



# Symposium 14

## Green Polymers, Reprocessing & Recycling



## Processing Polymers from Renewable Resources

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Generally, polymers from renewable resources can be classified into three groups: (1) natural polymers, such as starch, protein and cellulose; (2) synthetic polymers from bio-derived monomers, such as polylactic acid (PLA); and (3) polymers from microbial fermentation, such as polyhydroxybutyrate (PHB). Like most polymers from petroleum, polymers from renewable resources are rarely used by themselves due to either either poor performance or high cost. Blends and composites are extending the utilization of polymers from renewable resource into new value-added products. Processing these polymers and their blends/composites is much more complex than that of conventional polymers; for example polymers from renewable resources can have large variations in hydrophobicity requiring significant compatibilizing technology to be utilized and often multiple chemical and physical reactions are involved in their processing. In this presentation some key issues of processing the polymers from renewable resources will be discussed, in particular some new achievements in our group will be introduced: New technologies developed for studying the phase transition of natural polymer during processing. Property enhancement in natural polymers using nanotechnology. Enhancement of compatibilizer functions through controlling its distribution.

S14-837

## CHARACTERIZATION AND BIODEGRADABILITY OF BIODEGRADABLE POLYMER-WOOD FLOUR COMPOSITES

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Wood-polymer composites are widespread in the field of industrial applications, because of the several advantages they can assure in comparison with mineral filler-polymer composites: the low cost of wood based fillers; the reduced specific weight; the lower hazards for production workers in case of inhalation; the special aesthetic features; environmental issues. In the scientific literature, several studies are reported concerning polymer matrices like polyethylene and polypropylene, in combination with various natural-organic fillers. However, a limit of these composites is represented by the lack of a full biodegradability: this, in fact, regards only the filler, thus the environmental performance will generally be lower than expected. To overcome this limit, it is necessary to replace the traditional, non-biodegradable polymer matrices (typically, polyolefins) with biodegradable ones. An interesting solution consists in the use of biodegradable polymers like, for instance, those belonging to the Mater-Bi® class. In this work, a biodegradable polymer matrix, coming from the Mater-Bi® family, was mixed with wood flour, a widely used natural-organic filler. The study was focused on the relationships between the mechanical properties and the processing method, the filler type, the humidity content of the components. Morphological characterization was also carried out by SEM analysis, in order to get more data regarding some different behaviours shown by the different preparation variables. An investigation was also undertaken regarding the biodegradability of the materials and its relationships with the preparation, the processing parameters and the surface roughness.



## Crystallisation of PLA and PLA/Thermoplastic Starch blends under processing conditions

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Poly(lactic acid) (PLA) must be crystallised in order to increase its temperature resistance. Unfortunately, its crystallisation rate is relatively low and thus it is difficult to achieve a high crystallinity level in polymer processing conditions unless it is induced by strain. In this work, different strategies to promote PLA crystallization were investigated with the objective of increasing its crystalline content in typical polymer processing conditions. The effect of heterogeneous nucleation was assessed by adding talc, sodium stearate and calcium lactate and thermoplastic starch as potential nucleating agent. The PLA chain mobility was increased by adding Acetyl Triethyl Citrate and Polyethylene Glycol as plasticizers. The crystallization kinetics was studied using DSC analysis under both isothermal and non-isothermal conditions. The isothermal data showed that talc is highly effective in nucleating the PLA in the 80~120°C temperature range. The non-isothermal data showed that the combination of nucleant and plasticizer is necessary to develop significant crystallinity at high cooling rates. The nucleated and/or plasticized PLA samples were injection molded and the effect of mold temperatures on final part crystallinity was determined. It was possible to mold the PLA formulations using mold temperatures either below 40°C or greater than 60°C. At low temperature, the molded parts were nearly amorphous while at high mold temperatures, the PLA formulation with proper nucleation and plasticization were shown to achieve crystalline levels up to 40%, close to the maximum crystalline content of the material. Tensile mechanical properties and temperature resistance of the amorphous and semi-crystalline materials were examined.

S14-1254

## Structural BioComposites: An Overview on Processing and Applications

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Renewable materials from sustainable sources are becoming increasingly used in a variety of applications. Polymer matrix composites reinforced with natural fibers are one such example. There is need for fundamental and applied research into products and processes that are based upon biobased materials and transfer these technologies to industry. There is a growing interest in the use of natural/biofibers such as jute, kenaf, flax, industrial hemp, coir, henequen and pineapple fiber as reinforcing components for various thermoplastics and thermoset matrices. This presentation will discuss till date developed high volume processing of structural biocomposites with particular reference to extrusion, injection molding, compression molding, sheet molding compounding (SMC), and resin transfer molding processing along with their industrial applications.



## Renewable Hierarchical Composites: Processing and Properties

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Environmental friendly materials are now actively sought for to replace unrecyclable materials mainly to address the problems arising from materials end-of-life issues. Here we will present a novel route to create bacterial cellulose reinforced natural fibre reinforced renewable polymer composites, which are in principal fully biodegradable. Nano-scale bacterial cellulose fibrils were successfully attached to various natural fibre surfaces by fermenting a strain of cellulose-producing bacteria (*Gluconacetobacter xylinus*) in presence of the natural fibres. Scanning electron micrographs (SEM) of the surfaces of hemp fibres before and after the bacterial surface modification clearly reveal that bacterial cellulose fibrils of 50-100 nm in diameter cover almost completely the fibre surface. This surface modification led to a significant improvement in the interfacial adhesion between the modified natural fibres and renewable polymers cellulose acetate butyrate (CAB) and polylactic acid (PLA). This improved adhesion should enhance the stress transfer efficiency between the fibres and the matrix in a composite, in turn resulting in an improvement in actual composite performance. Unidirectional long natural fibre reinforced CAB and PLA composites as well as short fibre composites have been fabricated using the modified fibres. The modified fibres were found to yield improved mechanical composite performance as well as improved moisture resistance.

S14-236

## Modification of Degradation and Processing Characteristics of Polylactic Acid with Ionic Liquids

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In attempts to modify the degradation characteristics of polylactic acid (PLA) the addition of selected low MW ionic liquids having the same cation but different anions, at concentration up to 5 wt%, was shown to result in enhanced degradation rates accompanied by plasticization and lubrication. Hydrolytic and thermal degradation were studied via mass changes, gel-permeation chromatography, pH changes, acid number and visual observations. Lubrication and plasticization were tested by measuring melt viscosity, friction coefficient, T<sub>g</sub> and contact angle. The effects of the two different ionic liquids on properties and processability are explained in terms of their different chemical structures and extent of interactions with the polymer.



## Compatibilized Poly (lactic acid)/Thermoplastic Pulse Starch Blends with Nanoclay

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Maleic anhydride is used as a reactive compatibilizer to enhance interfacial adhesion of blends of Poly (lactic acid) (PLA) and glycerol plasticized thermoplastic pulse starch (TPPS). Organoclay (Cloisite 30B) is used to improve the mechanical properties of blends. Measurements of rheological and mechanical properties were performed on a Rosand capillary rheometer and Instron tensile testing machine. Thermal and morphological properties of blends were evaluated using differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). Water contact angles were measured using a goniometer equipped with a video camera and a computer with drop shape analysis software for calculating the contact angles. Maleic anhydride compatibilized blends showed higher tensile strength and modulus than simple PLA/TPPS blends. Nanoclay improved the mechanical properties and hydrophobicity of blends. At 150°C, all thermoplastic pulse starch/PLAgMA blends showed shear-thinning behavior. Tensile strength and modulus improved remarkably for blends of pea and lentil starch with maleic anhydride as a coupling agent in blends, but the improvement for blends for bean starch was slight. The addition of Cloisite 30B improved the tensile strength and modulus, but elongation at break decreased. The initial contact angle of a water droplet in the surface of thermoplastic pulse starch/ PLAGMA sample was less than 55°, but it increased to 75° as nanoclay (Cloisite 30B) was added to the blends up to 5% by weight.

S14-271

## Formation of Water-disintegrative Poly(l-lactic acid) Blends

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In this study it was attempted to generate materials with excellent mechanical properties but whose structure would easily disintegrate when immersed in water. The materials were prepared by melt-blending poly(L-lactic acid)(PLA) and butylene adipate-co-butylene terephthalate copolyester (PBAT) with a small amount of aspartic acid-co-lactide copolymer (PAL) as a degradation accelerator. In the present experiments, five kinds of PALs with different molar ratios of the aspartic acid (Asp) unit to the lactide (LA) unit were employed; PAL-1/5, PAL-1/20, PAL-1/30, and PAL-1/50, where the ratios denote the [Asp]/[LA] molar ratios. The degradation behavior of the blends in phosphate-buffered saline (pH=7.3) was investigated by gel permeation chromatography (GPC). The present study elucidated four important points: First, miscibility between PLA and PAL was enhanced in the order of PAL-1/5 < PAL-1/20 < PAL-1/30 < PAL-1/50. Second, in the [(100-X)/X/25 by weight] PLA/PAL/PBAT blends, addition of PBAT successfully modified brittle PLA to a ductile material in a range of X < 20. Third, hydrolysis of the blends was almost negligible in air, whereas it proceeded swiftly in water. Fourth, most notably, the degradation rate of PLA blends becomes higher for the blends containing PAL with the lower [Asp]/[LA] ratios, when different blends containing the same [Asp] concentration are compared. This implies that the distribution of PALs with lower [Asp]/[LA] ratios occurs at a smaller scale (e.g. at the molecular level) in blends so that the higher contact area of PAL with component polymers results in a swift degradation of the blends. Thus, in order to design materials with superb mechanical properties in air and a swift degradation process in water, a good distribution of PAL in the blends is essential, and this is controlled by the miscibility of PAL and the component polymers.



## High performance alloy of Bio-based thermoplastics PA11 and PLA

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A strong motivation appeared in our end-user customer to replace current commodity, engineering and even high performance thermoplastics by Bio-based materials. Petrol, which mainly comes from fossil fuel, was the preferred source of energy of the XX century, but it is a non-renewable resource. The massive and accelerated use of this product in the last half century has contributed to the planetary global warming. The current emergence of Bio-plastics is one of the answers of the strong trend to decrease the amount CO<sub>2</sub> emissions responsible for this global warming. For example, Polylactid acid (PLA) is a recent and well-known bio-based polymer currently emerging in the market, particularly within the packaging industry. However, PLA has 2 main drawbacks: low impact resistance and low thermo-mechanical performance, which dramatically restrict the applicative areas of this bio-based thermoplastic. On the other hand, polyamide 11, a high performance polyamide made from castor oil, has high mechanical properties. Adding PA11 into PLA can bring improvement in terms of mechanical properties without reducing the bio-based content : this is the aim of this study. The PA11 and PLA alloy, with PLA as the matrix, reveals a key improvement in mechanical properties when compared to those of pure PLA. We have clearly shown that the addition of PA11 in PLA leads to a ductile behaviour for this new blend whereas pure PLA is completely brittle in the same conditions. In addition, we have demonstrated that PA11 plays the role of nucleating agent for PLA. The consequence is a huge increase in thermo-mechanical properties above the T<sub>g</sub> of PLA. The high mechanical performance obtained with this new blend gives us the opportunity for the developments of new and innovative Bio-based alloys.

S14-358

## WATER VAPOURS ABSORPTION ON THE CHITIN-CONTAINING MATERIALS

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The goal of this paper is the experimental study and the mathematical modelling of the sorption process of water vapours on different natural polysaccharides. Chitin-glucan complexes isolated from native biomass of higher fungi, chitin from bees corpses, Arthropoda chitin and cotton cellulose were chosen for study. For the first time the theoretical model of this process has been proposed. According to proposed model, the water sorption occurs in volume of biopolymer. Moreover, three different modes of absorbed water molecules can appear during this process: a) matrix dissolved molecules; b) primary absorbed (strongly connected) molecules on active centers of biopolymer; c) secondary absorbed (cluster) molecules on active centers of biopolymer. Results show that analytical formula equation of absorption isotherm derived in the context of this model describes well this process for various chitin-containing materials in the wide range of humidity. Furthermore, base parameters of absorption isotherm were defined for studied samples. From analysis of experimental data absorption capacity has been found to be essentially higher in the case of chitin-glucan complexes of higher fungi than for cellulose and chitin of animal origin.



## Rheological and Molecular properties of organic modified induced recycled and virgin high density polyethylene

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Blow moulding grade recycled (R-HDPE) and virgin (V-HDPE) high density polyethylene were reactively extruded with various compositions (0.00- 0.15%) of different peroxides in a twin screw extruder. The aim was to improve the melt strength properties of a blow moulding grade HDPE homopolymer- a polymer resin comprising a significant part of the post consumer recycled plastic stream in Australia. Shear rheological tests were also carried out to study the structure of the modified materials within linear viscoelastic region. Viscoelastic parameters, such as storage moduli ( $G'$ ), loss moduli ( $G''$ ) and complex viscosity ( $\eta^*$ ) showed improvement at all frequency tested with increase in both peroxides' compositions. Higher improvements were experienced with OP2 modified V-HDPE and R-HDPE. R-HDPE showed greatest improvements in viscoelastic properties due the inclusion of low level of carbon black as stabilizer. However, increase in peroxide loading cause appearance of the divergence of complex viscosity profile from Newtonian plateau to non-Newtonian slope analogous to finite yield stress region. Uniaxial Extensional rheological study, using melt strength tester, was carried to evaluate the response of the modified material to the extensional deformations. Melt strength of V-HDPE and R-HDPE was enhanced with peroxide modifications. Extensibility was found to decrease with increased melt strength. Instabilities like draw resonance and ductile fracture were experienced with peroxide loading and results in the processing limitations. Extensional viscosity was found to increase with all modified samples. Moreover, this enhancement was further experienced with recycled modified materials. Environmental stress cracking resistance were measured to evaluate the modified material in terms of the targeted pipe application. Resistance to stress crack increased with peroxide modifications.

S14-508

## MECHANICAL AND DYNAMIC-MECHANICAL PROPERTIES OF BIODEGRADABLE EPOXY RESINS

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In the last decades, epoxy resins (EP), widely used as matrix for advanced composites, have been extensively investigated as demonstrated by the huge amounts of papers appeared in the scientific literature. These matrices are usually obtained from petrochemically derived monomers but, recently, the growing demand for petroleum-based products and the resulting negative impact on the environment, plus the scarcity of non-renewable resources, have encouraged the scientific community to find more sustainable and environmentally epoxy formulations. In line with this well established consideration, an increasing interest is nowadays devoted towards renewable sources. In particular, carbohydrate-based epoxy seems to be a promising alternative. Aim of this research was to investigate ultimate performances of networks derived by curing sorbitol-based diepoxides and sucrose-based monoepoxides in presence of amines such as diethylenetriamine (DETA) or diethyltoluene diamine (DETDA) have been considered. Products were compared with formulations based on the diglycidyl ether of bisphenol A (DGEBA) cured with the same amines under similar processing conditions. Preliminary results achieved by flexural and impact tests but also by dynamic-mechanical measurements emphasized a worthnoting competitiveness of carbohydrate-based epoxy resins especially in the case of sorbitol based ones.



## MORPHOLOGY AND MECHANICAL PROPERTIES OF PHYSICAL BLENDS OF DIFFERENT BIODEGRADABLE POLYESTERS TO BROADEN THEIR AREA OF APPLICATION

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The aim of this study is to better understand the performance of binary blends of biodegradable polyesters, in order to overcome some limitations of the PLA such as brittleness and stiffness. For this, different blends have been prepared using the complete range of blends compositions with P(L)LA (L-poly (lactic acid)) and PCL (poly (caprolactone)), PBSL (polybutylene-succinate-co-L-lactate) and PBHV(poly(hydroxy butyrate valerate)/PCL blend. The blends obtained created an intermediate biopolymer with a much more ductile mechanical behaviour. PCL and P(L)LA are the most known and studied biodegradable polymers (1). However PBSL (2) and PBHV/PCL have both recently been commercialized. All these materials have a large field of application (3), with medical care, agricultural and packaging being the most widely researched applications. Those polymers can be processed by traditional thermoplastic processing methods and can be disposed through composting. Binary blends were prepared by melt blending (in a twin screw extruder) and followed by injection moulding. The composition ranged from each pure biodegradable polymer. Initial modulus, elongation at break and impact toughness of those blends were investigated. In addition, morphological characterization was performed using Scanning Electron Microscopy and Differential Scanning Calorimetry. The results indicate it is possible to improve PLA mechanical properties in that PCL, PBSL and PBHV/PCL in general, act as polymeric plasticizers, enhancing the flexibility and ductility of the blend. Phase-behaviours were also studied for all blends, confirming that our biodegradable polymers are mainly immiscible. 1. K. Van de Velde, P. Kiekens, *Polymer Testing* 2002, 21 4332. Taniguchi, Nakano, Nakamura, El-Salmawy, Miyamoto, Kimura, *Macromolecular Bioscience* 2002, 2, 447-455 3. W. Amass, A. Amass, B. Tighe, *Polymer International* 1998, 47, 89

S14-593

## The Effect of Compatibilization on the Properties of Ultrafine Scrap Tire Rubber and Recycled Thermoplastic Blends

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Thermoset rubber products are more difficult to recycle as compared to thermoplastics. As a result, much of the waste rubber may be landfilled. Although a number of recycling methods exist for thermoset rubber compounds, including tire derived fuel and civil engineering applications, new recycling methods are needed. One method to recycle rubber is to produce crumb rubber by grinding, which can be used in asphalt, or blended with plastics to create rubber toughened products or novel thermoplastic elastomers. Blends of recycled rubber powder and thermoplastics offer the potential for a variety of new applications. The properties of the resulting blends depend on the particle size of the ground rubber, the type of thermoplastic, and compatibilization techniques. This work investigates the effect of ultrafine rubber particle sizes on the properties of a series of recycled thermoplastics and scrap rubber blends. The effect of particle size, loading, and compatibilization on a series of batch mixed compounds is discussed.





## Petrochemical feedstocks and syncrude production from plastic waste by pyrolysis

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The European Union's directives on plastic wastes management are getting sterner. These directives require developments of such new technologies from the member countries, which technologies are susceptible for the recycling of the enormous amount of plastic wastes. The problem might be solved with development of advanced recycling technologies, like feedstock recycling, e.g. with thermal or thermo-catalytic pyrolysis of plastic wastes. For utilization of plastic wastes it is necessary to define the proper parameters of pyrolysis, which make the technology suitable for producing feedstocks for refining and petrochemical industry. Syncrude had to have similar properties as the crude oil, because otherwise the integration to refinery streams would be too complicated. Moreover the pyrolysis of plastic wastes was investigated in the aspect of the derived product would utilized as petrochemical feedstocks. In this case the aim of the experiments was the production of paraffinic hydrocarbon fractions which consisted small amount of aromatic compounds. In our experimental work parameters of pyrolysis were investigated, which are required for producing high quality syncrude for refinery. A continuous pilot tube reactor with capacity of 70 tones per year was applied, which with the defined parameters can produce high quantity and quality syncrude or in the other case it can produce petrochemical feedstocks too. The pyrolysis products had advantageous properties for utilization e.g. research octane number (RON) range 80-90, Bureau of Mines Correlation Index (BMCI) range 15-20. In conclusion the proper parameters of the pyrolysis were determined as the reaction temperature range (500-550°C), residence time range (10-30 min), the raw material composition and the applied catalyst concentration.

S14-710

## MICROWAVE TECHNOLOGY APPLIED TO A VULCANIZED MODEL RUBBER COMPOUND: RECLAMATION AND RECYCLING ABILITY

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The objective of this work was to investigate the effects of a thermal treatment induced by microwaves (MW) and applied to a simple rubbery model system. It is the first step of a study aimed at finding an effective, industrially applicable, way to induce partial devulcanization in more complex systems. The final goal is to improve recycling capabilities of massive rubbery wastes, like end-use tyres, whose disposal constitutes a severe environmental issue. The chosen system was based on a styrene-butadiene rubber mixed with vulcanization agents. Such "uncured rubber" (UR) was vulcanized under static load to give the reference "vulcanized rubber" (VR), and finally processed in a MW oven to obtain a "treated rubber" (TR). All the materials were characterized in terms of gel-percentage and mechanical properties. In order to evaluate the effects of MW treatment on the recycling capability of the rubber, the UR was loaded with TR in a lab scale Banbury mixer, in the 20 to 100 phr compositional range, and then subjected to re-vulcanization. Besides the reference VR, also samples obtained by re-vulcanization of UR loaded with cryo-milled VR were considered for comparison. Rheological, calorimetric, stress-strain and dynamic-mechanical characterizations were performed on all the obtained compounds. By this way it was measured how the addition of either TR or cryo-milled VR to the virgin material influences the curing process and the properties of the final product. It was found that both systems showed less attractive mechanical properties than the original VR. However, TR-loaded compounds showed better performances than those containing analogous quantities of cryo-milled VR. Moreover, a significant increase of the glass transition temperature of the final material was observed, indicating that the "recycled" part was still able to participate in the second vulcanization process.



## STRUCTURE CHANGES IN STYRENIC POLYMERS UNDER FIRST USE AND MECHANICAL RECYCLING USING SPECTROSCOPIC AND SPECTROMETRIC TECHNIQUES

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Polymers are subjected to physical and chemical changes during their processing, service life and further recovery, and they may also interact with impurities that can alter their composition. Scientific knowledge about the degradation processes to which polymers are subjected during life cycle and the development of fast and reliable characterisation methods for the quality assessment of recycled plastics are basic to guarantee the performance of recycled products in new applications. Modelling of the first use and subsequent recycling of high-impact polystyrene (HIPS) has been performed using an integrated procedure by multiple processing and thermo-oxidation. The chemical changes in the microstructure have been evaluated using vibrational spectroscopy (FTIR and Raman spectroscopy), proving that the rubber phase is the initiation point of degradation processes in HIPS. The formation and/or release of low molecular weight compounds (residues of polymerisation, degradation fragments) during previous life and mechanical recycling have been monitored using chromatographic techniques. Advanced spectrometric techniques such as MALDI are a valuable tool to investigate the structural changes in polymer architecture and the formation of oxidised end-groups during recycling. The results of these advanced characterisation procedures will be correlated with the evaluation of macroscopic properties such as mechanical and viscoelastic properties.

S14-909

## Hybrid injection molding for natural fiber composites

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In recent years, there have been interests in natural fiber reinforced injection moldings for industrial products such as car components and home electronics. The use of only natural fibers as reinforcement, however, does not provide the composites with adequate mechanical properties. In this study, PP-based glass (GF) and jute hybrid long fiber pellets were fabricated by the pultrusion method and subsequently injection molded into specimens. The incorporation of GF (at 10 wt%) was intended to enhance the overall mechanical performance of the composite while preserving some 'green' content with the presence of up to 30 wt% jute fibers. Mechanical tests revealed that the tensile modulus increased linearly although there was minimal increment in tensile strength with increasing jute fiber content. The tendency of flexural properties was similar to that of tensile properties. In the case of notched Izod impact test, the impact strength increased with the incorporation of 5 wt% jute fiber, although subsequent increases in jute fiber content does not affect the impact strength values. Meanwhile, the un-notch specimens experienced a loss in toughness with increasing jute fiber content. This could be caused by the heterogeneous distribution of the jute fibers whereby large agglomeration was observed at the core section of the specimens, especially in the case of specimens incorporated with 30wt% jute.



## Fullerene C60 as advantage additive for recycling of polymer composites

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The aim of this study was to take advantage of the unique properties of fullerene C60 and explore its potential applications as stabilizer in the thermal or photo degradation of acrylic polymers, polystyrene, polyamide-6 and polyamide-6,6 ; essentially characterized by free-radical processes, and apply their use to recycling of polymers. The use of fullerene C60 as nanofiller in polymer composites to prolong their life time and be in use advantage additive for recycling. For acrylic polymers and polystyrene the presence of fullerene C60 leads to increase of yield of monomers at pyrolysis and to decrease of yields of by-products. For polyamide-6 the presence of fullerene C60 leads to moderate yields of  $\epsilon$ -caprolactam at pyrolysis. The conditions of pyrolysis of polymers and its influence on yields monomers are discussed.

S14-1228

## Film Casting of Renewable Resource Polymers

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Bio-based polymers show significant promise as an alternative to conventional fossil fuel-based materials, particularly for commodity applications such as single-use products. In particular, poly-lactic acid (PLA) and poly-hydroxyalkanoates (PHA) can offer similar properties to conventional plastics, yet they are derived from renewable resources and can degrade under the appropriate conditions. In this work, a DSM Xplore microcompounder with the cast film attachment is used to process films of PHA copolymers, PLA, and blends of the PHA and PLA materials. The films are then characterized to investigate the impact of material properties, such as blend composition, and processing conditions on thermal and mechanical properties. Processing variables include draw ratio and post-draw biaxial stretching parameters. A broad battery of tests, including DSC, WAXD, tensile testing, and SEM are used to investigate the final film properties. We report on structure-property relationships, interpret results in terms of processing history, and define effective processing windows for commercial applications.



## RECYCLING AND REUSE OF NATURAL FIBERCOMPOSITES

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Problems exist in the disposal of end-of-life composites. The best disposal method is under discussion. In the case of plastics there are different available methods: landfills, biodegradation, reuse and recycling. In this work, two different solutions have been presented: reuse and recycling. In the first approach flax fiber/vinylester composite were milled and mixed with virgin matrices to produce composites. The effect of this powder on the mechanical properties of a thermosetting (vinylester: VE) and a thermoplastic (polypropylene: PP) was studied. For VE flexural and tensile strength decreased with the addition of powder. For filler contents higher than 50%, the strength reached a constant value. Flexural and Young's modulus was independent on the powder contents. For PP, strength and modulus decreased when powder replaced fibers. Both, fibers and powder acted as reinforcement because modulus increased. Impact properties were improved with the addition of powder and fibers in comparison to the pure matrix. In the second one, the influence of multiple extrusion cycles on the behavior of 20 wt.% flax fibers / polypropylene composites was studied. Final fibers dimensions (length and diameter) were measured by optical microscopy. The mixing index was measured in order to do the analysis of the quality of mixing. Mechanical properties of matrix and composites were measured after each extrusion cycle. The elastic modulus of the matrix was higher after the first cycle than that of the virgin material, mainly due to chain scission. In the next cycles, the modulus kept constant. For composites, the elastic modulus after a single extrusion step was lower than that predicted by the Halpin – Tsai model probably due to a poor mixing and the low fiber/matrix adhesion. In the following two steps, modulus increased because of the better fiber dispersion. For the final two extrusion cycles, the slow decrease in this property was correlated with the darkening

S14-1303

## BAROPLASTIC ELASTOMER: IN DIFFERENT TOPOLOGIES AND USED AS COMPATIBILIZER

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Most plastic products today are manufactured and recycled by heating of virgin polymer resin close its melting point or above the glass transition ( $T_g$ , generally more than 200 oC), extruding or molding under pressure into desired forms, and cooling to solidify. This process has several disadvantages including the cost and environmental impact associated with heating and cooling the polymers and equipment. There is also the potential for thermal degradation of the polymers being molded. To address issues of energy consumption, thermal degradation and low recyclability encountered in thermoplastics manufacture, Mayes and Acar et al had developed a novel class of polymeric materials termed (Baroplastics, BP) di-block copolymers and core-shell polymer nanoparticles that can be processed mainly by the application of pressure at ambient temperature instead of high temperature. The processing is achieved by exploiting the pressure-induced miscibility of the low  $T_g$  and high  $T_g$  components. This opens the door for a class of plastic materials that become processable with the application of hydrostatic pressure at greatly reduced temperatures relative to traditional thermoplastic processing and complete multiple recyclability. To worth studying, having different topologies of polymers were investigated and experiments on the effect of pressure and time on the processability of the polymers with different topologies were achieved and also their compatibilizer possibility to process polystyrene and multiple recyclability were examined. Tri-block and star-block copolymers were shown baroplastic behavior that obtained by simple compression molding at room temperature only with the application of pressure and conditions were optimized. When pressure applied at room temperature, BP Elastomers (BPE) can be at least 5 times recycled 100% without degradation. In addition, BPE were used as compatibilizer to process polystyrene.



## PRODUCTION AND CHARACTERIZATION OF BIODEGRADABLE POLYMER BASED NANOCOMPOSITES

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The use of biodegradable polymers represent a useful solution to the environmental problem due to the plastic waste. The main problem concerning the application of biodegradable plastics is that at this moment the material properties are not enough for several industrial applications, and the costs are normally higher than tradition polymers. The use of nanofillers in polymeric matrices showed important results concerning the improvements of properties as for example thermal resistance, fire behaviour, barrier properties, mechanical properties. In this work Mater-Bi® based nanocomposites have been produced by melt intercalation procedure and analysed from a rheological point of view. The production process of thermoplastic polymers involves the flow of materials, for these reason the rheological analysis of the nanofilled systems is very important both for the analysis of processing ability of the materials and for the optimization of the manufacturing procedures. Mater-Bi® NF-01U kindly supplied by NOVAMONT was used as matrix, Montmorillonites and Sepiolites both compatibilized and pure were used as nanofillers. In particular Montmorillonites from LAVIOSA Dellite HPS (natural) and Dellite 43B, and Sepiolites from TOLSA PRG4 (natural) and PRG1 were used. The materials were processed by melt intercalation by using a twin counter-rotating screw extruder BAUSANO MD30 up to 3 extrusion cycles. Two nanofillers content were use: 3 wt% and 5wt%. The materials produced were analysed by a mechanical and morphological point of view and an important influence of the processing conditions was observed. Rheological measurements in both dynamic and steady conditions were performed and it was possible to observe that several rheological parameters are significantly affected by the processing conditions. Both viscosity and viscoelastic properties ( $G'$  and  $G''$ ) of the melt suspensions show different behaviour depending on the processing conditions and therefore on the dispersion level

S14-1315

## Green Polymer Packaging Containers for the Military

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The development of fiberboard is being researched by the U.S. Army for the Department of Defense's Strategic Environmental Research and Development Program (SERDP). The project, "Lightweight and Compostable Packaging for the Military" will help to reduce the amount of solid waste for the military. Shipping containers fabricated from fiberboard are necessary to transport and store food and other military items for all warfighters, including sailors on Navy vessels. However, there are numerous disadvantages in the process used to produce fiberboard: the process is costly, uses cellulose and hazardous chemicals, depletes natural resources in our environment, and creates hazardous waste. This study produces new green lightweight biodegradable fiberboard for Meal Ready-To-Eat (MRE) containers that can be converted to a valuable byproduct, compost. Two technologies are being used in this research effort to decrease the volume/weight of fiberboard used in military packaging. First, a novel fiberboard is being developed using a soy protein bioadhesive and natural fillers to reduce either density or thickness while maintaining needed mechanical properties and water resistance. Secondly, a variety of environmentally friendly coatings applied to paper and fiberboard are also being prepared by a variety of methods (spray, solution, extrusion coating) and evaluated to improve water and puncture resistance. Coating formulations varying the thickness of the coatings are being optimized. Both technologies have provided prototype fiberboard that is less weight and comparable water resistance to the existing MRE containers. Composting trials are ongoing throughout this program to determine how quickly the new fiberboard formulations biodegrade and if these packaging materials used in combination with other waste (e.g. military food waste, grass clippings, leaves, newspaper) can generate a compost product.



## Structure-property-degradation studies for thermoplastic starch polymers

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This paper reviews the development of biodegradable thermoplastic starch polymers at the University of Queensland. Biodegradable plastics are of significant current interest in the packaging and plastics industry. Starch-based thermoplastics are relatively cheap and more importantly manufactured using a renewable resource. However traditionally most thermoplastic starch polymers suffer from low water resistance and loss of mechanical properties when in contact with water. This paper will highlight the development of commercial grades of thermoplastic starch polymers via our research and via our spinoff company Plantic Technologies. In this work we will specifically highlight understandings from fundamental work on the genetics-structure-property relationships of model starch polymers [1] structure-property-biodegradation relationships of thermoplastic starch polymers [2], innovation in nanocomposite materials and reactive extrusion [3] scale-up of film blowing and injection molding grades [4].  
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S14-1345

## Environmental degradation of bio- and nanocomposites

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Environmental degradation is a summary of all those degradation factors that can decrease the life-time of polymeric materials outdoors. Chemical, physical, mechanical and biological factors have an impact on the materials and the degradation may occur quickly or at a rather slow pace. In many cases the degradation factors are effective synergistically or even consecutive. Usually chemical, physical and mechanical factors enables a later biodegradation where biofilms are particular notorious to appear on nearly every surface. Biofilm forms when bacteria adhere to surfaces in aqueous environment and begin to excrete a slimy, glue-like substance that can anchor them to all kinds of material – such as metals, plastics, soil particles, medical implant materials, and tissue. Composites, consisting of synthetic or biodegradable polymeric matrix and natural fibres as reinforcement have been successfully applied in various applications: automotive, packaging, construction, etc. Natural fibres present a series of advantages such as low density, high specific strength and modulus, renewable and biodegradable characteristics, and reasonable processibility at low cost. The presentation will address results from ongoing studies conducted in order to compare how both bio- and nanocomposite materials are affected by the environment. The materials were subjected to photo-oxidation, hydrolysis, thermal oxidation and a micro-organism environment in order to simulate the environments that the products might be exposed to. The focus of these studies was to investigate chemical-, physical- and mechanical property changes as well as emissions of particles applying various analytical techniques.



## PLA based composites: evaluation of the mechanical performance and aesthetics

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Due to several reasons, the world is increasingly gaining a green consciousness. Nowadays, everybody understands at least some of the problems and effects on the environment that the continuous use of non-renewable resources will lead us to. This is why scientists and engineers all over the planet are studying and developing new materials from renewable resources and non-polluting alternatives able to satisfy people's needs and at the same time avoiding further damaging on the environment. The main objective of this work is to improve the performance of PLA based composites, in terms of mechanical and physical aspects, in order to make them able to be used in automotive applications. A range of natural reinforced composites was evaluated for this purpose: PLA was composed on a twin screw extruder with different percentages of cellulose spent fibres. An attempt was made to use interfacial modification by free-radical grafting of maleic anhydride (MA) unto PLA, using two different methodologies, as a way to improve the composites ductility and stiffness. The materials were then pelletized and injection moulded. The mechanical properties of the produced composites were tested and their morphology was assessed using optical microscopy and SEM. Another important subject when addressing automotive industry is the design of the materials, meaning their capability of being coloured or their possibility to produce different patterns. In this work an attempt was made to create different visual aspects in terms of colours and patterns, on the studied PLA based composites.

S14-256

## Soy flour composites reinforced by natural fibers for environmental friendly applications

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Various commercially available petroleum-based plastics and composites pose a serious environmental threat due to their extremely slow degradation characteristics. Green materials are increasingly being explored as alternatives to the conventional plastics to improve the environmental sustainability. As a result, plant-based biopolymers are fast becoming viable alternative to petroleum-based polymers. Among various biopolymers, soy protein has been increasingly researched as a biodegradable resin and composite matrix due to its easy and worldwide availability as well as low cost. Soy proteins are commercially available in three forms: soy protein isolate (SPI), soy protein concentrate (SPC), and defatted soy flour (SF). These environmental friendly composites can be used in indoor applications, as cover panels on walls or doors wardrobe, lampshades, or structure parts of furniture. To process SF powder (containing 55% protein and 32% carbohydrates) into a suitable resin for fabricating "green" composites, it was mixed with distilled water in 1: 9 ratio, the pH of the mixture was adjusted to 11, using NaOH, and 40% GA solution was used as cross-linking agent. With the fast cross-linking reaction, the viscosity of the mixture increased rapidly. Desired amount of glycerol was added as a plasticizer. After evaporation of a large quantity of water, the dried resin was used to prepare composite sheets by hot pressing in a caver hydraulic hot press, at 120° for 25 minutes under a force of 50 Pa. The sheets contain two types of natural fibers, kenaf and caroà: short fibers are randomly distributed through the matrix, while long fibers are parallel aligned. The cured, GA cross-linked SF polymer sheets were conditioned before characterization: mechanical and thermal tests were carried on, morphological observations and adhesion properties were evaluated in order to well select the end uses of this green composites



## Comparative degradation level analysis of bio-based and synthetic materials when submitted to different environmental conditions

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The use of bio-based materials instead synthetics has being stimulated in different areas to attend the increase of the world environmental awareness. Within this context, the objective of this work is to evaluate comparatively the degradation level of synthetic and bio-based materials after being submitted to different environmental conditions. The following materials were selected to be evaluated in this study: bio-based - PLA (Polylactic Acid) and PA11 (PolyAmide 11); synthetic - PC/ABS (PolyCarbonate/ AcrylonitrileButadieneStyrene Blend). The PLA is a bio-based thermoplastic polymer made from 100% renewable resources like corn, sugar beets, wheat and other starch-rich products. The PA11 is a semi-crystalline thermoplastic combining high tensile strength and creep resistance with a rather low modulus/high flexibility. This material has been used by automotive, transport, textile, oil and gas, and electrical/electronic industries. PA11 is produced from castor oil, a renewable source. The PC/ABS is one of the most used polymer blends in electrical/electronic and car industry. Polycarbonate is used for its mechanical and thermal properties while ABS enhances the processability and low-temperature impact strength. It is employed if good dimensional stability and creep resistance is needed. PC and ABS possess relatively poor interfacial adhesion between the phases but miscibility can be improved with compatibilizers. Design of experiments was the methodology applied to test the samples in different conditions of temperature, humidity and time. After that the samples were submitted to FTIR analysis in order to evaluate the degradation degree of the different materials. PLA and PA11 have mainly shown hydrolysis process when submitted to the highest temperature and RH conditions. PC-ABS blend found to be primarily susceptible to hydrolysis and thermal oxidation.

S14-262

## Interface Improvement between Natural Fiber and Biopolyesters

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The focus of this work has been to investigate three techniques of improving the interface between polylactic acid (PLA) and wood flour: (1) surface treatment of wood flour; (2) adding coupling agent and (3) introducing a toughening agent into PLA phase. The composites were prepared by melt compounding using a twin screw extruder, followed by injection molding. The microstructure, mechanical properties and fracture of the composites were studied by DSC, DMA, SEM, tensile and impact testing. The influence of wood flour content and the techniques of improving the interface between PLA and wood flour were systematically studied. Surface treatment of wood flour through esterification and addition of a coupling agent have improved the interfacial adhesion between PLA and wood flour, resulting in composites exhibiting improved tensile properties. The addition of toughening agent into the PLA matrix did not improve the interfacial adhesion between PLA and wood flour, but improved the PLA matrix by increasing the elasticity of the host polymer. Surface treatment of wood flour has more influence on the modulus while the toughening agent improved the toughness of the composites more efficiently.





## Rheological Properties of Starches with Different Amylose/amylopectin Ratios

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In this study, corn starches with various ratios of amylose/amylopectin (80/20, 50/50, 23/77, 0/100) were initially extruded using a Haake parallel, co-rotating twin-screw extruder with a rod die. The extruded pellets were used to characterize shear stress and melt viscosity as functions of moisture content and extrusion temperature using a single-screw extruder (Rheomex 252p, Ø19, Screw 2:1, L/D 25) with a slit capillary die (20 × 1 mm). The screw speed used was between 30 to 180 min<sup>-1</sup> which is similar to industrial extrusion processing, and 6 points were recorded using cutting and manual entry measurement mode. It is seen from the results that the apparent viscosity decreased with increasing shear rate for all moisture contents. The apparent viscosity decreases generally with increasing moisture content in the range from about 19% to 27% for all experimented temperatures. A strong power law dependence of apparent viscosity on shear rate was observed, indicating the shear thinning behaviour of the melts under all conditions. The power law index *n* increased with temperature and moisture content in most cases, and decreased as amylose content was higher. The power law consistency “*K*” increased as moisture content and extrusion temperature decreased and amylose content increased.

S14-264

## Phase Transition of Starch-based Materials during Thermal Processing

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The starch granule is a heterogeneous material with much more complex microstructure than conventional polymers. Chemically, it contains both amylose and amylopectin. Physically, it has both amorphous and crystalline regions. Most granular native starches are a mixture of amylose, a linear structure of alpha-1,4 linked glucose units and amylopectin, a highly branched structure of short alpha-1,4 chains linked by alpha-1,6 bonds. The processing of starch-based materials is much more complex than that of conventional thermoplastics because the processing involves gelatinization, melting, volume expansion, molecular degradation, crystallization, and various physicochemical changes. In this presentation some key phase transitions during thermal processing starch-based materials will be discussed, in particular some new achievements in our group will be introduced: New technologies of studying starch gelatinization New technique of studying the thermal stability of starch during processing New techniques of detecting phase transition under shear stress.



## Gas Barrier and Thermomechanical Properties of Poly (lactic acid) (PLA)/ Poly (butylene succinate) (PBS)/clay nanocomposites

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Amita Bhatia, Rahul K Gupta and Sati N Bhattacharya Rheology and Materials Processing Centre, School of Civil, Environmental and Chemical Engineering, RMIT University, 124 Latrobe Street, Melbourne, Vic 3000 Australia A series of poly (lactic acid) (PLA)/ poly (butylene succinate) (PBS)/ layered silicate nanocomposites were prepared by simple melt extrusion of PLA/PBS/C30B (Cloisite 30B organically modified MMT) clay. Extruded and compression molded samples containing 1,3,5,7 and 10 wt% of clay and having 80 and 20 wt % of PLA and PBS respectively were prepared to evaluate barrier and mechanical properties of these biodegradable nanocomposites. Oxygen Transmission Rate (OTR) was measured by MOCON 2/21 unit. The O<sub>2</sub> permeability values for all the hybrids for clay loadings were found to be decreasing with clay content. X-ray diffraction was used to assess the periodic distance of the clay layers. X-ray diffraction showed no peak indicating possibility of exfoliated structure however Transmission Electron Microscopy (TEM) images showed that most clay layers were dispersed homogeneously in the polymer matrix, although some clusters or agglomerated particles of clay was also detected. Mechanical properties measured by Instron Universal Testing Machine, showed that tensile strength and Young's modulus initially increased up to 3 wt% of clay but then decreased with the introduction of more clay loadings. Thermo gravimetric analysis revealed that thermal stabilities of pure PLA, PBS and their nanocomposites. The PLA/PBS/clay nanocomposites showed higher degradation temperature than the unfilled polymer blend.

S14-305

## Green Acoustic Materials from Waste Plastics and Rubber

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Sustainable development is a means of achieving progress in society, the environment and the economy at the same time. This paper is based on this philosophy and presents a new-clean-continuous-less energy consuming-safe process to re-use waste plastic and rubber materials that are otherwise dumped in landfills at an increasing cost both to the economy and the environment and re-process them smartly into new added-value acoustic products that can be used to meet the growing public expectation for a quieter environment. Applications are widespread and include acoustic underlay, lagging and panels in buildings, noise barriers for motorways and railways tracks, acoustic lagging in industrial appliances and transport vehicles. The basis of this new process is about tailoring a porous structure so that the final material possesses particular acoustic properties. The operation is carried out in a cold (no heat is applied) extruder which conveys and mixes the particulates and fibers with a reacting aqueous binder. The extruder thus operates also as a reactor. The end result is a structure of bound particulates and fibers through which the CO<sub>2</sub> that has evolved during reaction adds extra-porosity. By controlling the size of the particulates and or fibres, the ratio of binder-water and the level of compaction in the extruder, we show how the structure is tailored to produce the desired acoustic properties. The process allows the design and production of 2-3 fold cheaper noise control products with desired physical properties and minimum environmental impact exploited in a single structure. As the extrusion is carried out cold and has the advantage of being a continuous process, this new production process will require 4-5 times less energy in comparison with that used for conventional commercial products. The paper presents structure-properties data from a comprehensive experimental programme undertaken jointly with an industrial consortium.



## Recycled HIPS and nanoclay in improvement of cement mortar properties

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The unabated growth in the use of plastics in recent years is of considerable concern because of the difficulties involved in waste disposal. Increasingly, plastics are replacing wood, glass, paper, and metal in numerous applications, especially in packaging. One of these plastics are high impact polystyrene (HIPS) which is a common component in consumer electronic housings and automobiles. For reducing its waste and decreasing environmental problems we can use it (HIPS) in modification of cement mortar. Cement mortar was modified using recycled high impact poly styrene (HIPS) in powder form. Mixtures with polymer–cement ratios of 10, 15, and 20 wt.% were investigated for changes in compressive properties and adhesion to steel rebar. Compressive tests indicated an increase in Young's modulus for samples with 10% and 15% HIPS. Adhesion strength to the steel rebar decreased on adding the HIPS. However, when the HIPS was treated with maleic anhydride, an increase in adhesion strength was obtained. The decrease in adhesion of the untreated HIPS-modified cement to steel was attributed to the disruption of the interface between the cement mortar and steel rebar. Addition of 5% nanoclay increased both compressive Young's modulus and Adhesion strength to the steel rebar.

S14-481

## Effect of the Mixing Condition on Structure of Thermoplastic polymer/tyre post-user blends

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One great part of the municipal solid waste (MSW) is composed of polymer mixed since commodity plastics, blend to polymer composite. The processing of plastics mixtures for recycling has been attempted with some success, but poor mechanical properties and uncertain economic value limit their more versatile reuse. Polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), poly(vinyl chloride) (PVC) and polystyrene (PS) are among the most common plastic waste, predominantly used in packaging food industry. One other problem that preoccupy to the society is the increase of tyre waste in the proportion of MSW. In Brazil, between 1999 to 2004, 39 % from 386 mil ton of tyre post-use were destined to cement Industry as source of energy. However that destiny produce one other problem, environment pollution, due to gas mixture emitted. Therefore, polymer blend from polymer waste is an alternative of reuse of these materials. Usually, enhancement of impact strength, dimensional stability, stress cracking and improvement of processability have been the prime goals of blending. However, there are little literature about mixtures thermoplastic polymer waste with tyre waste, therefore, the aim of this work is to mixture waste thermoplastic with shaving tyre waste and to study the influence of its size particle and content in the interfacial interaction between thermoplastic and shaving tyre waste. PP/tyre (90/10, 70/30) and HIPS/tyre (90/10, 70/30) were processed in a injection molding machine whose processing temperature used was 220 oC and tyre particle size used were of 500 and 1000 mm. These mixtures were characterized by physycal, morphologycal and mechanical properties. Preliminary results of tensile strength showed a decreasing of the thermoplastic/tyre blends when it compared with the only thermoplastic. All the results will be showed in the complete work.



## Modified Carboxymethyl Starch Derivatives for Metal Ion Scavenger from Water

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Environmental pollution caused by toxic heavy metals is one of the most pressing problems. The use of synthetic resins for chelating toxic metal ions in water and wastewaters is a possible approach for preventing environmental pollution. These resins are mostly petroleum based synthetic polymers that are non-degradable in natural environment. In general, after the adsorption process for metal ions the chelating resins are discarded in landfills or treated by incineration, resulting in secondary environmental pollution by contaminating the soil, water and air. Starch, a natural plant polysaccharide, is attractive for industrial use because of its renewability, biodegradability, and inexpensive unit cost. Since native starch itself has no appreciable flocculating, chelating or metal uptake capacity, several approaches have been made to utilize the starch as a flocculants and metal scavenger by introducing effective functional groups. Among various starch derivatives, starch substituted with carboxyl groups enhances water interaction property along with metal ion partitioning between the gel and the solution phase. In this study, native corn starch was chemically modified using sodium monochloroacetate to yield carboxymethyl starch (CMS). The aqueous solution of CMS was then irradiated using electron beam (EB) radiation and underwent radiation induced cross-linking, resulting in a cross-linked carboxymethyl starch (CCMS). The CCMS was characterized for gel content and swelling property. Structure of the CCMS was determined using SEM, wide angle X-ray scattering and FTIR spectroscopy. Metal removal efficiency of the CCMS was evaluated for extraction of copper (Cu) and cadmium (Cd) ions from aqueous solution by varying pH, metal ion concentration, adsorption time and the dose of adsorbent. Biodegradation property of the CCMS irradiated at various doses of EB was evaluated by using soil burial method.

S14-516

## Impact modification of degradable PLA-flax composites with natural rubber: The influence of flax fibre content and processing parameters on Impact strength.

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Poly-(lactic acid) is a fully biodegradable and versatile polymer, which can be processed similar to polyolefins. Its good mechanical properties e.g. high stiffness and high tensile strength combined with optical good properties (transparency) make PLA attractive for many packing and household applications. In order to introduce PLA also in the automotive industry and other high performance markets new composite recipes have to be developed, which overcome the low thermal stability and improve toughness. The goal of this study was to improve the impact strength properties of PLA by varying the natural rubber content and flax content as well as processing parameters e.g. rotational speed and flow rate in a parallel twin screw extruder. In a first attempt with PLA – natural rubber compounds the Charpy Impact strength of PLA increased from about 20kJ/m<sup>2</sup> to almost 80kJ/m<sup>2</sup> by varying the natural rubber content between 5% and 20%. To further improve the impact strength and stiffness Flax fibers of different lengths (4mm to 8mm) were added to the PLA-NR compounds. Compositions of PLA compounds with a fiber content ranging from 10% to 30% and the NR content from 5% to 30% were created and mechanically tested. As an overview the mechanical data of PLA-Flax, PLA-NR and PLA-Flax-NR compounds were compared in a diagram E-modulus versus Charpy Impact strength. The fracture mechanism of the samples was investigated with the aid of SEM pictures of a PLA-Flax, PLA NR and a PLA-Flax-NR compound.



## The Effect of Prodegradant on Accelerated Aging of Polyethylene-Poly(3-hydroxybutyrate) blends

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Plastic packaging accounts for around 40% of world plastic output and is growing faster than any other packaging material. At the same time, a very visible portion of municipal and industrial waste consists of polyethylene (PE) films utilized on a massive scale as packaging material. Full carbon backbone polymers, wherever occurring may sustain biodegradation in two steps. The first one (degradation step) would be a photo-and/or thermo-oxidation promoted by photo-active and thermo-active prodegradants, leading ultimately to oxidized fragments of substantially lower molar mass. These oxidized fragments may become vulnerable to microorganisms present both in solid and aqueous media with their conversion to water, carbon dioxide and cell biomass (biodegradation step). Improvement of PE degradation/biodegradation behaviour was studied by performing a statistical experimental design. Independent variables studied were the amount of poly(3-hydroxybutyrate) (PHB) and of two thermal prodegradant additives supplied by EPI-Canada. Samples were subjected to an accelerated thermal ageing in a static oven at 55°C by 60 days. Data from mechanical and thermal behaviour were analysed statistically as dependent variables. Blends containing EPI-TDPA prodegradants showed to be more brittle after aging under controlled conditions than the counterparts prodegradants-free. In general the tensile modulus of the blend increased with aging for pristine PE and formulations containing prodegradants. On the other hand, blends containing only PE and PHB showed almost invariable tensile modulus. Data showed that the degradation temperature (Td) decreased with aging time with more significant effect in samples containing prodegradants.

S14-527

## Characterization of the Biodegradable Composite: PHB/Sugar Cane Bagasse's Fibers.

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The objective of this work was to characterize a composite of biodegradable polymer PHB modified with a natural fiber, also biodegradable. The bagasse fiber was used the PHB produced industrially for PHB Industrial Inc. The sugar cane, that industrially started to be produced in Brazil, was supplied by the Edra Eco Ltda Systems. For the process of incorporation of the sugar cane bagasse fiber a screw profile was developed aiming at to the use of 20-40% of fiber (% mass), for two sizes of different fibers. After that, they were processed again in an injection molding machine, where the granules of the polymeric composites, prepared in the twin screw extruder, were processed in an injection molding machine Arburg All Rounder model 270V 300-120, with injection of test bodies ASTM of traction and impact. The compositions had been evaluated mechanically, thermally and morphologically. For this techniques had been used as DSC, Test of Impact and Tensile, GPC and SEM. Also assays of biodegradable, in organic composition, of the pure PHB and bagasse the PHB/fiber compositions had been carried through of sugar cane, in different periods, evaluating structural variations and of properties caused for the biodegradation. The gotten results show that the percentage (%) mass of fiber that presented better resulted in the preparation of the composites was of 30%, as much for the processing as for the properties. Already with the results of the biodegradation assays it proved biodegradable and the gradual loss of properties of the compositions for the different periods.



## Stabilizers consumption during polypropylene multiple extrusions

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Polypropylene when submitted to high shear rate, high temperature or ultraviolet (UV) radiation undergoes structural modifications, usually accompanied with deterioration of the physical and mechanical properties. Suitable stabilization systems can be used to prevent or inhibit these detrimental effects by interfering with degradation mechanisms. Usually the different types of stabilizers are mixed into the polymeric mass, in the molten state, via polymer extrusion. During the melt mixing, the stabilizers concentration decreases due to physical loss by pyrolysis and chemical reactions with the radicals present in the molten polymer. The consumption of stabilizers is dependent of the processing parameters, since they affect the formation of radicals and so the intensity of the degradation processes. In this study the consumption of different types of stabilizers during multiple extrusions of a random copolymer polypropylene in a modular twin-screw extruder was analyzed. It was prepared two formulations containing 0.2% w/w and 0.4% w/w of each additive. After multiple extrusions, the stabilizers were extracted by dissolution-precipitation method and their concentrations were quantified by size-exclusion chromatography (GPC). The hindered amine presented the higher consumption percentage, followed by the phosphite, the hindered phenol presented the lower consumption percentage. Besides the additives consumption with the increase of the number of extrusion cycles, it was also observed an increase in the retention time of the high molecular weight amine, possibly due to its molecular scission. This shift increases when the hindered amine was used at lower concentration.

S14-595

## Maghnite-H+, an ecocatalyst for cationic polymerization

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The polymerization of vinyl monomers catalysed by the Maghnite-H+ (Mag-H) was investigated. Mag-H is a montmorillonite sheet silicate clay, exchanged with protons. It was found that the cationic polymerization of Isobutylvinyl Ether (IBVE), N-vinyl-2-pyrrolidone (NVP), Isobutylene (IBu) and Styrene is initiated by Mag-H at various temperatures, in bulk and in solution. The effect of the amount of Mag-H, the temperature and solvent was studied. The polymerization rate increased with increase of the proportion of catalyst and the temperature. The solvent effect depends on the structure of the monomer. The results indicated the cationic nature of polymerization. It may be suggested that the polymerization is initiated by proton addition to monomer from Mag-H.



## CHARACTERIZATION OF VINYL PLASTISOLS BASED ON THE USE OF LOW ENVIRONMENTAL IMPACT PLASTICIZERS DERIVED FROM EPOXIDIZED LINSEED OIL

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PVC is one of the most important products of the chemical industry. As a building material, PVC is cheap and easy to process. It can be made more flexible by the addition of plasticizers. Common plasticizers used in industry are phthalates (DINP, DINCH, DOP). In this form, it is used to make flexible tubes, roofing membranes, electrical cables insulating... Despite it seems to be an ideal building material, the costs of PVC to the natural environment and human health are high, due to possible migration of phthalates and an insufficient thermal stability that causes the release of hydrogen chloride in non stabilized PVC. In the last years, a new type of plasticizers has been developed. This type of plasticizers can solve the problems cited previously. In the present study, we have chosen epoxidized linseed oil as an alternative plasticizer for PVC. It biodegrades quickly and comes from plants, a clean and renewable energy resource. With this purpose different concentrations of ELO have been added to PVC. The processing conditions (temperature and time of curing) are vital to determine the final properties of the material. A study of the processing conditions shows the adequate temperature and time to achieve the optimum properties. The results obtained for these conditions show an increment of thermal stability as ELO content increase. The tensile strength and elongation at break of the plasticized PVC/ELO vary as increase the percentage of ELO added. On the other hand the addition of ELO reduces the glass transition temperature of PVC. The use of ELO can be an effective solution to the problems of environmental health derived from the migration of phthalates and to the problem of the thermal stability and the possibility of the release of hydrogen chloride. Also the mechanical properties offer a similar behavior than traditional plasticizers.

S14-723

## microwave assisted recycling of polyester based polyurethane wastes

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Polyurethanes (PUR) are one of the most versatile groups of plastic materials. The variety of PUR types reaches from flexible foams and rigid foams over thermoplastic elastomers to adhesives, paints and varnishes. This variety is one of the reasons, why the development of cost-efficient recycling methods is very difficult. On the other hand, the production of PUR is rather expensive - compared to the mass-produced plastic materials like the polyolefins. This fact was the reason for the development of recycling methods for PUR since the 60s. Glycolysis, which is already used on a commercial scale, means the decomposition of PUR by diols and polyols at elevated temperatures through a transesterification reaction. The reaction products are polyols which are similar to the virgin components and can be directly used for the manufacture of new PUR. In the continuation of previous reports about the PU foam waste glycolysis, in this study, glycolysis reactions of methylene diphenyl-di-isocyanate (MDI) and polyester polyols based flexible PU foams are conducted with sorbitol solution using microwave as an energy source and polyester polyols recycled without hydrolysis of ester groups.



## **New polyurethanes based on aminolysis of polyethylene terephthalate waste**

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There are many methods of PET waste management among which chemical recycling (e.g. hydrolysis, alcoholysis, acidolysis, aminolysis and ammonolysis). In this investigation polyethylene terephthalate in the form of waste fibres and disposable soft drink bottles was subjected to depolymerisation through aminolysis using excess of ethanolamine in the presence of sodium acetate as catalyst. The product bis(2-hydroxy ethylene) terephthalamide (BHETA) obtained was in its pure form with sufficiently high yields. The purified product was characterised by IR spectroscopy, Nuclear Magnetic Resonance (<sup>1</sup>H NMR), (<sup>13</sup>C NMR). BHETA was investigated as a diol component for new polyurethanes synthesis by reaction with hexamethylene diisocyanate (HDI) and toluylene diisocyanate (TDI). The product was characterised by FT-IR spectroscopy, Differential scanning calorimetry (DSC). The process of reported here is economically viable since yield of polymer is high. References[1] Shukla, Ajay M. Harad, Polymer Degradation and Stability, Aminolysis of polyethylene terephthalate waste, 91 (2006) 1850-1854. [2] M. Kacperski, T. Sychai. Polym. Adv. Technol, Rigid polyurethane Foams with poly(ethylene terephthalate)/ Triethanolamine Recycling Products, 10 (1999) 620-624.

S14-746

## **The change in structure of ABS and ABS/PC polymers resulting from technological recycling**

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The problem of polymer wastes reusing is considered in this article. Estimation of the change in polymers structure during and after their processing allows to understand the process of polymer degradation, that have a significant influence on mechanical, thermal and other properties of molded parts made of recycled materials. In experiments two materials - ABS and ABS/PC blend (in 6/4 proportion) were reprocessed six times by injection molding. After multiple reprocessing the degradation of polymer was observed. Fracture patterns of parts made of multiple reprocessed polymers were examined by scanning microscopy SEM. Significant difference in parts morphology was found, especially for ABS/PC blend. Structure investigations were also carried out by permeation chromatography analysis GPC, using polymers dissolved in chloroform. This analysis showed small changes in structure of both polymers. Results of examinations can be useful when possibility of particular polymers reusing is estimated. Polymer wastes can be reused in the same production process, from which parts were obtained, or for manufacture of new, of lower requirements products. However, the change in polymer structure arising from multiple heating and cooling in successive injection molding cycles should be known to allow proper use of recycled materials.





## Using Simultaneous TG/DSC Analysis to Analyse the Degradation Kinetics of Polyethylene

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Polyolefins are one of the major chemical produced worldwide, with a tremendous impact on our daily life and, consequently on the generation of urban wastes. Chemical recycling of polyolefins is a potentially interesting alternative for the management of these plastic wastes. Thermal and catalytic degradation can be used to produce hydrocarbons in the gasoline range that can be used as fuels, mainly by a sequence of steps that are related to the cracking of paraffinic petroleum cuts. Thermal processes tend to have a relatively high reaction temperature but catalytic degradation allows the plastic cracking to be performed at lower temperatures and may also lead to a better control of the product distribution. This process has been raising increasing attention and several papers, dealing with the use of various catalysts, namely zeolites, for this type of reaction, have been published 1,2,3. In order to develop a suitable catalyst for this process, the kinetics of the cracking reactions has to be analysed. In order to follow the progression of the cracking reactions, since the reactant molecular weight is extremely high, there is a severe limitation in looking only at the gas phase products. The use of heat flow information, which will be able to provide a measurement of the rate of molecular bond breaking, with the weight or gas phase analysis information can supply a further insight into the reaction kinetics. In this work, the thermal degradation of high and low density polyethylenes is analysed using simultaneous TG/DSC analysis. The results obtained in the thermal degradation are compared with the catalytic degradation using transition metals supported in NaY; these latter catalysts have been shown to be efficient for the reverse reaction, i.e. ethylene polymerization<sup>4</sup>. These catalysts were prepared by either ion-exchange or by incipient wetness method on the parent NaY zeolite.

S14-768

## REINFORCEMENT OF STARCH-BASED BIODEGRADABLE RESIN BY HEMP FIBER

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This work describes the development of biodegradable resins using hemp fiber and more particularly boon (peeled hemp). The boon is a part of hemp reed that is not very used. Due to their low density and low cost in comparison to conventional fibers, boon fibers composites have great potential for different uses. Used on its own, starch material has poor mechanical properties. Yet, it has good high strength properties when mixed into polymer matrix. In order to better understand interfacial phenomenon between fiber and matrix, we used two different types of starch : wheat and potato starch. Blends were made in a twin-screw extruder. Viscoelastic properties at melt and solid states have shown how interactions develop within the composite thanks to rheological analysis. We studied more particularly the adhesion of the fiber to the matrix and an eventual way of compatibilization. The two types of starch showed different behaviors. Mechanical properties such as tensile and flexural strengths were led versus rate of boon fiber. Fracture surface after tensile testing illustrated the degree of adhesion quality versus tailoring parameters. The purpose of this approach is to make a starch-based biodegradable composite for cushion in packaging.



## Starch blends reinforced with cellulose nanowhiskers and nanoclays for biopackaging

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In the world of packaging, the use of bioplastics as a substitute for petroleum materials has increased during the last decade due to the more environmental consciousness. The use of polymers based on natural resources are a possible alternative, however, to enhance the material properties is necessary the development of nanobiocomposites using different nanoreinforcements such as nanofibres or nanoclays, because the mechanical and barrier properties of biopolymers are not competitive with oil based polymers.(1)The purpose of this project is the study of these reinforcements into a biodegradable matrix like potato starch, in order to become this biopolymer in an alternative to oil derived plastics.Reinforcement used are, two types of cellulose fibres: Microcrystalline cellulose (MCC), Cellulose whiskers obtained by acid hydrolysis of MCC(2) and Sodium montmorillonite clay.Previously to processing steps, a morphological characterization of the nanofillers were performed. Several experiments have been carried out to improve the dispersion of the fillers within the polymeric matrix, and to obtain an optimum combination of fillers to enhance material properties.The films obtained have been characterized by DSC, X-Ray Diffraction, Tensile tests, Oxygen and Water Vapour transmission rate The results conclude that the use of nanofillers in polymeric matrices show important results concerning the improvement in properties as for example, barrier properties, thermal and mechanical properties(3). (1) Ching,C, Kaplan.D, Thomas.E: “Biodegradable Polymers and Packaging”, First Edition,Technomic,(1993). pp 43-51.(2)Bondenson.D, Mathew.A, Oksman.K: “Optimization of the isolation of nanocrystals from microcrystalline cellulose by acid hydrolysis”, Cellulose (2006).13:171-180.(3) Lever A.E. & Rhys J.A. “The Properties and Testing of Plastics Materials”, Third Edition, Temple Press Books (1968).pp 37-157.

S14-836

## Maghnite, a new green catalyst for the synthesis of Poly (D,L-lactic Acid)

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The development of synthetic biodegradable polymers, such as poly( $\alpha$ - hydroxy acid), is particularly important for constructing medical devices, drug delivery systems, including scaffolds and sutures, and has attracted growing interest in the biomedical field. Here, we report a novel approach to preparing poly(D,L-lactic acid) (PDLA) as a biodegradable polymer. We investigated in detail the reaction conditions for the simple direct polycondensation of lactic acid, including the reaction times, temperatures, and catalyst. The molecular weight of synthesized PLA is dependent on both the reaction temperature and time. The optimum reaction condition to obtain PDLA by direct polycondensation using Maghnite-H<sup>+</sup>, a proton exchanged Montmorillonite clay, as catalyst was thus determined to be 120°C for 28h with a molecular weight of 7970. The method for PDLA synthesis established here will facilitate production of PDLA of various molecular weights, which may have a potential utility as biomaterials. Keywords : Direct polycondensation, D,L-lactic acid, PDLA, maghnite- H<sup>+</sup>.



## Moisture Sorption Characteristics of Thermoplastic Starch: a Kinetic Evaluation on the Dependence of Water Activity

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Thermoplastic starch (TPS) is a biodegradable material providing environmental benefits including utilisation of renewable resources. High amylose starch is preferred for extruded film and sheet formation due to its thermoplastic properties. Formation of TPS by extrusion requires swelling, plasticisation, melting and gelatinisation of the native starch granules. These processes require water to promote particular structural and phase changes. Water plasticisation, thermal energy and mechanical shear allow starch molecules to be released from the granules to form an amorphous state that behaves similarly to a thermoplastic melt. TPS film formed in this process retains hydrogen-bonded water in its structure. The affinity of water toward starch has implications on the function and performance of TPS film, therefore the amount and availability of water is critical. The aim was to investigate the state of water in the TPS and changes initiated by variation in water activity ( $a_w$ ) under controlled environmental humidity (saturated salt solutions). The TPS was exposed to a series of water activities from of 0.50→0.75→0.84→0.75→50→0.33→0.0. At each stage, the equilibrated TPS was heated at 2 °C•min<sup>-1</sup> in a thermogravimetric analyser to desorb the water from the starch. With increased water activity, the TPS sorbed up to 15% water at  $a_w = 0.84$ . The amount of water retained in the structure after exposure at the highest  $a_w$ , was higher than the initial water content. For instance, at 0.75, water desorption was 13.8% and 14.6%, before and after  $a_w = 0.84$ . The difference is attributed to swelling of the amorphous starch structure, leading to an increase in sites exposed for hydrogen bonding to water. This phenomenon has been described as occurring in other types of gel materials. Non-isothermal kinetics will be applied to the dehydration at each water activity to derive the kinetic parameters {activation energy (E), pre-exponential factor (A) and the order of reaction (n)}.

S14-902

## Molecular Simulation for Processing of Starch System

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Pure starch does not melt. Its melting temperature is higher than decomposition temperature. However processing of starch is possible when we add water to starch system. Water plays a role of plasticizer to destabilize hydrogen bonded crystal system of starch molecules. Recent experiments on temperature controlled milling of rice particles shows that temperature and shear with small content of water affect crystallization of milled rice particles. In this study we perform molecular simulation that examines process of crystallization control in system of starch molecules. Modeling and simulation method will be proposed.



## Reactive Blending of Polypropylene and Nylon Films from Commingled Plastic Wastes

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Reactive extrusion for recycled PP/nylon blends from commingled plastic wastes was investigated through thermal, morphological, mechanical and rheological studies. From SEM investigation, we found improved surface morphologies with homogeneous domains in the recycled 75/25 PP/nylon blend compatibilized with copolymers containing maleic anhydride (MA) as a reactive functional group; SEBS-g-MA, PP-g-MA. Especially, SEBS-g-MA thermoplastic elastomer which is highly reactive with amine terminal group of nylon, resulted in a large increase of impact strength above nearly 200%. This compatibilization effect resulted from the increase of interfacial adhesion and the reduction of domain size of dispersed phase in PP/nylon blend system. To confirm the existence of this network structure, we measured a dynamic rheological properties.

S14-932

## Recycling of Cross-linked Polyethylene Using Supercritical Fluids Process

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The cross-linked polyethylene has been widely used as an insulating material for electric wires and cables because of its high insulating characteristics. XLPE does not dissolve in solvents and melt by heat owing to the cross-linking network structure. However, it is very difficult to reuse such a thermosetting resin, therefore, in present, most of waste cross-linked polyethylene have been incinerated or disposed of in landfills. We investigated the method to recover thermoplastic polyethylene from cross-linked polyethylene using supercritical fluids. The cross-linked polyethylene foam can be completely re-plasticized in supercritical water and methanol in a short time, and the effect of several process parameters was investigated. The degree of cross-linking, molecular weight and thermal properties of products were analyzed using GPC(Gel Permeation Chromatography), DSC(differential scanning calorimeter), TGA(Thermogravimetric Analysis), and FTIR(Fourier-Transformation Infrared). Observations of phase morphology were performed using SEM(Scanning Electron Microscopy). All specimens were manufactured by Minimax Molder. Measurements of physical properties of specimens were carried out by Impact Tester, Instron Tensile Tester and TMA(Thermal Mechanical Analyzer). Successful recycling of cross-linked polyethylene was achieved by supercritical fluids.



## Films based on chitosan and $\beta$ -cyclodextrin/eugenol for fruit packaging application

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Films based on chitosan and  $\beta$ -cyclodextrin/eugenol for fruit packaging application Barbara Immirzi(1), Mario Malinconico(1), Salvatore D'Aquino(2), Mario Schirra(2), Adele Cutignano(3)(1)Institute on Chemistry and Technology of Polymers – National Research Council - Via Campi Flegrei, 34, Pozzuoli, Italy.(2)Institute on Science of Food Production – National Research Council – Via dei Mille, 48, Sassari Italy.(3)Institute on Biomolecular Chemistry – National Research Council – Via Campi Flegrei, 34, Pozzuoli, Italy. Chitosan is a polysaccharide mainly extracted from shell wastes of shrimps and lobsters. Chitosan acts as a preservative coating when sprayed on plants and vegetables. It is insoluble in water, but dissolves easily in diluted acid, showing good film forming capability. Eugenol is an essential oil, slightly soluble in water, used in medicine as antiseptic and shows an inhibitor effect on *Penicillium citrinum*. Cyclodextrins make up a family of oligosaccharides and are able to form host-guest complexes with hydrophobic molecules, so enhancing their solubility in water. This study was undertaken to prepare films based on chitosan with different amount of cyclodextrin-eugenol to be used for fruit packaging application. We provide information on chemical-physical and mechanical properties of cast films for packaging application; moreover, the release of eugenol in different conditions is reported.

S14-965

## THE INVESTIGATION OF BIODEGRADABLE POLYCAPROLACTONE(PCL) / STARCH BLENDS

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The starch was degraded by various kinds of acid (oxalic acid(OA), succinic acid(SA)) with various concentrations (0.1, 0.5, 1.0M ). The melt flow index (MFI) of PCL/ST blend could be increased from 2.73g/10min to 66.90(g/min) as the starch was degraded by 0.5M oxalic acid solution. The elongation of O1, O2, O3 blends could be increased about 2.0 times higher than that of PCL/ST blend. SEM graphs show that the phase separation phenomenon between PCL and starch could be improved by adding high concentration (0.1, 0.5, 1.0M) oxalic acid solution treated starch to the blends. keywords: starch, biodegradable, modified starch.



## Effect of Plasticizer and Plasma Treatment on

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In this study, poly(vinyl alcohol) and starch were used as mainly raw materials for producing biodegradable plastics by the single screw extruder. Effects of plasticizers and plasma treatment on the mechanical properties, physical properties and the biodegradability by composting of composites were investigated. As starch plasticized by H<sub>2</sub>O or acid, the interphase between PVA and starch could be improved. After PVA treated by plasma treatment, the maximum stress of starch(m-50%,adipic acid)/PPVA is achieved to about 16MPa.

S14-971

## CHARACTERIZATION OF LIGNIN/POLY(VINYL ALCOHOL) HYDROGELS

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The incorporation of the natural polymer in the synthetic matrix is an alternative way to reduce polymer waste production, the demand energy, risks and costs. These offers on one hand the possibility to obtain a broader application range of the usual polymers and on the other hand to produce new material with defined properties or with a life cycle well controlled. In this idea, the present study offers the possibility to synthesis new hydrogels from green polymers. These were obtained by the covalent cross-linking of steam explosion lignin from aspen wood or epoxy-resin of it, with poly(vinyl alcohol), in the presence of the epichlorohydrin. It has been established that the lignin nature significantly influences the swelling process. The hydrogels were characterized by elemental analysis, FTIR spectroscopy, scanning differential calorimetry (DSC) and thermogravimetry method.



## LIGNIN CONTAINING INTERPENETRATED NETWORKS

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Interpenetrating polymer network (IPNs) are defined as a combination of two or more polymers in network form that are synthesized in juxtaposition. It is known that the most IPNs do not interpenetrate on a molecular scale; they may form divided phases of only tens of nanometers in size. Many IPNs exhibit dual phase continuity, which means that two or more polymers in the system form phases that are continuous on a macroscopic scale. In this study the polymer networks based on poly(vinyl alcohol) and various lignin type by crosslinking reactions with epichlorohydrine have been prepared. The interactions between components were examined by a comparison of rheological and reaction kinetic changes. Phase morphologies of the IPNs analyzed by electron and atomic force microscopy. The formation of simultaneous interpenetrating network materials is indicated by FT-IR and mass spectroscopy.

S14-1003

## Compression Molding of Fiber Reinforcement Plastics based on Papermaking Method with Extracted Carbon Fiber from FRP Waste

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Today, the effective utilization of FRP (fiber reinforcement plastics) waste is a large concern. FRP recycling technology by unsaturated polyester decomposition under ordinary pressure is useful to extract reinforcement fiber from FRP waste. In this study, we investigated molding of thermoplastic composite materials reinforced by carbon fiber extracted from FRP waste. As raw material of matrix resin, we used polyester fiber waste discharged from textile factory. In order to make sheet shape of preform, papermaking method was applied to carbon and polyester fiber. Obtained preform was laminated in metal mold and compressed at 300°C. The mechanical properties of composite board was investigated.



## Compression Molding of Fiber Board by Using PET/PE Sheath/Core Fiber as Binder

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The compression molding method of fiber board was to bind base fiber with low melting chemical fiber (PP). These fiber boards are thought for various applications. For industrialization, Optimum shape of binder fiber must be argued because mechanical properties derive in solidification morphology. In this study, PET/PE sheath core fiber was used as binder. By melting only the sheath material (PE), boards were molded and evaluated for bending properties. As a result, bending properties of boards using PET/PE binder had similar trend with boards using PP binder by increasing densities, however lower in value. By microscopic study, it was found that using PET/PE sheath core fibers as binder results the growing in fiber crossing numbers. This was because where PP fiber melt away, PET/PE fiber leaves PET fiber as linkage and PE connects base material and PET fiber. After bending tests, solids of PP were found broken or with cracks in boards using PP binder while PET fiber pull-out and small amount of PE breakage was found in boards using PET/PE binder. PE is known for poor adhesion and the result of the PET fiber pull-out is one of this cases. Although fiber pull-out occurred, the morphology of PE binding PET and base fiber worth special mention. As from the results observed by the boards using PET/PE fiber boards, sheath core fiber was capable for binder use.

S14-1016

## PALM OIL BASED EPOXIDES AS PVC PLASTICIZERS: SYNTHESIS, CHARACTERIZATION AND INCORPORATION ON INDUSTRIAL FORMULATIONS

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This century opens new opportunities for the engineering of chemical reactions involving renewable materials, coupled with product design requirements as specified by the polymer processor. Environmentally conscious design of transformation process is a necessity for the plastics industry. Colombia as the fourth palm oil producer in the world has an increasing crop of palm per hectare. Palm Olein, a product of palm oil refining, was epoxidized by the in-situ production of peracetic acid from hydrogen peroxide and glacial acetic acid using acid catalysis. The effect of several process parameters were studied to improve the epoxide yield (oxirane value 3.3), thus favoring the plasticizing effect of the functionalized triglyceride. Epoxide was then incorporated on current formulations used by PVC industry (in the andean region) using di-octyl phthalate (DOP) as primary plasticizer. By varying the amount of DOP/epoxide ratio and through a statically design of the experiment, the insertion of the epoxide during PVC extrusion, allowed the replacement of 30-50% of DOP content as plasticizer. Selected thermomechanical properties were measured including the glass transition temperature, T<sub>g</sub>, which for the PVC-Plasticizer mix was adjusted by the use of the Cox-equation, allowing the thermodynamical validation of the mixture. Long term stability is currently being measured. Due to high variation in crop composition the same study was performed with oil produced from different regions of Colombia. The determination of the large scale viability for the incorporation of palm oil epoxides on PVC will be made by industrial extrusion trials that are going to be performed with Colombian PVC processors. The expected production cycle will be robust enough in order to respond not only to price variations in crude oil but also to the struggle between vegetable oils as their prices rise, a direct consequence of the biofuels boom.





## **Ternary blends of chitosan /poly(vinyl alcohol)/poly(lactic acid) produced by oil-in-water emulsion processing.**

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Recently the interest in producing blends of chitosan with other polymers has increased due to renewable character and antimicrobial activity of chitosan. Chitosan is a cationic polyelectrolyte when dispersed in slightly acid aqueous media. Thus, the blends of chitosan and water soluble polymers can be prepared by blending the polymer solutions. Poly(lactic acid) (PLA) is a biodegradable polymer that has attract much attention due to its potential use in several applications such as packaging and textile fibers. PLA is soluble in organic non-polar solvents and its direct solution blending with chitosan is not possible. Blends of PLA with chitosan have been prepared by the oil-in-water emulsion process sowing poor miscibility (Sébastien, F., et al., Carbohydr. Polym., 65, 185, 2006). In this work a ternary blend of chitosan /poly(vinyl alcohol) and poly(lactic acid), were produced by W-O process using PVA as a compatibilizing agent. The polymers used were, chitosan from crab shell with (85 % deacetylation), poly(vinyl alcohol) from Aldrich (89 % hydrolysis) and PLA L 9000 from Biomer. The blends were prepared by mixing solutions of chitosan in aqueous acetic acid (1%), poly(vinyl alcohol) (PVA) in water and of PLA in chloroform using a high shear mixer (Ultra-Turrax) at 12.000 rpm. The blended solutions were poured on glass Petri dishes and the films resulted by solvent evaporation at 40oC overnight. The produced blends where characterized by electron scanning microscopy (SEM), differential scanning calorimetric (DSC) and by dynamic mechanical analysis (DMA). The data were organized in a ternary phase diagram where it is possible to identify the regions of partial miscibility. Further work is necessary in order to test other PVA grades (molecular weight and hydrolysis degree). The use of C5 to C8 normal alcohols as co-solvents which could act compatibilizers are under course. \* Antonio J. F. Carvalho.

S14-1079

## **Microstructure and mechanical properties of solvent cast composites of thermoplastic biopolymer and coffee residues**

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Nowadays there is simultaneously a growing interest in both the development of new materials from renewable resources and composite materials with nanosized reinforcement. Since more than 10 years, bionanoparticle from biological source with great success and outstanding reinforcement have been prepared and characterized. The tropical agro-industrial residues such as coffee pulp and coffee husk are generated in large amounts during the processing and their disposal rather causes serious environmental problems. The aim of this work was investigate the microstructure and the mechanical properties of polyhydroxybutyrate-hydroxyvalerate (PHB-HV) and coffee pulp and polyhydroxybutyrate-hydroxyvalerate (PHB-HV) and coffee husk. Polyhydroxybutyrate-hydroxyvalerate (PHB-HV)/ coffee residues composites in rations of 10 to 40% of mass were prepared by chloroform solutions. The results showed that the coffee residues could be used as an excellent reinforcing material for some specific composite application, mainly in biodegradable products. And they are also able to satisfy both the economical and ecological interests.



## Viscoelastic properties and morphological characteristics of bitumen modified with recycled polymers

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The state of dispersion and viscoelastic properties, having the greatest influence on polymer modified bitumen blends behavior, were thoroughly investigated. Blends of bitumen 50/70 with 4, 6 and 8% recycled polyethylene from processed bags-PErec. and SBR were prepared in a specially designed mixer. These blends were characterized by optical microscopy, DMTA and other conventional methods. Photomicrographs indicated that dispersions with entirely different morphology, depending on the polymer modifier in bitumen/polymer blends were obtained; while PErec gave dispersions with almost spherical polymer particles, in the case of SBR lamellar domains were observed. It should be also emphasized that no phase separation at temperatures up to 130 oC in all cases was noticed. From the DMTA measurements in a solid state isochrones curves of the storage and loss moduli  $E'$  and  $E''$ , and mechanical loss angle vs. temperature for pure and modified bitumen were established. These curves confirmed enhanced viscoelastic properties of modified blends with much higher values of  $E'$  and  $E''$ ; sometimes these values were 3 to 4 times higher compared to neat bitumen. Blends modified with SBR showed a significant increase resistance to cracking at low temperatures due to which a shift of the glass temperature from -13.6oC to -34 oC was noticed; this effect was negligible in the case of PErec. Contrary, PErec gave better results at higher temperatures whereas as a result of the increased resistance to permanent deformation the softening point of the modified bitumen was shifted from 52 to 72oC. Thus, with this modification process improvement in deformation resistance, both, permanent deformation and cracking, was achieved; most likely that is due to the different morphology. Also, tensile properties and other conventional parameters were considerably changed. Overall, the modification process of bitumen was successfully carried out using recycled polymers.

S14-1082

## EVALUATION OF RHEOLOGICAL PROPERTIES OF THE SOLID STATE POLYMERIZATION PROCESS IN RECYCLED PET

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One way to increase the molar mass (MM) of recycled poly (ethelene terephtalate) – PET consist of solid state polymerization (SSP) make bottle-to-bottle recycling feasible. Although the rheological properties are extremely important to polymer processing, few studies have been done to study this properties in recycled resin and mainly in resin after SSP process. Then, in this work, rheological properties of post-consumer recycled PET after SSP process were evaluated in dynamic flow, steady state flow and transient flow, even about determination of intrinsic viscosity (IV) and carboxyl end groups concentration. The occurrence of degradative processes resulting from polymer recycling was shown by the increase in carboxylic end group concentration, the decrease in IV and MM values, as well as the results of rheological properties. All of these alterations are related to degradation by chain scission that may have occurred either in preparing the material for reprocessing, e.g., in grinding or in reprocessing owing to the high temperatures used, in addition to catalytic agents like humidity and oxygen involved in these processes. Furthermore, the results of complex viscosity as a function of frequency and time, as well, the results of  $G'$  and  $G''$  values as a function of frequency, shown that the SSP process promotes an increase in the MM values upper than virgin resin. With the rheometry results can obtain valuable informations about polymer molecular structure. Because the techniques used are extremely sensitive to MM variation, as demonstrated by its ability to detect the slightly superior molar mass of PET, after SSP process, compared to the virgin resin, which could not be determined by IV results. The purpose of SSP process was to increase the MM values of recycled polymer until similar values to the virgin resin. Then if the accompaniment of this process was realized by rheometry techniques in contrast of IV, could decrease the time of SSP process.



## Characterization of Rubber Tire Scraps (SRT-r) Devulcanized by Microwaves

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Rubber recycling is still a major problem in our modern society. Vulcanized rubber is a typical thermoset material, that is, unlike thermoplastics, can not be remolded by simple heating; it is first necessary to destroy the crosslinks between the polymer chains, making it moldable. Several techniques of devulcanization are described in the literature, using, among others, chemicals, ultrasound and microwaves. In this work, scraps rubber of the tire industry, was ground and devulcanized in several conditions (exposure time microwave; varied from 1 to 4 min). The resulting materials (SRT-r) were characterized in terms of its granulometry, gel content and thermal properties. The highest amount of the powder is in the range of 35 to 65 mesh (0.425 to 0.212 mm). Only 3% of the particles of SRT-r are higher than 0.60 mm. It was detected a decrease on the gel (insoluble) content as the irradiation time is increased, indicating certain degree of devulcanization. In DSC thermograms of SRT-r there is no exothermic peak in the region of 200oC, showing that the amount of residual accelerators and/or sulfur is not sufficient to cause sample vulcanization. The endothermic peak in the range of 100oC is due to sulfur melting (melting point 112.8oC). TGA was run in two conditions: in inert and in oxidant atmosphere. TGA thermograms in inert conditions, showed that the mass loss (58%), at 357 and 452oC, is due to the degradation of the elastomer (SBR). For the determination of the carbon black content, data were obtained from another TGA run, in oxidant atmosphere. In this thermogram, the mass loss (23.3%) at 535oC was due to carbon black decomposition. For the devulcanized SRT-r powders were observed that the more aggressive the microwaves treatment, the lower the relative amount of the SBR and the higher the amount of carbon black, indicating degradation of the polymer chains.

S14-1086

## Characterization of composites with addition of elastomeric vulcanized ground scraps

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Disposal of waste rubber is a serious environmental problem because elastomeric materials do not decompose easily. Mechanical recycling of vulcanized rubber scraps is a low-cost alternative in the search for the recovery of this kind of industrial solid waste. The aim of this work is to incorporate SBR (styrene-butadiene rubber) industrial scraps into a base formulation used in the fabrication process of extruded profiles (the original cycle production of waste rubber). SBR extruded profile scraps were ground under ambient conditions. The obtained powder (SBR-r) was physically and thermally characterized. Five formulations with different proportions (10 to 50 phr) of SBR-r were prepared and the results were compared with the original formulation without SBR-r. Rheometric characteristics and mechanical properties (tensile and tear strength) of developed compounds were evaluated, according to specific ASTM procedures. The obtained powder had a particle size distribution below 0.60 mm. Therefore, it is suitable for incorporation in new formulations. Thermogravimetric analysis showed the presence of 27.6% of SBR in the scrap rubber. With the ground scraps incorporation the vulcanization time decreased, when compared with compounds without ground scraps. The incorporation of 20 phr of SBR-r in the base formulation maintained the mechanical properties of the elastomeric device.



## **Biocomp - Composites from Renewable Resources – Progress of a European Project**

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Innovative environmental friendly approaches to materials use biocomposites the development of which has to be knowledge-based. Important issues are resource saving, variability in properties and functionality, light weight, low costs and eco-efficiency in all stages of the product life cycle. These are requirements to be met using raw materials of biomass, fibres, wood extraction constituents and biopolymers to supply branches of mass consumer goods, automotive and electronic industries in the future. The research project BIOCOMP funded by EU investigates engineering thermoplastic and thermoset materials from natural resources with contribution from 24 partners of industry and research institutes. Thermoplastic matrices are lignin from the paper industry and of the biopolymers polylactide, polyhydroxy-butyrates and starch. Reinforcement occurs by use of natural short fibers from hemp, flax and wood. Beneath standard methods of processing like extrusion, compression moulding and injection moulding advanced processing techniques like film stacking with aligned fibers and single step processing LFT-D-ILC. Thermoset processing involves furan resins and crops oil derivatives with vacuum infusion, SMC and BMC processing applied. Short and long fibers are investigated and woven and non-woven cellulose fibres and fibre mats used. On-line quality control uses Near Infrared Spectroscopy for controlling the composition. Crops oil based resins are developed to obtain fiber plates by compression moulding. Various model products and demonstrators are developed from the involved industrial branches and show the benefits of the materials and their limits of use. In more detail, a thermoplastic part is investigated processed by LFT-D and a thermoset model aerial vehicle the matrix of which is a furan resin.

S14-1138

## **Cure characteristics and mechanical properties of devulcanizable SBR ground scraps compositions**

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The recycling of waste rubber has very important significances, such as protection of the environment and conservation of energy. Considering that most of published works concerning this subject are about tire recycling, the objective of this work is to develop and characterize SBR industrial scraps devulcanizable formulations with technological applications. Firstly, SBR extruded profile scraps were collected in accordance with the standard ASTM E 300-03. The scraps were ground under ambient conditions. The obtained powder (SBR-r) was physically, thermally and chemically characterized. A homogeneous powder, suitable for utilization as raw material in devulcanizable compositions was obtained. From the devulcanizable SBR-r, two compositions were elaborated, varying exposure time of the powder in the microwave (3 and 4 min). These compositions were compared to a control sample, with the same formulation of the SBR scraps. This sample was supplied by the industry where the SBR extruded profile scraps were collected. Vulcanization parameters were determined by oscillatory disk rheometry, to obtain specific test specimens for proposed tests. Vulcanized compositions were characterized by crosslink density and physical-mechanical properties (density, tensile strength, tear strength and hardness). Mechanical properties of the compositions, being around 25% of the tensile strength of control sample and 41% of the tear strength. Crosslink density was definitive in the study, once that justifies the mechanical properties of compositions.



## CHARACTERIZATION OF SOLID AND CELLULAR COMPOSITES WITH RUBBER SCRAPS

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The problem of vulcanized rubber scraps is of high importance nowadays, and the solution to minimize this problem is the recycling and recovery in new materials. The residue used in this study is a expanded poly(butadiene-co-styrene) (SBR), resulting of the process of cutting insoles. This residue is a cross-linked material, since its natural degradation occurs over long time periods due to the presence of cross-linking, stabilizers and other additives. The SBR scraps were ground and obtained a powder (SBR-r). This powder was physically, thermally, morphologically and chemically characterized. Compounds with virgin SBR and SBR-r were developed with the objective to obtain solid and cellular composites. The amounts of the SBR-r varied from 0 to 30 phr. The structure foam was obtained by using the foaming chemical agent: azodicarbonamide. The compounds were prepared on a two roll mill and manufactured using compression molding. The rheometric, physical, chemical, mechanical, thermal and morphology properties of the composites were evaluated before and after accelerated ageing. It was observed that properties are improved with the incorporation of SBR-r content up to 20 phr. The result showed that the incorporation of gas cell inside rubber matrices affect their internal structure to be caused by cross-link destruction. Properties obtained with cellular composite depends of the quantity of elastomeric compound, parameters control process and SBR-virgin/SBR-r ratio. The cellular composites samples exhibit apparent density of 0,47 to 0,52 g.cm<sup>-3</sup>, closed cell, smaller cell size (less than 10 µm) and uniform cell distribution in elastomeric matrix.

S14-1164

## PROCESSING AND MECHANICAL CHARACTERISATION OF RECYCLED PBT CLAY NANOCOMPOSITES

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Polymeric nanocomposites are novel materials of huge interest due to their favorable cost/performance ratio with low amount of nanofillers, increasing thermal resistance, flame retardancy and mechanical properties of polymers. Polymer clay nanocomposite systems were successfully prepared by melt compounding using several thermoplastics (commodities and specialties), but none data were found to date in the literature on the use of recycled plastics as matrices. In this work, primary recycled PBT is being used to be reinforced with organic modified montmorillonite clays (MMT). Melt compounding with a twin-screw extruder was used to prepare recycled PBT/MMT compounds as a function of screw speed and grade of nanoclay. A fine balance between processing temperatures, shear, residence time and chemical affinity between clay and polymer is required for recycled PBT to minimize degradation phenomena and to get a good dispersion of the clay tactoids in the polymer matrix. Morphological analysis (TEM and XRD) suggested that a partial or initial exfoliation of the nanoclay in the PBT compounds was achieved when using the grade Cloisite 25A, less organophylic, but an intercalation when using Cloisite 20A. Injection moulded specimens were prepared for mechanical characterisation. It was found that tensile and flexural strength of the recycled PBT were improved when using nanoclays, but regarding impact strength no significant differences were found.



## MECHANICAL PROPERTIES OF COMPLEX BLENDS CONTAINING VIRGIN AND RECYCLED SYNTHETIC POLYMERS

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In the last few years, the interest in the recycling of plastics has increased significantly as a result of a growing awareness of their environmental impact. Plastic waste is to be found in higher proportions in refuse from industry, trade and household, so the state of the waste from different waste classes is very different due to the different history of that. Wastes from production and from polymer processing are often type-clean and in general polluted hardly, whereas plastics in waste from building sites or municipal waste stream are much polluted and contaminated with other materials. In this study, blends of recycled polypropylene (PPr) and polyamide 6 (PA6r), polymers obtained as waste in processing operation, were prepared by melt mixing process and a small amount of elastomer, namely ethylene-propylene-diene monomer (EPDM), was added. The ternary blends were compatibilized by addition of various grafted polymers containing functional reactive groups, such as maleic anhydride (PP-MA), acrylic acid (PP-AA) and bismaleimide (PP-BMI). In a second step, 20 wt% of the recycled binary (66.67PPr/33.33PA6r) and ternary (60PPr/30PA6r/10EPDM) blends was introduced in virgin polypropylene matrix and the effect of the type and concentration of compatibilizer, on the dynamic rheological and mechanical properties of the final blends was investigated. The results obtained from the evaluation of dynamic parameters, tensile and impact tests indicated that addition of PP-BMI and PP-MA allows for a marked improvement of physical/mechanical performances of studied blends.

S14-1259

## EFFECT OF SZE REINFORCEMENT ON THE BEHAVIOR OF BIODEGRADABLE POLYMER BASED COMPOSITES

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In this work composites of polycaprolactone (PCL; Mn=80000) with 5 wt.% of agricultural cotton (macro); cellulose (micro) and nano-cellulose and also two different commercial clays (nano): one unmodified (MMT) and another organically modified (C30B) were prepared by melt-intercalation. Cellulose micro-fibres were obtained from cotton and nanocellulose were prepared by acid hydrolysis. It was determined that, whereas the macro and micro reinforcement produced a decrease on the crystallinity of the matrix, the nano-scale filler did not affect it. On the other hand, a clear decrease on the theoretical melting point took place in all cases; due to the presence of more heterogeneous nucleation that reduce the perfection of polycaprolactone crystallites but the effect was remarkable for higher-scale filler. The induction time, as well as, the half-crystallization time diminished when reinforcement was incorporated to the pure PCL; the higher the reinforcement scale, the higher the effect on both parameters. In the case of the nanocomposite; the clay dispersion degree, which is related to the filler/matrix compatibility, also affects both parameters. From the tensile tests; it is clear that the incorporation of all the fillers, except the nanocellulose, drive to a decrease on the tensile strength as well as an increase on the Young's modulus. Also, stiffens enhancements were related with several factors: the scale and the aspect ratio (l/d) of the filler, the matrix/filler adhesion and, also associated to their compatibility, the dispersion of the filler between the polymeric chains; and the rigidity of the new phase. In our study we have to consider all of these factors for the complete understanding of the mechanical behavior of the composites.



## Hybrid Wood Plastic Green Composites from Polyhydroxybutyrate-co-valerate (PHBV), Wood fiber and Talc

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Polyhydroxybutyrate-co-valerate (PHBV) is a widely recognized renewable resource based biodegradable copolyester from the passel of polyhydroxyalkanoates (PHAs). Physical properties of PHAs spread from stiff and brittle thermoplastics to elastomers, based on the characteristic of chain length, type of functionality and degree of unsaturataion in their branched chain. Natural fibers and fillers such as mica, kaolin, calcium carbonate, and talc are already functional and sustainable reinforcing agents in the thermoplastic matrix due to their abundant availability, low cost, and coherence with the nature. Nucleating capacity of talc in PHBV matrix had already been concluded but the effect of bulk quantity on mechanical properties of PHBV is not extensively studied. The high density of the talc can be offset by the low density of wood fiber thus generating the hybrid composite of the improved specific mechanical properties. In the present investigation, hybrid composites from wood fiber, talc and a bioplastic polyhydroxybutyrate-co-valerate (PHBV) were fabricated using the extrusion-injection molding technique. Synergistic improvement in the mechanical properties of micro sized talc reinforced PHBV was done with the incorporation of maple wood fiber. The hybrid green composites showed a pronounced leap in the Young's and flexural modulus with the dual reinforcement of 20 wt% of talc and 20 wt% of wood fiber in PHBV matrix. Morphological analysis of the hybrid composite was carried out using the scanning electron microscopy (SEM) to study the interfacial interactions among the different components in the hybrid composite. This investigation also attempted to establish the structure-property-processing co-relationship of the hybrid composites. This research is financially supported by USDA-CSREES under the McIntire-Stennis program of Michigan State University.

S14-1299

## Poly- $\epsilon$ -caprolactone/clay nanocomposites prepared by High Energy Ball Milling: mechanical, thermal and barrier properties

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Demand for degradable and biocompatible polymers is rapidly increasing, especially in the packaging sector where is highly encouraged by environmental management policies. The main limitations that prevented the degradable polymers widespread industrial use are they high cost and they poor mechanical and barriers properties. One of the most promising strategies to improve physical and mechanical properties of polymers and blends is the addition of small quantity of inorganic material, like clay, dispersed at nanometric level. The obtained nano-hybrids composites possess very unusual properties, very different from their microscale counterparts. In this work we propose an alternative method for the preparation PCL-Starch-Clay composites, which involve a solid-state mixing at room temperature: High Energy Ball Milling (HEBM). The clay dispersion was promoted by the energy transfer between milling tools (generally balls) and polymer/clay mixture, which in turns results grinded and intimately mixed. The structural organization and physical (mechanical, thermal and barrier properties) were studied and correlated with the milling processing. It has been proved that HEBM of powders, constituted by organic polymers and fillers, has been proved to be an alternative and efficient technique to produce novel composites.



## CHARACTERIZATION OF POST-CONSUMER POLYETHYLENE-TEREPHTHALATE (PET) BOTTLES

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Polyethylene-terephthalate (PET) bottles of different colors were sorted and separated from other house-hold post-consumer plastics such as high density polyethylene (HDPE) bottles and polystyrene (PS) disposable cups and plates. After sorting all PET bottles from other plastics, bottle caps which are mainly made of HDPE were removed manually. Bottles were then crushed into small flakes in order to accommodate for further processing steps. The main objective of the current study was to investigate the effect of pretreating of the PET flakes, prior to melt processing and compounding into pellets, on the properties of final products. Results of this study have shown that contaminants found with untreated PET flakes significantly influence its thermal properties which lead to multi phase immiscible system. On the other hand, PET flakes pretreated by washing with ordinary water resulted in pure PET single phase system

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## LIGNOCELLULOSIC FIBERS FROM THE CITRIC AGROINDUSTRY, IN THE ELABORATION OF BIODEGRADABLE PLASTICS

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Several cast films based on orange peel, pectin and polyvinilic alcohol (PVA), were prepared to study their biodegradability, mechanical and barrier properties. An additional study, was carried to observe the effect of sodium benzoate in the barrier properties. In laboratory, all films were totally mineralized after 306 hours, whereas in soil garden exposure, the films showed progressively fragmentation from 15, 30, 45, 60 days; after 90 days recuperation was not possible. The highest percent elongation and tensile strength ( $P < 0.05$ ) were 10% and 41 MPa, respectively, corresponding to the formulation with the highest level of PVA. The water vapor permeability ( $\text{gH}_2\text{O}\cdot\text{h}/\text{mm}^2$  at  $25^\circ\text{C}$  after 7 hrs) decreased with the PVA addition, from  $6.15 \times 10^{-6}$  to  $1.64 \times 10^{-6}$  ( $P < 0.05$ ). The addition of sodium benzoate, do not showed statistical significance in the permeability results. The cast films based on orange peel showed good mechanical and permeability properties, although less than synthetic plastics as polyethylene; however they can be an option for specific applications like mulching and packaging. By other hand the use of renewable residues is a very important way to produce environmentally friends products, mainly without any previous treatment, as in this case.





## NEW POLYMER CONCRETE CONTAINING FLOOR-COVERING RECYCLATES

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Polymer concretes are very attractive because of their capability for using recycled waste products as fillers. However, only a few examples of use of floor-covering recycle as fillers have been reported [1,2]. The aim of this work was the preparation of new polymer concrete which was formulated with floor-covering recyclates. The floor-covering wastes of polyamide 66 or polypropylene were applied as fillers for polymer concrete. The mechanical recycling of pre-consumer (cut-offs) floor-covering wastes was applied. The wastes were ground and added to polyester resin to obtain new materials with tailored mechanical and physical characteristics. For this purpose, the different mixture formulation of the materials were used. Then the physical and mechanical properties as moisture absorption, density, abrasion resistance, flex resistance and compression resistance of the obtained polymer concrete were investigated. The results indicate on the possibility of application of the floor-covering wastes of polyamide 66 and polypropylene as fillers for polymer concrete. [1] Y.Wang, A. Zureick, B.S. Cho, D. Scott, "Properties of Fibre Reinforced Concrete Using Recycled Fibres from Carpet Industrial Waste", *J. of Materials Science*, 29 (16), 1994. [2] Y. Wang, "Reuse of Carpet Industrial Waste for Concrete Reinforcement", in *Disposal & Recycling of Organic and Polymeric Construction Materials*, Edited by Y. Ohama (E&FN Spon, London) 1995, p.297

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## Mechanical and morphological evaluation of modified PP, starch plastized with glycerol from biodiesel and their blends

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Synthetic polymers have been used on short-life products, which have presented a harmful consequence for the nature, due to the low degradation rate reached by most common polyolefins, such as the polypropylene. By this way, the incorporation of pro-oxidants has been shown nice results to the bio-assimilation of the common polymers. The aim of this work is to obtain a modified polypropylene (PP) by the incorporation of pro-oxidant agents and the influence of the addition of thermoplastic starch biodegradable plastic (TPS) to PP. TPS was obtained by the incorporation of glycerin (sub-product of biodiesel), in a proportion of 80/20 (wt. starch / wt. glycerin) processed into an extruder (zone temperatures of 120°C and 140°C). PP was added using a masterbatch contained, individually, calcium stearate (SCa) and magnesium stearate (SMg) using temperatures of 200/210°C. It was reached a final amount of stearate of 0.2% in the blend. The blends with TPS and modified PP were prepared with a thermal profile of 200 and 210°C. The following compositions (modified PP/TPS - w/w) were prepared: 100/0, 95/5, 90/10, 80/20 and 70/30. Tensile tests were done according to ASTM D-638/99. The speed of stretching was 50 mm/min. The melting flow index was performed in an extrusion plastometer using temperature of 190°C and pressure of 2.16 kg (ASTM-D-1238/99). The samples were analyzed, by MEV, and it was observed a changing on the morphology with the addition of TPS. The addition of TPS progressively decreased the mechanical properties for all the blends. The formulations 80/20 and 70/30, presenting SMg and SCa respectively, reached the highest values of Young's Modulus, which were almost 20% higher than the pure PP. The MFI for the blends in the presence of TPS has increased its value for the polyolefin and the formulations 80/20 and 70/30, in the presence of SMg, reached values 30% higher than the pure PP. The degradation was more sensible to the samples containing SMg than SCa.



## CMC/EVA BLENDS COMPATIBILIZED WITH TRANSESTERIFICATION

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Blends based on poly(ethylene-co-vinyl acetate) (EVA) and carboxymethyl cellulose (CMC), have been obtained by reactive blending in a Brabender mixer and their physico-chemical properties as well as mechanical and rheological behaviours were evaluated. These blends represent a new type of biodegradable material and resulted promising for industrial application in several fields such as packaging and agriculture. Environmentally degradable polymers and polymer systems are important for modern technology as ecologically safe materials. Blends of starch or cellulose derivatives and certain synthetic polymers hold the lead among some new materials that have been used successfully. CMC is a natural organic polymer that is non-toxic and biodegradable. It is a polysaccharide which is widely used in many industrial sectors. These properties make it ideal for industrial applications and one of the most promising materials for biodegradable plastics. However, CMC has some limitations such as poor mechanical properties and processability for practical applications. Polymer blending is one of the easiest and most cost efficient ways to produce new material with the desired properties from each component and many researchers express considerable interest in compatibilization and in reactive compatibilization of immiscible polymers. The polyester family has the possibility to create chemical reactions because of its ester bonds and because the transesterification is the major reaction in polyesters. Researches about the exchange reaction of polymer blends commonly concentrate on polyester blends whose constituent ester bonds exist in their backbones. On the contrary, there are a few polymer investigations whose reactive groups exist in branching chain, such as EVA. EVA provide good mechanical properties, excellent ozone resistance, good weather resistance and relatively lower material cost.