that crystallinity of PBAT decreased slightly with increasing GNP loading while crystallinity of PLA increased markedly. The glass and melting temperatures of the matrices did not vary considerably with GNP incorporation. Electrical permittivity of both PLA and PBAT increased with increasing GNP loading. However, while dielectric constants of both systems had comparable values for the same concentration of GNPs, PLA nanocomposites exhibited higher values of dielectric loss than PBAT nanocomposites for filler loadings of 9-15 wt%.

FACILE FABRICATION OF VERSATILE PMMA/CNF-NaYF4:Yb/Er COMPOSITE MICROSPHERES BY PICKERING EMULSION SYSTEM

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Herein, we report a straightforward method to fabricate multifunctional model drug methyl red-loaded polymethyl methacrylate (PMMA)/cellulose nanofiber (CNF)-NaYF₄:Yb/Er CRs by Pickering emulsion system. The CRs obtained with relatively uniform size distribution exhibited both strong upconversion and downconversion luminescence and fine drug release performance. Considering the facile operation process and versatile properties of the CRs, this work offers an easy and universal method to prepare various multifunctional CRs for meeting the requirements of diverse applications.

Introduction: Composite microspheres (CRs) have drawn increasing attention because of their attractive and combined optical, catalytic, electronic and magnetic properties. Rare-earth upconversion nanoparticles (UCNPs), which can convert a near-infrared excitation into a visible emission, are attractive luminescent nanomaterials due to their low auto-fluorescence and toxicity, absence of photo-damage, and high light penetration depth. On the other hand, cellulose nanofibers (CNFs) possess high specific stiffness and strength, low density, excellenty biodegradability and biocompatibility, which make them promising for applications in drug delivery and tissue engineering. Despite significant progress on CRs in recent years, however, the CRs based on the combination of UCNPs and CNFs have rarely been reported.

In this work, we present a simple and effective method to direct preparation of multifunctional model drug methyl red (MR)-loaded PMMA/CNF-NaYF4:Yb/Er CRs by Pickering emulsion system. NaYF4:Yb/Er nanoparticle was chosen as a representative UCNP, because it has been demonstrated as one of the most efficient UCNPs.

Methods: For synthesis of MR-loaded PMMA/CNF-NaYF₄:Yb/Er CRs, typically, 1.5 mL of the aqueous dispersion of 0.1% (w/w) CNFs and 0.05% (w/w) UCNPs was used as water phase. Subsequently, 0.5 mL of the dichloromethane solution of 2% (w/w) PMMA and MR (2 mg/mL) as oil phase was added into the water phase. After hand-shaking emulsification, the stable O/W Pickering emulsion co-stabilized by CNFs and UCNPs was obtained. After evaporation of dichloromethane from the emulsion by shaken at 40 °C for 48 h, MR-loaded PMMA/CNF-NaYF₄:Yb/Er CRs were obtained. For comparison, Pickering emulsion only stabilized by CNFs was prepared according to the above method.

Results: We have demonstrated an easy and viable strategy to preparation of versatile MR-loaded PMMA/CNF-NaYF₄:Yb/Er CRs through Pickering emulsion system by using water-dispersible UCNPs and CNFs as stabilizers. The obtained CRs simultaneously exhibited strong upconversion and downconversion luminescence and excellent drug release property (see Fig.1). There is no doubt that this approach can be extended to prepare other functional CRs. This study thus provides opportunity to fabricate multifunctional CRs for various applications.

Discussion: The upconversion luminescence spectra of the MR-loaded PMMA/CNF-NaYF₄:Yb/Er and PMMA/CNF CR were measured under excitation of 980 nm. As depicted in Fig. 4a, the MR-loaded PMMA/CNF-NaYF₄:Yb/Er CRs presented four obvious emission peaks at 407, 524, 542 and 656 nm, which are assigned to the ${}^{4}H_{9/2}$ - ${}^{4}I_{15/2}$, ${}^{2}H_{11/2}$ - ${}^{4}I_{15/2}$, ${}^{4}S_{3/2}$ - ${}^{4}I_{15/2}$ and ${}^{4}F_{9/2}$ - ${}^{4}I_{15/2}$ transitions for Er³⁺, respectively. In contrast, no emission peak can be detected for the MR-loaded PMMA/CNF CRs. Moreover, the PMMA/CNF-NaYF₄:Yb/Er CRs can also exhibit strong downconversion luminescence with the emission peak at 584 nm because of the introduction of MR (Fig. 4b). Based on the dual modal luminescence property, the PMMA/CNF-NaYF₄:Yb/Er CRs with potential tracking capability hold great promise for advanced biomedical applications.



Fig. 4. (a) Upconversion luminescence spectra of the MR-loaded PMMA/CNF-NaYF₄:Yb/Er (1) and PMMA/CNF (2) CRs (λ_{ex} = 980 nm). Inset: Photographs of water dispersion of MR-loaded PMMA/CNF-NaYF₄:Yb/Er CRs under daylight and excitation of 980 nm laser. (b) Emission spectrum of the MR-loaded 490 nm).

Keywords: Composite materials; Functional microsphere; Cellulose nanofiber; Luminescence; Upconversion nanoparticle

HYBRID COMPOSITE USING CARBON NANO TUBE AND NATURAL FIBER

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Natural fibre composites (NFCs) are widely used in the construction, automotive, aerospace and packaging industries due to their several environmental and structural advantages. Compared to synthetic-fiberreinforced composites they are environmentally friendly, inexpensive to synthesis and possess high specific strength. However, the hove some drawbacks which limit their application. Hybrid composites using natural fibre and nanoparticles have been an area of intensive research over the last few years due to their capacity to improve the properties of the natural fibre composite by nanoparticles. In the present work, a hybrid composite was prepared with natural fibre from plant resources and nanoparticles either MWCNT or Glassflake reinforced in unsaturated polyester. The major issue is the preferential reaction of curing elements in thermoset resins with the natural fibre cells instead of participating in the polymerization reaction, where it was found to delay the curing reaction of thermoset resins (polyester, vinylester and epoxy) by decreasing the peak exothermic temperature and increasing the time to peak. Depends on the resin type, selecting a suitable surface treatment for the natural fibre was observed to mitigate this effect and improve the rate of curing reaction. It was also reduced the degradation temperature of the natural fibre composite. Besides, natural filler loading deteriorated the water absorption of the polymer composite. While it was



Low abrasion resistance with rough surface in worn area for neat polymer



Higher abrasion resistance with smooth surface in worn area for hybrid Composite

improved the wear resistance, the more filler, the less mass loss rate resulted. However, utilizing MWCNT as nanoparticles improved the resistance of hybrid polymer composite in both water absorption wear test.



Reduction in the rate of curing reaction of thermoset resins due to the reaction of catalyst with natural fiber instead of polymer



Natural fiber reduced the degradation temperature of natural fiber composite

Keywords: natural fiber composite, carbon nano tube, water absorption, abrasion test, curing rate of polyester

CRYSTALLIZATIONBEHAVIORANDMORPHOLOGYOFOCTAVINYL-POLYHEDRALOLIGOMERICSILSESQUIOXANESREINFORCEDPOLY(ETHYLENESUBERATE)NANOCOMPOSITESVANOCOMPOSITES

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Introduction: Polyhedral oligomeric silsesquioxanes (POSS) possess a structure of cube-octameric frameworks consisting of an inorganic cube-like core and eight organic corner groups, which may not only increase the thermal stability and mechanical properties but also act as nucleating agent for the crystallization of semicrystalline polymers. To our knowledge, poly(ethylene suberate) (PESub) and octavinyl-polyhedral oligomeric silsesquioxanes (ovi-POSS) nanocomposites have not been reported so far. In this work, the PESub/ovi-POSS nanocomposites at low ovi-POSS loadings were prepared via a solution mixing method; moreover, the effects of ovi-POSS on the crystallization behavior and morphology of PESub in the nanocomposites were studied in detail.

Methods: The PESub/ovi-POSS nanocomposites with 0.5, 1 and 2 wt % of ovi-POSS were prepared via a solution casting method and investigated with several techniques.

Results: The dispersion and morphology of ovi-POSS in the PESub matrix were first investigated with SEM on the fractured surfaces of the nanocomposites. A fine dispersion of Ovi-POSS was observed in the PESub matrix; moreover, the cubic crystals of ovi-POSS were also found in the polymer matrix. The nonisothermal melt crystallization behavior of PESub/ovi-POSS nanocomposites was studied with DSC at a cooling rate of 5 °C/min. The overall isothermal melt crystallization kinetics of PESub/ovi-POSS nanocomposites was investigated with DSC in a wide crystallization temperature range and analyzed by the Avrami equation. The crystalline morphology and crystal structure of PESub/ovi-POSS nanocomposites were studied with POM and WAXD.

Discussion: The nonisothermal melt crystallization behavior of PESub was enhanced in the nanocomposites, as the nonisothermal melt crystallization peak temperatures were higher in the nanocomposites than in neat PESub. The overall isothermal melt crystallization rates were faster in the nanocomposites than in neat PESub, although the crystallization mechanism remained unchanged. Both the nonisothermal and isothermal melt crystallization behaviors of PESub in the nanocomposites were apparently affected by the ovi-POSS loading. At a ovi-POSS loading of 0.5 wt%, the nanocomposite exhibited the highest nonisothermal melt crystallization peak temperature and fastest isothermal crystallization rate. With further increasing the ovi-POSS loading, the crystallization rates of the nanocomposites slightly decreased but were still faster than that of neat PESub. The crystalline morphology study revealed that ovi-POSS obviously increased the nucleation density of PESub spherulites in the nanocomposites, indicating the nucleating agent effect. The crystal structure of PESub was not modified in the nanocomposites.

Keywords: Crystallization, Morphology, POSS, Nanocomposites

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BIO-ACTIVE CLAY BASED HDPE NANOCOMPOSITES: A POTENTIAL FUNCTIONAL PLASTIC

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The ever-increasing concern for improvement of well-being and hygiene in our daily life owing to improved living standards throughout the world impacted the overall global research attention. In such times, investigation on antimicrobial materials has emerged as one of the primary research fields. Polyethylene represents an important class of commodity plastics having wide range of applications in our daily life and current living status demands high quality functional products of HDPE. Target applications are everyday commodity plastic items such as kitchen dustbins, crates that are used for transportation and storage of food items, baby toys, pipes, buckets and mugs, inner linings of washing machines etc.

Human history has seen clay being used in various applications because of its advantageous high ion absorption capacity along with its non-toxic nature and easy availability. Two types of antimicrobial clays, a copper based and a silver based has been synthesized by ion exchange reaction with sodium montmorillonite (Na-MMT) clay. The modification is confirmed by characterization techniques like XRD which revealed a disordered intercalated morphology and EDX which quantified the amount of copper and silver loading on these clays. Antibacterial assay and minimum inhibitory concentration (MIC) of synthesized two types of antibacterial clays is studied and compared. Both types of modified clays showed excellent bioactivity and low values of MIC.

Further, the synthesized clays were incorporated into HDPE to prepare antimicrobial HDPE nanocomposite films via melt mixing route in a twin screw extruder with varying clay concentrations. The nanocomposites were characterized using tools such as SEM and XRD which suggested uniform dispersion of clays in HDPE matrix. Tensile testing of the nanocomposites revealed the reinforcing effect of clays on the host HDPE matrix. The nanocomposites exhibited exceptional antibacterial activities of approximately 99.8% and a comparative analysis has been performed between the two types of HDPE nanocomposites to evaluate their effect against harmful bacteria. These bioactive materials can be potential candidates for replacing some commodity applications of HDPE plastics.

Keywords: HDPE, MMT, Nanoclay, Nanocomposites, Antibacterial

RHEOLOGICAL BEHAVIOR OF HDPE/NATURAL NEEDLE LIKE CLAY NANOCOMPOSITES UNDER SHEAR AND EXTENSIONAL FLOW

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In the present study, high density polyethylene (HDPE)-based composites containing different amounts of sepiolite [1-10 wt %] and different types of compatibilizers, PE-g-MAH [Optim and Fusabond] were prepared by melt compounding in a corotating twin screw extruder. These composites were prepared through masterbatch route containing 20% sepiolite with HDPE. The effect of sepiolite loading and compatibilizer type on the rheological behavior of HDPE-sepiolite nanocomposites was investigated with a strain-controlled rheometer. The melt-extensional properties such as extensional viscosity melt strength and drawability were investigate by using Rheotens set up and extensional viscosity was examined by using two different methods i.e. Rheotens set up and capillary Rheometer. High shear viscosity and melt fracture analysis were also carried out using Capillary rheometer.

It was found that the storage modulus, loss modulus and complex viscosity in oscillatory rheometry were highest for nanocomposite prepared using 10% w/w sepiolite. Incorporation of varying amounts of sepiolite enhanced the melt strength and extensional viscosity with slight reduction in drawability at high filler loading. These properties were further increased significantly with the addition of compatibilisers to the HD/Sepiolite composites. Extensional viscosity calculated from Wagner's master curve using Rheotens data as well as calculated by modified Cogswell method using convergent flow analysis from capillary data exhibited good agreement. High shear viscosity increased upon increasing filler content with slight decrease in onset of melt fracture at 10% w/w sepiolite loading. On the other hand, incorporation of compatibilisers did not affect the shear viscosity with slight increase in the onset of melt fracture.

Keywords: HDPE, Sepiolite, PE-g-MAH, Extensional properties, Melt fracture

EVALUATION OF DAMAGE TOLERANCE ON FILAMENT WOUND CFRP LAMINATES SUBJECTED TO LOW-VELOCITY IMPACT

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Introduction: Composite pressure vessels are nowadays used as fuel tanks of fuel cell vehicles and hydrogen filling stations. Although they have advantages such as high specific strength and stiffness, it is difficult to predict impact damage behaviour and associated residual properties. Therefore high cost cyclic pressurization test on an impacted vessel have been conducted. In this study, alternative test method for cyclic pressurization after impact is proposed. Filament wound composite laminates simulated as shoulder part of composite pressure vessels were subjected to low-velocity impact. Damage propagation was examined by destructive and non-destructive inspection. Residual tensile strength was measured with a tensile test and compared to virgin specimens.

Methods: Carbon-epoxy composite laminates were fabricated with wet filament winding as illustrated in Fig. 1 and separated from mandrel after cure. Stacking sequence of laminates was $[\pm 18]_5$. Low-velocity impact test was carried out with a drop-weight impact test apparatus. The impactor had a mass of 5 kg and a 16 mm hemispherical nose. The impact energies were 5 and 8 J that induce barely visible impact damage. Damage propagation was examined by microscopic observation to cross-section and X-ray photographs. Tensile test was carried out with universal testing machine for the specimens with and without impact.

Results: From cross-section and X-ray photographs, the specimen impacted by 5 J impact energy had a few matrix cracks and longer splitting with wide crack opening on the back face while specimen by 8 J had many matrix cracks and shorter splitting with narrow opening. The damage through-the-thickness showed pine-tree-pattern both 5 and 8 J. Results of tensile tests showed that no clear difference in tensile strength among each condition, as shown in Fig. 2.

Discussion: Although there were differences in damage formation between impacted at 5 and 8 J, both tensile strengths were similar to the result without impact. It seems that all impact damages were matrix damage such as crack and splitting which do not affect tensile strength considerably. **Keywords**: Composites, Filament winding, Low-velocity impact







IMPROVEMENTOFPHOTODEGRADATIONPOLYPROPYLENE NANOCOMPOSITES

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Introduction: As well as known, the photodegradation of isotactic polypropylene (iPP) materials is a serious problem for extending their applicability. In this work, we investigated the additional effects of carbon nanodots (CDs), showing obvious UV absorption, on the photodegradation of iPP by examining the change in tensile properties on irradiation.

Experimental Methods: The CDs particles with ca. 10 nm in diameter were prepared from the aqueous

solution of citric acid and ethylendiamine. iPP $(M_w=38\times10^4, M_w/M_n=4.9)$, free from photo-stabilizers, was used as base polymer. The iPP based nanocomposites were kneaded by mixing rollers with a fixed amount (60 to 600 ppm) of CDs in which a polycarbonate (PC) resin was used as compatibilizer. The iPP nanocomposites were then pressed at 180°C and under 200 kg·cm⁻², and quenched into a 100°C water bath to prepare the sample sheets with 100 μ m thickness.

Irradiation tests were carried out using ATLAS, SUNTEST cps plus. The sheets were irradiated with xenon lamp ($550W/m^2$) at $63^{\circ}C$ for 24 h. The tensile properties of the sample sheets were investigated at $25^{\circ}C$ and under the elongation speed of 20 mm/min.



Fig.1 Stress-strain curves of virgin iPP, irradiated iPP, and irradiated iPP/CDs nanocomposite.

Results and Discussion: Fig.1 compares the stress-strain curves of photoirradiated iPP and photoirradiated iPP/CDs nanocomposites (600 ppm) with that of virgin iPP. It was found that the virgin iPP is embrittled by photodegradation after 24 h irradiation, whereas the addition of nano CDs particles drastically improves photodegradation, and their elongation and strength are comparable with those of the virgin iPP. This is because CDs act as inhibitor of photodegradation due to their high ability of UV absorption. Furthermore, we examined the effects of the CDs contents on photostability of iPP. The photo-stability became gradually poor with the CDs contents less than 240 ppm.

Keywords: nanocomposite, polypropylene, carbon nanodots, photostability

EFFECTS OF MOISTURE ON THE PROPERTIES OF UNCURED AND CURED EPOXY-ANHYDRIDE BASED THERMOSETS

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Epoxy resin is a widely used material when preparing polymeric matrix composites, providing excellent mechanical strength, good adhesive properties and convenient processing routes. In many industrial applications the epoxy resin is cured with anhydrides (e.g. hexahydrophthalic anhydride) after the addition of metal-organic or amine accelerators. However, the resin and the anhydride hardener are sensitive to moisture absorbance, what affects the shelf lifetime of the uncured system. Furthermore, the mechanical properties of the final thermoset change when the resin / anhydride composition is stored under humid conditions before curing.

In this work, the influence of humidity on the shelf lifetime of the uncured epoxy / anhydride system was investigated. Moreover, the effect of moisture absorption on the final properties of the thermoset was investigated. Characterization of the effects of moisture absorption was done by rheological investigations, NMR spectroscopy and infrared spectroscopy. To characterize the curing behavior as well as the thermomechanical properties of the cured system various analytical methods, such as differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and infrared spectroscopy were employed.

The high sensitivity of the anhydride hardener to moisture results in the formation of a dicarboxylic acid, which is - in contrast to the liquid anhydride - a solid material. Thus, an increase of viscosity during storage under humid environment can be monitored. Upon hydrolysis of the anhydride the acidic product can also catalyze the curing reaction, what leads to a decreasing shelf lifetime. Differences in mechanical and thermal properties of the resulting thermoset become more pronounced with longer storage of the uncured system under humid conditions; this is due to altered curing behavior of the dicarboxylic acid with the resin compared with the anhydride / epoxy reaction when cured with a metal-organic or amine accelerator.

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EFFECT OF TOUGHNESS-ENHANCING ADDITIVIES ON THE HIGH TG THERMOSET RESIN FOR CARBON FIBER REINFORCED COMPOSITES

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Carbon fiber-reinforced polymer composites with the superior mechanical properties and low density have been considered as one of the promising lightweight materials for structural parts. Recently, automotive industry requires a mass production system of the composite parts, in which cost reduction and fast speed of manufacturing process are needed. Liquid molding-based process is one of approaches for high speed process of composite products and some companies have already produced the composite parts including a matrix resin with a low glass transition temperature (Tg). The parts can show a problem of dimensional stability especially when they are painted and dried at a high temperature oven. Therefore, there is a demand for developing a new thermoset resin which has a high Tg as well as fast cure characteristic. In this work, we develop a new thermoset resin exhibiting a high Tg/fast-curing property. The resin system consists of general epoxy resins, multifunction epoxy resins and amine hardeners. However, since the resin has poor toughness due to the brittle characteristics, a toughness-enhancing additive is necessary. The mechanical properties such as tensile, compressive, and shear properties for the composites as well as resin itself are measured. The Tg of resin and corresponding composites was measured by DSC and TMA. Experimental

results showed that the resin system could be cured at ~ 120° C and simultaneously have a high Tg of more

than 160°C. In particular, effect of toughness-enhancing additives on the toughness of the developed resin is discussed. The resin system is applied to the fabrication process, HP-RTM and the feasibility as a matrix resin in the structural composite materials for automotive is evaluated. From this work, we can provide a new resin system which is suitable for automotive composite parts.

Keywords: Thermoset resin, Glass transition temperature, Toughness, Composites

CHARACTERIZATION OF RHEOLOGICAL PROPERTIES OF PCS (POLYCARBOSILANE) IN THE VICINITY OF CAPILLARY NOZZLE OF MELT SPINNING PROCESS

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Silicon carbide (SiC) fibers have attracted the attention of many researchers as a high-performance reinforcement material due to their excellent thermos-mechanical properties such as high tensile strength, high wear resistance, low thermal expansion, etc. at high temperature of over 1000°C Melt spinning process is one of the most useful commercial spinning processes to produce thermoplastic fibers. It has been reported that SiC fibers can be produced from thermoplastic polycarbosilane (PCS) precursors by using the melt spinning process, followed by the curing and pyrolysis, and the precise control of structure and formation of PCS as-spun fiber in melt spinning process has emerged as one of important elements to obtain high-performance and high value SiC fibers. However, the studies on the fiber formation and rheological behavior of PCS in melt spinning process is relatively still rarer. In this study, the characteristic rheological behaviors of PCS in the vicinity of capillary nozzle under industrial melt spinning conditions was investigated. PCS was melted by using single-screw extruder under an atmosphere of N_2 gas, and extruded through spinning nozzle by metering gear pump. Hole diameter of capillary nozzle in the spinning nozzle was 0.3mm with L/D 5.0. Entrance pressure (ΔP) of molten PCS in the vicinity of capillary nozzle was measured with a pressure sensor positioned between the gear pump and the nozzle by changing throughput rate (shear rate) and nozzle temperature. Shear rate at wall and nozzle temperature were controlled in the industrial spinning conditions of 2000 ~ 3500 sec⁻¹ and 280 ~ 295°C, respectively. Apparent dynamic viscosity (poise) of molten PCS in the capillary nozzle were calculated by using Hagen-Poiseuille Eq.. Poise of molten PCS showed drastic decrease from 1,303 to 324 g/(cm·sec) as nozzle temperature increased from 280 to 295°C at the shear rate of 3500 sec⁻¹. It is also interesting to note that the PCS showed a shear thickening behavior as shear rate increased from 2000 to 3500 sec⁻¹ at the nozzle temperature of 280°C and the behavior showed a tendency to decrease as nozzle temperature increased. These characteristic rheological behaviors are rare behaviors cannot be generally observed in the commercial thermoplastic polymer such as PET, Nylon, PP, etc., and it is speculated that these results seemed to be cause by the unique and complex non-linear molecular structures with various branches of PCS polymer.

SiC fibers, polycarbosilane, rheology, melt spinning

SALT-TOLERANT HYDROGEL-COATED MESH WITH SUPERHYDROPHILIC/UNDERWATER SUPEROLEOPHOBIC PROPERTY FOR EFFECTIVE OIL–WATER SEPARATION

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Introduction: Extraction of oil from seawater is a worldwide urgent issue due to frequent oil spill accidents and increasing oily waste water, which have bad influence on human health and marine environment. Recently, based on wettability. However, oil-water separation in complicated and harsh environment such as high salt Figu

concentration of seawater is challenging. In nature, surface of seaweed *S. Japonica* is inherently superoleophobic in highly saline conditions. Here, taking advantage of alginate gel as a bioinspired material of seaweed, we fabricated hydrogel-coated mesh with calcium alginate. Alginate-coated mesh exhibits effective separation of oil/water mixture without oil pollution.

Methods: Polyester mesh was cleaned and hydrophilized by KOH treatment. Hydrophilic mesh was firstly dipped into polyethyleneimine (PEI) solution. After dried by air flow, the mesh was immersed into sodium alginate solution and subsequently gelled in CaCl₂.

Results: Water contact angle in air (Fig. 1a; $<5^{\circ}$) and underwater oil contact angle (Fig. 1b; 160°) indicate that alginate-coated mesh possesses superhydrophilicity and underwater superoleophobicity. Moreover, oil–water separation was carried out by putting alginate-coated mesh between two



Figure 1. Photo images of (a) water in air and (b) oil underwater deposited on alginate-coated mesh.



Figure 2. Separating the mixture of oil and water (dyed with brilliant blue).

glass pipes. 200 mL of oil-water mixture is poured into the mesh and the separation is achieved solely by gravity with separation efficiency >99%, where water penetrates through the mesh while oil is rejected.

Discussion: Superhydrophilic/underwater superoleophobic property of alginate-coated mesh indicate that the mesh has higher affinity to water than that to oil. Retained water on alginate gel blocks the permeation of oil to realize efficient oil–water separation without polluted by oil contamination.

Keywords: oil-water separation, underwater superoleophobicity, hydrogel, calcium alginate

ONE STEP FORMATION OF JANUS TEXTILES AND GRADIENT FUNCTIONAL FILMS VIA SPRAY DISTANCE CONTROL OF NANOPARTICLES/POLYMER COMPOSITE

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Introduction: Bioinspired by lotus leaves, many researchers have attempted to impart superhydrophobic properties both for scientific interest and commercial applications. Despite considerable efforts, only limited success has been achieved in terms of mechanical durability. To overcome these problems, our group previously reported mechanically durable superhydrophobic surfaces by spraying nanoparticles/polymer composite. Recently, we discovered spraying distance between sprayer and substrate (SD) can strongly affect on nanoparticles/polymer ratio, surface roughness, and penetrance of spraying solution into fibril substrates. Here, we newly developed 2 types of advanced superhydrophobic material using SD controlled one step spraying; 1. an asymmetric superhydrophobic/superhydrophilic Janus textile is designed by controlling the wettability and penetrance of spraying solution. 2. Gradient density superhydrophobic coating is designed by continuously SD changing spray method (Gradient spray method). These advanced coatings and a coating method can contribute to scientific and industrial fields.

Methods: A cocktail of hydrophobic SiO_2 nanoparticles and ethyl-alpha-cyanoacrylate (EAC) in acetone is sprayed for composite coating. EAC was used to enhance the mechanical durability. We changed a SD ranging from 10 to 60 cm and measured water contact angle (WCA), surface morphology, and the penetrance into textiles.



Figure a) Photo image of superhydrophobic/ superhydrophilic Janus membrane. b) Elemental distribution of gradient density superhydrophobic coating in depth-probe.

Results: Water contact angle value and surface roughness of coatings are increased as the increase of a SD; i.g. the coating of SD=10 cm performed hydrophilicity (WCA=75.0°) and smooth structure (R_{rms} =1.097 µm) whereas the coating of SD = 30 cm performed superhydrophobicity (WCA=154.5°) and roughened structure (R_{rms} =20.256 µm). Moreover, the penetrance of the solution become small as the increase of a SD, that textile became both side superhydrophobic in case of SD=10 cm while textile showed Janus property in SD=30 cm (Figure a). Furthermore, we designed gradient density structure by changing SD from 10 cm to 50 cm continuously. The depth directional elementary revealed the gradient density (Figure b).

Discussion: The changes along with SD are induced by the evaporation ratio of solvent and following instant polymerization of EAC (i.e. SD: high = solvent evaporated and EAC polymerized mixture deposits on substrate).

Keywords: superhydrophobicity, spray, mechanical durability, Janus, gradient

A BIOLOGICALLY INSPIRED ATTACHABLE, SELF-STANDING NANOFIBRE SHEET FOR VERSATILE USE IN OIL–WATER SEPARATION

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Introduction: Oil pollution in water is a worldwide problem, causing long-term effects on the health of living organisms and the environment. Recent approaches to oil–water separation are based on the selective

wetting of oils, chemicals and water onto 2D or 3D porous materials. Although the development of selectivewetting materials enabled highly effective separation, there are still challenges of practical use in terms of cost, scale and material dimension limiting the strategy. Here, Uloborus walckenaerius spider webs provided the inspiration for attachable, self-standing nanofibre sheets (NF-S). The developed product adds selective wettability against oil–water mixtures to both 2D and 3D materials by attaching or covering them, leading to successful separation through a facile, scalable and low-cost process.

Methods: The NF-S was fabricated by an electrospinning of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and ethyl-alpha-



cyanoacrylate (Et-CA) mixture to adjust strength and elastic properties. The threshold of wetting/de-wetting were analysed by measuring contact angle of EtOH/water mixture varying surface tension γ with ratio. In addition, wetting/de-wetting behaviours on the NF-S were observed by time-lapsed imaging of air/water/oil/NF-S interfaces.

Results: Contact angles measurement with different surface tension liquid (Fig. (a)) reveals that there is a threshold of wetting/dewetting between 36.1–38.6 mN m⁻¹. Thus water (γ =72.8mN m⁻¹) does not penetrate the NF-S whereas gasoline, Decane, *n*-Dodecane, Hexadecane, Toluene (γ =21.6-32.0mN m⁻¹) penetrate the surface.

Discussion: The results revealed wetting/de-wetting threshold to study separation conditions of single liquid/NF-S interfaces. We further considered a case of oil/water coexisting on NF-S. When oil was cast on NF-S, we found a part of oil being infused on NF-S to form oil layer whereas most oil penetrates NF-S (Fig. (b), left). Thus, oil infused NF-S blocked water penetration because liquids were immiscible (Fig. (b), right) to realize successful separation from mixture.

Keywords: oil-water separation, electrospinning, nanofibre, slippery surface

Fig. shows (a) Contact angles of liquids with different surface tensions and (b) photo images of oil on NF-S (left) and water on oil-infused NF-S (right).

COPPER PLATED NANOFIBERS AS TRANSPARENT ELECTRODE VIA AUTOCATALYTIC ELECTROLESS DEPOSITION

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Introduction: Transparent Conductive Electrode (TCE) is widely used in optical and electrical devices like touch panel and solar cells. Recently, not only Indium-doped Tin Oxide (ITO), but also ITO alternative such as metal nanowires are attracted because ITO has problem in depletion. TCE is also promising material as a heater for de-icing and de-fogging in automobile windows. Using metal nanowires (NWs) for heater is sometimes undesirable because high conductive metal such as Ag or Cu is highly sensitive to oxygen and humidity. In this study, we fabricated Cu nanowire including a little amount of Ni and P by electroless deposition and investigated heater properties. This electrode can be applied to automobile windows as a de-icing and de-fogging heater.

Methods: Procedure of fabricating Cu plated nanofibers is shown in scheme 1. Poly vinyl butyral (PVB) and SnCl₂ was dissolved in ethanol and electrospun onto PET substrate. After that, substrate with nanofibers was activated in PdCl₂ aqueous solution. As a copper plating bath, CuSO₄·5H₂O was dissolved in ion exchanged water (IEW) with NiSO₄·6H₂O. Activated nanofibers were immersed in plating bath.

Results: Figure 1 shows scanning electron microscopic images and energy dispersive x-ray spectroscopic images of Cu plated nanofibers. The average diameter of nanofiber before plating was 143 nm. After plating, the average diameter increased to $1.78 \mu m$. Additionally, we demonstrated de-icing test to evaluate heater property.

Discussion: By controlling electrospinning and plating time, transmittance and sheet resistance were tuned. From fig. 1, Cu is plated along with PVB nanofibers with Ni and P. The weight ratio was 84.7%, 10.4%, 4.9%, respectively. Cu plated nanofibers including Ni and P can improve anti-corrosive property.

Keywords: nanofiber, electrospinning, electroless deposition, heater, de-icing



Scheme 1. Fabrication method of copper plated PVB nanofibers



Images and Energy Dispersive X-ray Spectroscopic Images of nanofibers.

OPTIMIZATIONOFACIDHYDROLYSISFORNANOCRYSTALLINECELLULOSEPRODUCTIONFROMRICEHUSK PULP USINGRESPONSE SURFACE METHODImage: CelluloseImage: Cellulose

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Introduction: Nanocrystalline Cellulose (NCC) is one of the most abundant renewable bio-nano-materials, produced in massive quantities from lignocellulosic biomass. For the production of NCC, the classic and most widely used method is acid hydrolysis of a purified cellulose starting material. Different inorganic acids, most commonly sulfuric and hydrochloric acid, have been used for this purpose under various process parameters. The choice of process conditions and parameters inevitably affect NCC yield. The most efficient way to optimize a production process and maximize yield is the Design of Experiments (DOE) method. DOE is a systematic approach for determining the relationship between different process parameters (x_1 , x_2 , x_3 etc.) and process outputs (y_1 , y_2 , y_3 etc.). In this study, three factors was used to analyse the production of NCC from rice husk pulp by sulfuric acid hydrolysis to elucidate the relationships between the acid concentration (X_3), hydrolysis temperature (X_2), hydrolysis time (X_1) and NCC yield.

Methodology: The Box-Behnken experimental design of acid hydrolysis for NCC production from delignified rice husk pulp was performed by response surface method (RSM). Fifteen experimental runs (Table 1) were performed at different time, temperature and acid concentrations in order to optimize the process.

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Experiment	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Time (X ₁)	155	10	300	155	155	155	300	10	155	300	10	10	155	300	155
Temp. (X ₂)	100	100	70	70	70	100	70	40	40	100	70	70	40	40	70
Conc. (X ₃)	70	60	70	60	60	50	50	60	70	60	70	50	50	60	60

The production of NCC was considered as a main response from this experimental investigation as denoted by Y in the Equation 1. The experimental data were analyzed by the response surface regression procedure using the following second order polynomial equation:

Results and Discussion: Response surface plots and contour plots are based on the model equations obtained in the regression analysis. The response surface plots of NCC production indicate that the response passes through a maximum and then decreases. Figures 1(a, b) and 1(c, d,) represent the contour and response surface plots of the NCC production. The optimized conditions for maximum NCC production are time (200 minutes), temperature (50 $^{\circ}$ C) and concentration (60 %).









(a) NCC vs X_1 , X_2

(b) NCC vs X₁, X₃

(c) NCC vs X_1 , X_2



Figure 1: Contour (a, b), and surface (c, d) plotting of NCC at various parameters

The model Eq. 2 was obtained for all responses, where X_1 , X_2 and X_3 are the parameters such as time, temperature (temp.) and concentration (conc.), respectively. The factors with positive coefficients have a positive effect on the NCC production and vice versa. From these responses it can be seen that NCC production first increased, reach a maximum and then decreased as the process parameters increased. R^2 value is the percentage of response variable variation that is explained by its relationship with one or more predictor variables. The R^2 values for this study was 0.72. For the model to be valid, R^2 should be greater than 0.8. The value achieved for R^2 in this study is an indication of moderately fitting of experimental data by the response surface method.

Keywords: Modeling, Optimization, Acid Hydrolysis, Cellulose Pulp, Response Surface Method

NUMERICAL SIMULATION OF SLOT-COATING FLOWS OF CONCENTRATED DISPERSION SYSTEMS OF DISC-LIKE PARTICLES USING STOCHASTIC COMPUTATION FOR PARTICLE MOTION

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Slot coating flows of concentrated dispersion systems of disc-like particles were numerically simulated. In this simulation, stochastic simulations of the orientation motion of disc-like particles were coupled with the macroscopic computation of coating flows. In addition, the effect of evaporation of solvent from the film interface was considered.

In the stochastic simulation of the particle motion, disc-like particles were approximately described by oblate spheroidal particles, and the interaction among the particles was expressed using a Maier-Saupe type mean field potential function. Furthermore Brownian configuration field method was applied to compute the particle orientation field. The macroscopic calculation of coating film flows was performed using the finite element method. The SUPG/PSPG method was employed to numerically stabilize the flow computation.

In the present study, slot-coating flows of concentrated suspension of disc-like particles were numerically analyzed. The present simulation captured that the particles highly oriented to make the direction of its rotation axis nearly perpendicular to the flow near the free surface of a film just downstream of a die exit. The orientation relaxed as the particle flowed downstream. However, the increase in the particle concentration due to solvent evaporation from the film surface derived the phase transition from isotropic states to nematic states and hence the particle orientation was fixed and the degree of the orientation increased again and kept relatively high values.

The orientation distribution of particles can be evaluated from the simulation results. The change in the orientation distribution along the flow provided detail information of processes such as the particle orientation near the die exit, the orientation relaxation, and re-orientation due to the solvent evaporation. Such information is a characteristic result of the stochastic simulation considering individual behavior of

particles and is useful for the analysis of the processing of functional coating films. The coupling of the stochastic simulation for microstructures of dispersion system and the macro flow computation is therefore an effective methodology of the numerical simulation of polymer processing considering flow-induced structures in materials.

Keywords: Disc-like particles, Dispersion systems, Coating flows, Orientation distribution, Stochastic simulation



ENHANCEMENT OF MECHANICAL PROPERTIES FOR POLY(METHYL METHACRYLATE) BY ADDITION OF LOW-MASS COMPOUND

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Introduction: PMMA is widely employed owing to its high transparency and high modulus. However, further enhancement of the rigidity is required for various applications to avoid the hard-coating process. In this study, a small amount of a low-mass compound (LMC) is added into poly(methyl methacrylate) (PMMA) and several measurements are performed to study the effect of LMC. The antiplasticizing behaviour of PMMA is observed, and the storage modulus *E*' at room temperature is increased.

Methods: A commercially available PMMA and poly(ethylene terephthalate) oligomer (C_2Ph) were meltmixed in an internal batch mixer at 200 °C. After mixing, flat sheet samples were obtained by using a compression-molding machine. The temperature dependence of the oscillatory tensile moduli in the solid state, such as storage modulus *E*' and loss modulus *E*'', was measured from -100 to 180 °C using a dynamic mechanical analyzer.

Results: Fig.1 shows the temperature dependence of dynamic tensile modulus at 10 Hz for PMMA and PMMA/C₂Ph (90/10). The glass-transition temperature (T_g), defined as the peak temperature in the E" curve, is shifted to low temperature by adding C₂Ph, which is known as a plasticizing behaviour. Moreover, it should be noted that the storage modulus E' at room temperature for the blend is found to be higher than that for the pure PMMA.

Discussion: A conventional plasticizer is known to decrease the modulus due to the increase in the free volume fraction of a polymer. In contrast, C₂Ph enhances the modulus in the glassy region, which is known as antiplasticizing behaviour. Furthermore, it is obvious that the C₂Ph addition barely affects the \Box relaxation mode, i.e., localized motion, which is different from the antiplasticized polycarbonate.

Keywords: poly(methyl methacrylate), antiplasticization



Temp. $^{\circ}C$) **Fig. 1** Temperature dependence of (circles) tensile storage modulus E' and (diamonds) loss modulus E'' for (closed symbols) PMMA and (open symbols) PC/C₂Ph at 10Hz.

EVOLUTION OF FIBRE MORPHOLOGY AND RHEOLOGY IN A POLYMER COMPOSITE

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The purpose of this work is to understand the effects of changing fibre orientation on the rheological behaviour of molten glass fibre/polymer composites. Pellets containing 30% by weight of short glass fibres in a polyamide-6 matrix were compression moulded at 250°C to prepare 25mm diameter discs for rheological testing. A rotational rheometer with a parallel plate configuration was used with the gap set between 1mm and 2mm to ensure that gap effects are negligible. Samples were subjected to steady shear rates ranging from $0.01s^{-1}$ to $10s^{-1}$ in the clockwise direction and the transient rheological response provided quantitative evidence of the viscosity overshoot and the steady state viscosity. Once the viscosity reached a steady state, the sample was cooled to room temperature using a fan blower and carefully removed from the rheometer for morphological analysis. Fibre orientation and volume fraction data were captured using an X-ray Computed Tomography (X-CT) machine with a voxel resolution of 2µm and power rating of 2W. Post processing of the X-CT images was carried out using VGStudio Software to measure the extent of fibre orientation at steady state conditions. With an increasing shear rate, it was observed that the magnitude of the viscosity overshoot and steady state viscosity decreased while the extent of fibre orientation at steady state increased in the shearing direction. Samples containing different fibre orientation states were then subjected to dynamic oscillatory shearing between 0.01rads⁻¹ to 100rads⁻¹ using a strain amplitude that lay within the Linear Viscoelastic Region (LVR) of the sample. Following validation of the Cox-Merz rule, shear viscosity for a particular shear rate and state of fibre orientation was obtained from the oscillatory testing results. Using this data, an attempt will be made to develop a constitutive model to predict the transient rheological behaviour incorporating shear rate, shear stress, fibre orientation and time.

Keywords: Fibre orientation, Transient viscosity, Computed tomography, Polymer composites

CARBON/IRON OXIDE COMPOSITE NANOFIBER AS SELF-STANDING ANODE FOR LITHIUM ION BATTERY

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Introduction: Lithium ion batteries (LIBs) are the most popular energy storage in the various fields. LIBs demand more energy density for improving performance. Most studies were related to two types of approach. First one is the use of the active materials having higher theoretical capacity like iron oxide and silicon than graphite (372 mAh/g). The problem is that those materials are difficult to be used because of volume changes while charge and discharge. Second approach is the reduction of the non-active materials like conductive agent, binder, separator, electrolyte. However the electrode should have good conductivity itself. Here, based on both approaches, we fabricated pressed iron oxide/carbon composite nanofibers

(ICNF) as self-standing anode for LIBs. We investigated for the effects of pressure and temperature in carbonization which is important to conductivity.

Methods: Bicomponent nanofibers were fabricated via electrospinning of polyacrylonitrile (PAN) and Iron(III) Nitrate Nonahydrate dissolved in N,N-dimethylformamide. The nanofibers were first pressed and then heated in two steps to obtain pressed ICNF. The morphology and crystallinity and electrochemical performance were analysed.

Results: While press treatment increased junctions of fibers which improved conductivity, the surface morphology of the pressed ICNF was rough which can be caused by high density of iron oxide near by surface. The highest discharge capacity of ICNF and pressed ICNF was 609.3 mAh/g and 572.7 mAh/g, respectively. The discharge capacity of ICNF maintained 60.5% at 2500 mAh/g compared to the highest one at 100 mAh/g. Press treatment increased the density of fibers which improved capacity per volume from 138.2 mAh/cm³ to 325.8 mAh/cm³.

Discussion: It was found that press treatment changed crystallinity and surface morphology. This probably decreased rate performance of pressed ICNF nevertheless press treatment improved conductivity.

Keywords: electrospinning, carbon nanofiber, Li ion battery

Figure 1. Scanning Electron Microscope images of pressed ICNF (left) and ICNF (right).



Figure 2. Discharge capacity of pressed and without pressed ICNF at various currents.



IMPROVEMENT OF THE PERFORMANCE OF SELF-STANDING ANODE FOR LITHIUM ION BATTERY BY OPTIMIZING ELECTRODEPOSITION OF IRON OXIDE ON CARBON NANOFIBER

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Introduction: The improvement on specific capacity of lithium ion battery (LIB) is required. Iron oxide is a promising material for its high theoretical capacity and abundance. However, iron oxide is difficult to be used because of volume changes while charge/discharge and poor conductivity. In order to overcome these problems, composition of iron oxide and carbon nanofiber

(CNF) has been studied. CNF fabricated by heating electrospun polymer nanofiber has good conductivity and can accommodate expansion of iron oxide. In this study, electrodeposition was used because it is simple way and polymer nanofiber can be carbonized at high temperature without catalysis effect of iron oxide which enables to improve conductivity. The CNF deposited by iron oxide can be selfstanding electrode which does not require non-active components. Here, we investigated the effects of temperature parameters during the fabrication process of CNF on the conductivity and fiber structure. Effects of pH in solvent and



Figure 1. Sheet resistance of CNF.

Figure 2. Coulombic efficiency of CNF treated at 1000°C.





applying voltage were also studied to control morphology of deposited iron oxide.

Methods: Polyacrylonitril dissolved in N,N-dimethylformamide was electrospun. The electrospun nanofiber then stabilized and carbonized at 1000°C. Iron oxide was electrodeposited in FeSO₄ (pH=4.1). And then, CNF was annealed to get CNF deposited by iron oxide. Morphology and electrochemical measurement of the fiber was performed.

Results: Sheet resistance of CNF decreased from $3.7 \times 10^6 \Omega/sq$. (700°C) to $4.1 \times 10^2 \Omega/sq$. (1000°C) (Fig. 1). Coulombic efficiency of CNF treated at 1000°C was 100.8% after 100 cycles (Fig. 2). From these results, it was found that treatment at higher temperature can improve the performance of the battery. Deposited iron oxide with needle-like morphology was on the CNF (Fig. 3(a) (b)).

Discussion: It was found that conductivity of CNF increased with treatment at high temperature, which can improve rate capability without any conductive agents. From Fig. 3(b), while surface area increased by nanorods structure, the thickness of iron oxide was not uniform.

Keywords: lithium ion battery, iron oxide, electrodeposition, carbon nanofiber

NEAR-INFRARED REFLECTIVE FILM FOR HEAT SHIELDING WINDOWS VIA LAYER BY LAYER METHOD

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Introduction: Energy saving is one of the most important worldwide issues in our environment. Especially, heat shielding for windows is highly demanded because a main source of energy consumption

in buildings is cooling devices which is used for maintaining comfortable room temperature. In order to reduce the energy used for cooling inside buildings, it is effective to shut off near-infrared (IR) light passing through windows from outside sunlight. In this work, we fabricate layer by layer deposited thin polymer films with designed film thickness and refractive index to selectively reflect near IR light for the application of heat shielding window.

Methods: Aqueous solution of cationic Titanium(IV)-bis-(ammonium lactate)dihydroxide (TALH) and anionic Poly(diallyl dimethyl ammonium chloride) (PDDA) was alternatively adsorbed onto cleaned glass substrates by electrostatic force as a high refractive index layer (H-layer). Colloidal dispersion of SiO₂ and PDDA solution was likewise deposited on the substrates to form low refractive index layer (L-layer).

Results: In order to reflect IR light with wavelength (λ) of 900 nm, film thickness (*d*) should be designed as $d=\lambda/4n$ where *n* is refractive index of H- and L-layer. Therefore, desirable parameters are as below: n=1.7 and d=132 nm for H-layer, and n=1.3 and d=173 nm for L-layer. We measure



Figure 1. Film thickness and refractive index with different number of bilayer (a: High refractive index layer, b: Low refractive index layer). (c) Measured and calculated transmittance of the film.

film thickness and refractive index of H- and L-layer with different number of bilayer to decide optimal number of bilayer (Fig. 1a,b). When we piled up H- and L-layer 5 times alternatively, the film showed nearly 50% reflection at the wavelength of 1200 nm (Fig. 1c).

Discussion: Reflection peak at around 1200 nm in transmission spectra was observed, which was larger than that of theoretical value (900 nm). We considered that this was due to the change of film growth in the latter part of film deposition.

Keywords: near infrared reflection, layer by layer, optical thin film, heat shielding

NOVEL EXTENSION OF CONTINUOUS MULTI-LAYERING CO-EXTRUSION TECHNOLOGIES TO TUBULAR STRUCTURES

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Layer-multiplying co-extrusion of incompatible polymers was developed in the 1970s by Dow and has recently evolved to the fabrication of multi-layered nanostructures with thousands of layer, with individual layer thickness down to a few tens of nanometers. This yields much improved barrier, thermal and mechanical properties and has opened up a whole new range of applications, from GRIN lenses, to ultrahigh barrier packaging, to optical storage, among others. However, when the differences between the viscosity and/or elasticity of the coextruded materials are relatively high, flow instabilities arise during the processing that lead to non-uniform layers and non-useful multilayered films. We have recently developed a new multi-layering die that largely overcomes this issue and is able to layer melts with up to 10:1 viscosity ratios and 100:1 elasticity ratios and still maintain layer integrity.

In this presentation, we expand this work for the first time away from planar structures, i.e., sheets and films, to the multi-layering of rheologically matched and mismatched tubular structures, which opens a completely new world of applications yet again, from ultra-high barrier blow-molded parts, to medical devices.

Keywords: Multi-layering co-extrusion, rheology mismatch, high-barrier tubes and pipes

POLYETHYLENE MODIFICATION EFFECT OF THE SIDE CHAIN CRYSTALLINE BLOCK COPOLYMER WITH HAVING THE DI (ETHYLENE GLYCOL) ETHYL ETHER ACRYLATE IN THE FUNCTIONAL SITE.

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Introduction: The Side Chain Crystalline Block Copolymer (SCCBC) is composed with a side chain crystalline monomer unit and a functional monomer unit. It can be adsorbed to a polyethylene (PE) crystalline surface through crystalline supramolecular interaction.

In this time, we polymerized new functional SCCBC and measured its function.

Methods: The block copolymer was polymerized by living radical polymerization method. Behenyl acrylate (BHA) was selected as the side chain crystalline monomer and the Di (ethylene glycol) ethyl ether

acrylate (DEEA) was selected as the functional monomer. first step polymerization, behenyl acrylate (2.03g) was with butyl acetate (4.01g), and then added block builder (0.162g) as an initiator. The temperature was set to 105°C polymerization was carried under a nitrogen atmosphere. hours, the DEEA solution (12.0g was diluted with 12.0g acetate) was added. After 72 hours, we stopped the polymerization and obtained yellow powder (9.31g). The polymer was analyzed by FT-IR and elemental analysis.



Fig.1 IR spectrums of SCCBC1 (black), DEEA (red) and behenyl acrylate (blue).

The PE film was modified by dipping method with 0.5wt% SCCBC/ butyl acetate solutions. The dipping time was 60 second. We also modified PE film by coating the SCCBC solution. Evaluation for modifying functionality of SCCBC was measured by contact angle.

Results: Fig.1 shows the FT-IR spectrums of polymerized SCCBC and each component monomers. Comparing of these spectrums, the SCCBC spectrum have both specific peaks of each component

monomers. The results of elemental analysis shows that the molecular weight of each unit was about 3,800g/mol (BHA): 93,000g/mol (DEEA). Fig2 shows the results of contact angle measurement. The contact angle of original film was 83.3°. The contact angle of dip modified film was 69.7° and coat modified film was 60.8°.



Discussion: From the results, we polymerized new functional SCCBC by living radical polymerization. And by using this SCCBC, we can modify the surface properties of PE from hydrophobic to hydrophilic.

Keywords: Side Chain Crystalline Block Copolymer (SCCBC), living radical polymerization, contract angle, polyethylene (PE), surface modification.

THE EVALUATION OF POSSIBILITY; APPLICATION OF SIDE CHAIN CRYSTALLINE BLOCK CO-POLYMER (SCCBC) FOR PRETREATMENT PROCESS OF NON-ELECTROLYTIC PLATING

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Introduction: The non-electololytic plating is widely used as an affective primer technique for nonconductive material. Especially in etch process, acrylonitrile butadiene stylene (ABS) dipped in cronic-acid sulphic solution is generally method. However, it is well known that the harmful wastewater, including chronic acid has generated. In this study, we investigate the possibility of substitute the side chain crystalline block co-polymer (SCCBC), which has the alkane-block and tertiary amine- block, for etch process.

Methods: The degreasing polyethylene (PE) sheet was dipped into modifying solution (SCCBC butyl acetate solution) at room temperature, pulling and dried, to adsorb Pd-Sn colloid. D was precipitated t HCl. The Pd catalysed PE sheets was coated by non-electlolyic Ni plating.

Results: The results of observation, the color of Pd catalysed PE film were changed white to brown. It shows that, the alkane-block had been adsorbed at the PE surface and the tertiary amino-block have covered PE, thus, Pd-Sn colloid had adsorbed at PE surface. On the other, after non-electrolytic plating, metal layer had been formed on PE surface, although, many crack have been occurred and detached from PE. This results from the coating film stress by metal layer.



Figure.1 The image of appearances for un-treated (a), Pd-catalyzed (b), afuter non-electrolytic plating (c), 80° C annal (d), and 120° C anneal (e).

Discussion: After metal layer detached from PE, the surface turned white. It seems that, the SCCBC coated on PE surface, couldn't withstand the coating film stress by Ni layer. Accordingly, the SCCBC coated PE was annealed (80° Cor 120° C × 1h). The 80° C annealed sample had not have a change, but the 120° C annealed sample had the point that held a metal layer.

Keywords: PE, block co-polymer, non-electlolyic plating, coating film stress

INFLUENCE OF SELF-ORGANIZATION PROCESS TO THE POLYIMIDE MEMBRANE PROPERTIES

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Introduction: Polyimide (PI) is known as the typical super engineering plastic with having high glass transition temperature and elastic modulus. These high physical properties come from the strong aggregation force between PI molecules. From the fact, the physical and structural properties of PI film much depend on the self-organization process in the casting process of poly amic acid (PAA) solution. In this time, we investigated the holding time dependence in the casting process to membrane structure with using different viscous PAA solution.

Methods: In this time, we used BPDA (acid) and ODA (amine). The molar ratio is 1:1. BPDA and ODA dried at 80°C, 24 hours. At first, we dissolved ODA with NMP and stirred for more than 20 minutes at 40 °C. After that, we added NMP solution of BPDA little by little to completely dissolve to BPDA. Under the nitrogen atmosphere, we stirred for about 3 days with mechanical stirrer at 40 °C. By this process, we polymerized PAA solution. For the creation of PI membrane, at first, we casted PAA solution about 30µm thickness by using an applicator on the glass plate. After settling various holding times (0, 10, 60min) as the self-organization process, we peel off the PAA gel film from the glass plate. And then the gel film was fixed with a tenter and heated at 300 °C 30 minutes to produce the PI film. The propertied of PI films were analyzed by X-ray diffraction and Scanning Electron Microscope.

Results: The Figure shows the X-ray diffraction patterns of PI films. The settled direction of the film is parallel to the draw direction of PAA solution. From this figure, at 0 minute holding time, the X-ray diffraction pattern from 10 to 20 degree is almost flat and there is not specific peak in the scattering profile. On the other hand, with increasing the holding time to 10 minutes, some peaks begin to appear around 15 to 20 degree. With increasing the holding time to 60 minutes, there begin to appear a clear shoulder



around 25 degrees. These results indicate that with increasing the holding time at the stage of PAA solution casting, the PAA molecules begin to coagulate each other, and create some self-organized structure. The structure does not destroy in the process of imidization. In addition, almost the same results are obtained in the perpendicular direction to the draw direction.

Discussion: High viscosity PAA solution will make better structured film than low viscosity solution.

Keywords: Polyimide, Self-organization.

LARGE SCALE FLOW-MEDIATED FORMATION AND POTENTIAL APPLICATIONS OF SURFACE NANODROPLETS

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Microscopic droplets located on a solid substrate in contact with an immiscible liquid promise a broad range of applications in miniaturised analytical techniques, fabrication of antireflective coatings, high-resolution near-field imaging techniques and many others. A simple method of producing oil nanodroplets with desirable morphology is a bottom-up approach called solvent exchange, where nanodroplets nucleate and grow, as a good solvent of oil is displaced by a poor solvent. In this work, we have achieved the production of surface nanodroplets over a large surface area on planar or curved surfaces, guided by the principles of the solvent exchange. The droplet size is uniform over the entire surface of a planar or curved substrate or tuneable by varying the local flow rate. The production rate is extremely high at 10^6 nanodroplets per second. This advance in the nanodroplet production provides a general platform for droplet-based applications. Here we demonstrate that the application of surface nanodroplets in microextraction of hydrophobic solute (dye) from its highly diluted aqueous solution and in-situ detection of the dye in a simple process, and in fabrication of highly ordered array of microlens arrays and polymer-capped microstructures by simply processes.



Keywords: Nanodroplets, solid-liquid interface, solvent exchange, large scale

EFFECT OF MOLECULAR ORIENTATION ON MECHANICAL PROPERTIES OF PERFECTLY BIOABSORBABLE BONE FIXATION DEVICE

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Introduction: A composite material that is compounded with bioabsorbable polymer and bioactive ceramics have been self-reinforced by drawing to improve mechanical properties. Therefore, effect of molecular orientation on mechanical properties of the composite material should be investigated. The purpose in this study is to investigate effect of orientation in matrix on mechanical properties of the composite material.

Methods: Effect of molecular orientation on mechanical properties of poly(lactic acid) (PLA) which is bioabsorbable polymer was investigated before that of composite material. PLA screws as specimens are prepared through a series of routes including casting, extrusion drawing and forging. Shear strength, torsional strength, orientation function and crystallinity of PLA screws were measured.

Results: As a results, shear strength of PLA screw increased with extrusion ratio, while torsional strength decreased. The investigations of higher order structure were shown that orientation function increased with extrusion ratio and crystallinity did not change.

Discussion: Shear strength and orientation function increased with extrusion ratio. Therefore, drawing is effective method to improve shear strength of screw, where fibrous structure which was formed during extruding resisted shear stress in cross-section perpendicular to screw axis. On the other hand, decreasing torsional strength might be because that the fibrous structure could not hold shear stress in screw axis direction. It was guessed that this fibrous structure was obtained in matrix of drawn composite material. Therefore, shear strength in drawn composite material might increase.

Keywords: Poly(lactic acid), molecular orientation, mechanical properties

PELLERIZE CONDITION DEPENDENCE OF WASTE CONTAINER AND PACKAGE PLASTICS – COMPARISON OF A PRESENCE OF MOLTEN RESIN RESERVOIR

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Sample number	Granulation temperature (°C)	Screw rotation speed (rpm)	Water temperature (°C)
1	200	100	room temperature
2	200	200	room temperature
3	230	100	room temperature
4	230	200	room temperature
5	250	100	room temperature
6	250	200	room temperature
1	200	100	ice-cold
8	200	200	ice-cold
9	230	100	ice-cold
10	230	200	ice-cold
1	250	100	ice-cold
(12)	250	200	ice-cold



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Introduction: The environmental impact of a growing volume of wastes, effective recycling of various products and materials has become an important challenge. The poor physical properties of the material-recycled plastics had been believed as due to the chemical degradation. Such chemical degradation is irreversible because it is associated with the fracture of molecular chains. However, we have recently found that the main reason of this poor physical properties arise from physical degradation. In this time, we investigated pelletize condition dependence of recycle containers and package plastics and comparison of a presence of molten resin reservoir.

Methods: Recycled waste containers and packaging plastic pellet was offered from ECO FEEL Co. LTD. The pellet was not sorted and that was a mixture of polypropylene and polyethylene. We re-pelletized the pellet by using twin screw extruder. Tensile test pieces were molded by injection molding.

Results: Table 1 shows pelletize conditions. Fig. 1 shows tensile fracture elongation results of injection molded tensile test pieces. From this result, tensile fracture elongation results with molten resin reservoir are higher than without reservoir.

Discussion: From the results, the physical properties of injection molded sample are much depend on the pelletize condition and pelletizer form. Especially, the molten resin reservoir is important.

Keywords: Waste container and package plastics, Pelletize condition, Material recycle