## All-PP composites based on β and α polymorphic forms: mechanical properties

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Nowadays considerable efforts are being made to improve the properties of Poly(propylene) (PP) (versatile thermoplastic) matrices by reinforcing it with fibres. Although excellent mechanical properties have been achieved in this way, life cycle assessment does not yield favourable results for PP composites when they are "traditionally" reinforced with glass fibres. Self-reinforced composites represent an effective alternative to the traditional fibre reinforced composites where the matrix and the reinforcement are from the same polymer, thereby supporting the ease of recyclability. This topic has gained interest since the production of "single polymer composite" from polyethylene fibres and polyethylene matrix. Later on another group succeeded to convert a part of such fibres into matrix in which the residual fibres were embedded via "hot compaction". This material is nowadays commercially available as Curve®. The creation of highly oriented, co-extruded PP tapes allows the production of recyclable "all-polypropylene" (all-PP) composites, with a large temperature processing window (20-40°C) and a high volume fraction of highly oriented PP. This concept explored by researchers in the last years and was commercialised under the trade name PURE®. The most recent development with all-PP composites is to exploit the polymorphism- related difference in the melting range of  $beta(\beta)$ -(matrix) and alpha( $\alpha$ ) -phase (reinforcement) PPs carried out in the author's laboratory. Note that the  $\beta$ -PP has a markedly lower melting point than the alpha version. In this work, all polypropylene (all-PP) composites were manufactured from  $\alpha$ -PP tapes and  $\beta$ -PP matrix. The mechanical performance of the composite was investigated in a range of frequencies and temperatures using dynamic mechanical thermal analysis (DMTA). The volume fractions of matrix and reinforcement were estimated using optical microscopic images. Both the DMTA and the static flexural bending tests revealed that the  $\alpha$ -PP tapes act as an effective reinforcement for the  $\beta$ -PP matrix. Time temperature superposition (TTS) was applied to estimate the stiffness of the composites as a function of frequency ( $f = 10^{-9....}10^{20}$ ) in the form of a master curve. The Williams-Landel-Ferry (WLF) model described properly change in the experimental shift factors used to create the storage modulus vs. frequency master curve.

Key words: all-PP composites,  $\alpha$  and  $\beta$  polymorphic forms,mechanical properties, DMTA, time-temperature superposition

#### Studies on processing of styrene butadiene rubber-CaCO<sub>3</sub> nanocomposites by different mixing techniques and their performance properties

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Nano particles of CaCO<sub>3</sub> were synthesized by matrix mediated growth under controlled conditions and was used as filler in styrene butadiene rubber (SBR). The particle size of the synthesized nano CaCO<sub>3</sub> (35-60 nm) was determined by XRD and transmission electron microscope (TEM). The confirmed by SBR-CaCO<sub>3</sub> nanocomposites were prepared by using a Brabender Plastograph. The mechanical and physical properties of the nanocomposites were determined .The fracture surface of the nanocomposites was observed on a scanning electron microscope (SEM). The properties of the Brabender processed SBR-CaCO<sub>3</sub> nanocomposites were compared with two-roll mill processed SBR-CaCO<sub>3</sub> nanocomposites. The results showed that CaCO<sub>3</sub> nano-filler enhanced the properties of SBR as compared to pristine  $CaCO_3$ - SBR composites in both the techniques. Substantial improvement in properties was observed in the case of Brabender processed SBR-CaCO<sub>3</sub> nanocomposites as compared to pristineCaCo<sub>3</sub> based and two-roll mill processed SBR-CaCO<sub>3</sub> nanocomposites. The enhancement in properties was observed in Brabender processing technique owing to the higher shear rates which resulted in proper dispersion and mixing of nano CaCO<sub>3</sub> in SBR polymer matrix and to proper wettability of the inorganic particles by the polymer matrix.

**Key words:** - styrene butadiene rubber (SBR), nanocomposites, Brabender Plastograph, scanning electron microscopy (SEM)

## Studies on pressure sensitive adhesives based on blends of natural rubber and polychloroprene rubber modified with phosphorylated cashew nut shell liquid prepolymer

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Effect of variations in composition and processing on the T-peel adhesion strength of rexin specimens bonded with phosphorylated cashew nut shell liquid prepolymer (PCNSL) based pressure sensitive adhesives (PSAs) containing natural rubber (NR) and polychloroprene rubber (CR) has been studied. Increase in adhesion strength above that of a commercial sample of PSA has been observed with the increase in solids content of the PCNSL based PSA from 15% to 25%. Also, considerable increase in adhesion strength has been obtained with the increase in storage time prior to testing of the specimens from 1 to 7 days which indicates the time dependent diffusion behavior of PCNSL based PSA facilitating wetting and bond formation with the substrates. Irrespective of the solids content and the type of PCNSL, a maximum in T-peel adhesion strength is obtained at a CR dosage of 90 phr in the blend. Typical cohesive failure along-with high strength is obtained with PSAs based on PCNSL having a higher degree of phosphorylation / oligomerization. Uniform and almost complete wetting of the substrate has been confirmed by the optical stereo micrographs of the failure surfaces of the test specimens and the results of viscosity obtained from rheometry.

**Key words :-** pressure sensitive adhesives, natural rubber / polychloroprene rubber blends, phosphorylated cashew nut shell liquid prepolymer, peel adhesion, cohesive failure

## Aromatic-aliphatic co-polyester poly (butylene adipate-coterephthalate) bio-nanocomposite: Influence of organic modification on structure and properties

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Bio-nanocomposite hybrids based on poly (butylene adipate-co-terephthalate) (PBAT) and layered silicates were prepared by melt interaction technique using co-rotating twin screw extruder having blown film unit. Sodium montmorillonite (Na<sup>+</sup>MMT) along with three different commercially available nanoclays i.e., Cloisite30B (C30B), Cloisite20A (C20A), Bentonite (B109) was used. Wide Angle X-Ray Diffraction (WAXD) studies indicated an increase in d-spacing of the nanoclays in the biohybrids revealing formation of intercalated morphology. nanocomposites Morphological studies using transmission electron microscopy (TEM) also confirmed that nanoclays were finely dispersed in the PBAT matrix and there was presence of partially exfoliated clay galleries along with intercalated structures in the bionanocomposite hybrids. Mechanical tests showed that the bio-nanocomposite hybrids prepared using Bentonite nanoclay exhibited higher tensile modulus. Functionalization of PBAT matrix upon grafting with maleic anhydride (MA) resulted in further improvement in mechanical properties. The existence of interfacial bonds in grafted bio-nanocomposite hybrids is substantiated using FTIR spectroscopy. Thermal properties of bio-nanocomposite hybrids employing DSC and TGA also revealed improved Tg, Tc and thermal stability over the virgin polymer. Dynamic Mechanical Analysis (DMA) indicated an increase of storage modulus (E') of PBAT biopolymer with incorporation of nanofiller. The biodegradability of PBAT bio-nanocomposite hybrids showed an increase in the rate of biodegradability with addition of Na<sup>+</sup> MMT due to hydrophilic nature of the nanoclay.

**Key words:** poly(butylene adipate-co-terephthalate), TEM, DMA, MA-g-PBAT, bionanocomposites

#### Uncompatibilized and reactively compatibilized ternary polymer blends of PA6/PP/ABS: Morphological investigation

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Morphological investigation was carried out with melt mixed ternary polymer blends of polyamide 6 (PA6)/ polypropylene (PP)/ acrylobutadiene styrene (ABS) in order to understand the role of compatibilization in morphology developments. Uncompatibilized 80/10/10 PA6/PP/ABS blends exhibited matrix- dispersed droplet type morphology in which the dispersed phases (PP & ABS) found to exhibit core-shell type of morphology. The difference in morphology type may be due to a difference in surface energy between the matrix and one of the dispersed phases. Eventually it was found that "core-shell" type of morphology changed to "co-continuous" type on increasing the concentration of the PP and ABS in the ternary blends. In this context styrene maleic anhydride (SMA) co-polymer was found to act as a compatibilizer in PA6/PP/ABS ternary blends manifested in finer domain size or smaller ligament size in the respective ternary blends. Dynamic mechanical characterization has been carried out in order to understand the relationship between morphology and mechanical properties of PA6/PP/ABS ternary blends.

Key words: ternary polymer blends, core-shell morphology, styrene maleic anhydride copolymer, DMA, compatibilizer

#### Thermal and mechanical properties of poly (vinyl chloride)/ microscale and nanoscale calcium carbonate composites via melt intercalation

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Calcium carbonate was synthesized by *in situ* deposition technique and its nano size (35 to 60 nm) was confirmed by transmission electron microscopy (TEM). Composites of the filler CaCO<sub>3</sub> (micro and nano) and the matrix poly (vinyl chloride) (PVC) were prepared with different filler loading (0-5 wt. %) by melt intercalation. Brabender torque rheometer equipped with an internal mixer was used for preparation of composites. The effect of filler content, both nano and micro level on the nanostructure and properties is reported here. The nanostructures were studied by wide angle X-ray diffraction (WAXD) and scanning electron microscopy (SEM). The mechanical, thermal and dynamic mechanical properties of PVC/ micro and nano CaCO<sub>3</sub> composites were characterized using universal testing machine (UTM), thermo gravimetric analyzer (TGA) and dynamic mechanical analyzer (DMA). The results of thermal analysis indicated that the thermal stability of PVC/nano-CaCO<sub>3</sub> composites was better as compared with the corresponding microcomposites and that of pristine PVC and maximum improvement was obtained at 1 and 3 phr loadings. However, tensile strength decreased significantly with increasing loading of both nano and micro CaCO<sub>3</sub> while storage modulus and glass transition temperature increased significantly.

Keywords: poly (vinyl chloride), nanoparticles, TEM, WAXD, thermal stability, DMA

#### Effect of nano TiO<sub>2</sub> in conducting polyaniline composites for smart corrosion prevention coatings

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Among various inherently conducting polymers, polyaniline (PANI) has been the most widely studied due to its acceptable chemical stability together with relatively high electrical conductivity, environmental stability, ease of synthesis, handling and processing. In recent developments, PANI especially is expected to impart self healing properties in corrosion resistant coatings due to its redox behaviour. The passivation of metal surface responsible for corrosion protection by PANI has been reported recently. The use of PANI in nano size and incorporation of nano metal oxides would lead to improved barrier and corrosion protection properties. This paper reports the synthesis, characterization and corrosion resistance properties of this combination of materials viz. PANI with nano TiO<sub>2</sub>. The composite coating dispersion were made containing medium doped PANI and rutile grade nanoTiO<sub>2</sub> additives in the concentration range of 0 to 4.2 wt% in PVB with total solids content of 10 %. These were coated by dip coating method on steel substrate and dried at room temperature followed by baking in air circulated oven at 50°C for 4 h. The corrosion resistance of the coatings was studied by accelerated test in hot saline (3.5% NaCl solution at  $(65^{\circ}C)$  followed by electrochemical impedance analysis such as Tafel Plot and electrochemical impedance spectroscopy recorded periodically after exposure. The shift in open circuit potential (OCP) and low frequency impedance with time was noted for each composition. These results show that the corrosion resistance of coating is tremendously enhanced by the addition of nano-TiO<sub>2</sub>. This has been explained on the basis of improved barrier properties as well as formation of nano-TiO<sub>2</sub> layer which acts as noble metal. The n-type nano-TiO<sub>2</sub> and p-type PANI also forms p-n junction which gives potential barrier to charge transport. The role of PANI in the corrosion protection is seen in self healing effect even after the initiation of corrosion due to dopant release and ion capture process thus making these 'smart' coatings.

Key words: nano TiO<sub>2</sub>, PANI, corrosion protection, electrochemical impedance analysis, smart coatings

# Swelling behaviour of hydrogels based on crosslinked NR/PEG block copolymers.

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Hydrogels are multi-component hydrophilic polymeric networks that imbibe enough water to cause macroscopic changes in the sample dimension. A striking feature of hydrogel is its swelling degree that can be controlled by modifying the polymer backbone structure or crosslink density. Similarly volume phase transitions can be achieved in hydrogels by varying the crosslink density or by changing the surrounding conditions such as pH etc.

Focusing on these points, we zeroed in on swelling studies using a series of block copolymers based on non-polar natural rubber (NR) and polar polyethylene glycol (PEG) of molecular masses 4000. The synthesis was carried out by solution polymerization. Varying crosslink density in the block copolymer was attained by varying the NCO/OH ratio. The synthesised block copolymers were then subjected to swelling studies in water and at varying pH, viz., pH 4, pH 7 and pH 9. The swelling experiments have been used to determine the equilibrium uptake values, the transport coefficients, mechanism of sorption and sorption kinetics.

The results indicated that the hydrogels gave maximum equilibrium uptake in the sample with NCO/OH ratio 1.1 due to the increase in polymer mobility, free volume and existence of better interactions. Ample support for this observation could be provided by considering the sorption coefficient values, which was especially high in sample with NCO/OH ratio 1.1. The equilibrium uptake of water by the samples was found to be high at pH 4 compared to pH 7 and pH 9. Dynamic swelling curves of copolymer hydrogels with higher NCO/OH ratios and under acidic, neutral and basic media exhibited remarkable overshoot. This can be attributed to the relaxation-controlled (anomalous) transport. The transport of water in the hydrogels followed first order kinetics. Thus noticeable changes were brought in hydrogels by varying the crosslink density and pH, which, in itself, is an indication that if fine tuned, these sensitive hydrogels can find applications in drug delivery systems, separation systems etc.

Key words: hydrogels, swelling behaviour, NR/PEG block copolymers, sorption coefficient, transport of water

#### Synthesis, curing and characterization of tetraglycidyl epoxy resin

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Epoxies generally out-perform most other resin types in terms of mechanical properties and resistance to environmental degradation, which leads to their large scale use in aircraft components. It has outstanding thermal and adhesion properties. Some of these resins can be cured at room temperature, but heat can be used to accelerate the cure of the epoxies. Among the high temperature epoxy resins, tetraglycidyl diamino diphenyl methane can provide high crosslinking density, so that hardened bodies obtained from the known composition exhibits both high modulus and high heat resistance which are inevitable for matrix materials for the advanced composites used in aerospace, electronics, automotive and other industries. In the present investigation, tetraglycidyl diamino diphenyl methane was synthesized through glycidation of 4, 4'-diamino diphenyl methane with a large excess of epichlorohydrin under controlled reaction conditions. Diamino diphenyl methane (specifically increases temperature and chemical resistance), diamino diphenyl sulphone and triethylene tetramine were used for curing. The formulated curing mixture was cured as per the curing schedule described. The molecular structure of tetraglycidyl diamino diphenyl methane was confirmed by nuclear magnetic resonance spectroscopic technique. The degradation behavior of cured samples was studied by thermogravimetric analysis. The resin was cured with the above mentioned three amine curatives and their properties were compared using differential scanning calorimetry (DSC).

**Key words:** tetraglycidyl epoxy; curing; nuclear magnetic resonance spectroscopy; fourier transform infrared spectroscopy; thermogravimetry; differntial scanning calorimetry

#### Development of epoxy based material for rapid tooling applications

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For minimizing the mould making cost for plastic parts production, epoxy modified tooling material was developed. In epoxy resin we added different proportions of aluminium powder, sphericglass and liquid silicone rubber. This study first analyzed the best material which is good in properties such as thermal conductivity, tensile, compressive and flexural strength. Then the best proportion of the above mentioned materials with all such properties is analyzed for thermal fatigue. If the material is to be used as a substitute for tooling applications, thermal fatigue is very much desired. Hence this was studied with temperature higher than 200°C. This study also focuses on the machinability behavior for the best proportions.

Key words: rapid tooling, epoxy composite, tooling material, thermal fatigue, machinability

#### Preparation of polyvinylalcohol based thin film composite nanofiltration membranes: Application in the removal of hardness from brackish water

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Pressure driven membranes have acquired a significant position in the area of separation science and technology. Nanofiltration (NF) membranes are relatively new class of charged pressure driven membranes. Due to preferential selectivity towards ions, lower operating pressure and higher flux, NF membranes have wide scope of applications in water and waste-water treatment. Hard water is probably the most common water problem found not only at home but also in the industries causing scaling in boilers, cooling towers, pipelines and other industrial equipments. Treatment of hard water with nanofiltration membranes may be a unique solution to produce soft water. Polyvinyl alcohol (PVA) being a water soluble biodegradable polymer has immense potential as a membrane material because of its high water permeation and film forming characteristics. Additionally presence of innumerable number of hydroxyl groups in this polymer may impart a charge effect in the closer vicinity and make the membrane suitable to act as nanofiltration membranes with preferential rejection towards multivalent ions than the monovalent ones.

In this work PVA (degree of hydrolysis 86-87%) crosslinked with maleic acid (MA) has been used successfully as barrier layer of polysulphone (PSF) based thin film composite membranes. The crosslinking of PVA and its presence in PSF matrix has been established by FTIR and contact angle study. The effect of variation of crosslinker (MA) dose, cure time and temperature on membrane performance (flux and rejection of inorganic salts) have been studied and the optimum membrane compositions were evaluated. Such membranes show differential rejection among the sulphate and chloride salts. On an average 65% difference exists between the rejection of MgSO<sub>4</sub> (70-90%) and NaCl (15-35%). The overall trend of rejection by such membranes is  $R_{Na_2SO_4} > R_{MgSO_4} > R_{NaCl} > R_{MgCl_2} \cong R_{CaCl_2}$  (R = Rejection). The average molecular weight cutoff (MWCO) of such membranes varies between 250-450 Dalton. These membranes may be useful for the removal of dissolved sulphates (salts) and partial desalination of brackish water.

Key words: nanofiltration membranes, PVA based thin film, FTIR, contact angle, desalination

# *In-situ* generation of silica in epoxy matrix and modified epoxy matrix via sol-gel process

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Epoxy resin /silica organic-inorganic hybrid materials were prepared by using sol-gel technique. Tetraethoxysilane was used as the precursor for the in-situ generation of silica. The choice of epoxy resin as a matrix was made because of its highly reactive nature which can interact with the *in-situ* generated silica. The sol-gel reaction was carried out at room temperature by using ethanol as mutual solvent. Epoxy resin modified with amine containing polydimethylsiloxane also taken as matrix for *in-situ* generation of silica. An aliphatic amine was used as a curing agent. The resultant hybrid material was characterized by using fourier transform infra-red spectroscopy (FTIR), differential scanning calorimetry (DSC), thermo gravimetric analyzer (TGA) and atomic force microscopy (AFM). Infra-red spectroscopic studies were used to indicate the occurrence of chemical interaction within epoxy resin/silica organic-inorganic hybrid material. The shift in glass transition temperature (Tg) was determined by using DSC. The filler content and thermal stability were studied using TGA. Particle size and its distribution were determined by using AFM. The mechanical reinforcement within the hybrid material was demonstrated through the flexural behavior of the material.

**Key words:** *in-situ* generated of silica, modified epoxy matrix, organic-inorganic hybrid, sol-gel technique, amine curing

#### Use of deproteinized and normal skim rubbers for property improvement in natural rubber

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Skim natural rubber latex is a protein rich by-product obtained during the centrifugal concentration of natural rubber latex. Skim latex has very low dry rubber content (4-8 %) and rubber particles are smaller in size. It has higher proportion of non-rubber solids which is mostly proteinaceous in nature. The proteins in skim latex can be decomposed by proteolytic enzymes. The proteolytic enzyme, stabilized liquid papain, was used for deproteinization followed by creaming. This results in quick and easy coagulation of skim latex. The type and level of non-rubbers present in the same give rise to rather slow and often scorchy cure resulting in high modulus vulcanizates. The latter can be considered to arise at least in part due to the protein present in the rubber acting as a reinforcing filler and participation in the curing process. Despite these adverse features, skim rubber has low dirt content, often accompanied by light colour and relatively low cost. Blending natural rubber with skim rubber is a method of taking advantage of the relatively low price of skim rubber while minimizing its disadvantages. In addition, it seems possible that in such blends the fast curing characteristics of the skim can be utilized.

In this paper we have examined the cure behaviour and technological properties on adding 20 phr (parts per hundred rubber) each of deproteinized skim rubber (DPSR) and skim rubber to ISNR 20 mix without further addition of curatives and comparing the properties to that of a similar ISNR 20 mix. Two cure systems, one which contains the usual dosage of accelerator and antioxidant and the other system which contains comparatively lower level of accelerator without any antioxidant were studied. In the former case, the cure characteristics showed that there is attainment of good level of cure and cure rate even after addition of 20 phr skim rubber or DPSR to ISNR 20 with no extra curatives, compared to the conventional ISNR 20 mix. Also ISNR 20 vulcanizate and the vulcanizate containing additional 20 parts of skim rubber showed comparable values of moduli, tensile strength, tear strength and abrasion resistance and these values were higher than that observed for ISNR 20 vulcanizate containing 20 parts DPSR. Skim rubber incorporated mix showed a slightly higher resistance to crack initiation and crack failure when compared to ISNR 20 mix. However, comparable flex resistance was obtained for ISNR 20 mix and 20 parts DPSR incorporated mix. Comparatively lower values of resilience and higher heat build-up and compression set were recorded for the mix containing 20 parts of skim rubber.

The blend which contains 20 parts DPSR showed slightly better dynamic properties and improved air ageing characteristics as compared to normal skim rubber. For the mixes which contain lower level of curatives, cure characteristics were comparable but the values were lower than that which contains the usual dosage. The same trend was observed for the mechanical properties and ageing characteristics. The study has shown that incorporation of 20 parts skim rubber or deproteinized skim rubber to ISNR 20 imparts cure characteristics and mechanical properties similar to that attained by ISNR 20 without the incorporation of additional curatives.

**Key words:** deproteinized skim rubber, natural rubber, enzymatic deproteinisation, cure rate, mechanical properties

#### Photodegradable polypropylene film – Natural weathering studies

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Polypropylene (PP) is an attractive and widely used material for packaging due to its low cost, higher tensile strength, gloss and versatility and hence, their consumption increases thereby littering, which leads to environmental pollution. To solve these problems, out of the various technologies available, photodegradation seems to be a better choice due to the freely available sunlight. The polymers that degrade by peroxidation followed by bioassimilation of the oxidation products are more environmentally acceptable than the biopolymers. In the present work, in order to enhance the photodegrabbility of PP, transition metal salt of stearic acid was synthesized as prodegradant (MF01) and incorporated in PP. The virgin polypropylene and its blend with 0.2 % MF01 were extruded into films of 60 micron thickness. The films were exposed to natural weathering from December 2006 to March 2007 (winter season) and May 2007 to July 2007 (summer season). The photodegradation behaviour was studied using fourier transform infrared spectrometry (FTIR), universal testing machine (UTM) and scanning electron microscope (SEM). A steep increase in the various indices like hydroperoxide, hydroxyl, carbonyl, vinylidene, lactones, ester, carboxylic acid and crystallinity were noted for virgin PP after 50 days of exposure whereas these values increased after 15 days of exposure for the prodegradant added PP. The sudden decrease in the elongation at break (%) for the materials signifies chain scission. PP films having higher carbonyl index values showed surface cracks in the scanning electron micrographs, indicating the degradation of the material.

Key words: photodegradation, polypropylene, natural weathering, FTIR, SEM, photodegradant

## Effect of organic modification on the compatibilisation efficiency of Poly (trimethylene terephthalate) PTT/m-LLDPE blend nanocomposites

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Poly (trimethylene terephthalate)(PTT) and metallocene linear low density polyethylene (m-LLDPE) blends and its nanocomposites were prepared using melt blending technique in a batch mixer. Organically modified nanoclays; Cloisite 20A(C20A), Cloisite 30B(C30B) and Bentone 109(B109) have been used as nanoscale reinforcement to prepare blend nanocomposites. The blend composition of PTT/m-LLDPE of 70:30 has been optimized based on the mechanical performance. Further, characterization studies such as DMA, DSC/TGA, TEM and WAXD have been made to evaluate the effect of incorporation of nanoclays into the blend matrix. WAXD studies revealed a significant increase in  $d_{001}$  spacing of clay galleries in the blend nanocomposites indicating intercalated morphology. From DSC, it was observed that Cloisite 30B with 5 wt. % shows higher crystallization temperature as compared with PTT Virgin and other modified clay systems. Further, with the increase in the scanning rate, crystallization temperature of PTT virgin polymer as well as nanocomposites decreases. TGA thermograms indicated that the thermal stability of the blend increases with the incorporation of Cloisite 20A. DMA measurements reveal that the Cloisite 30B nanocomposite has maximum modulus as compared to the other nanocomposites. It is interpreted from DMA results that PTT/m-LLDPE blend is immiscible due to observation of two peaks and shifting of Tg outward. Nanocomposites show higher tensile strength and modulus as well as flexural strength and modulus as compared to the optimized blend. The effect of m-LLDPE content on the mechanical properties of PTT has also been investigated. It is found that m-LLDPE functions as impact modifier to enhance the impact properties of neat PTT and prepare rubber-toughened blend.

**Keywords**-: poly (trimethylene terephthalate), polymer blend and nanocomposites, compatibilisation efficiency, modified nanoclays, mechanical properties

#### Intercalated poly (methyl methacrylate) layered silicate nanocomposites: Effect of organoclay structure

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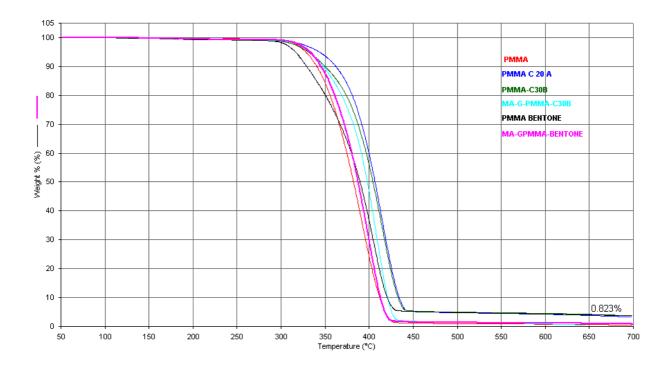
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Poly (methyl methacrylate) / layered silicates nanocomposites were prepared using melt intercalation technique. Commercially modified nanoclays such as Cloisite 30B, Cloisite 20A and Bentonite have been used as organoclays for the preparation of nanocomposites. Maleic anhydride (MA) has been used as a compatibilizing agent for improving the interfacial adhesion between organoclays and PMMA matrix. PMMA matrix with 5wt % of Cloisite 30B nanoclay exhibited optimum tensile properties. The tensile modulus of PMMA/Cloisite 30B 5% nanocomposite increases to about 35% as compared to virgin PMMA matrix. Thermal measurements employing differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) also showed improved thermal stability and marginal increase in glass transition temperature of PMMA matrix with the incorporation of nanoclays. The morphological studies concerning wide-angle x-ray diffraction (WAXD) revealed an increase in d-spacing from 18.5 A<sup>0</sup> in C30B nanoclay to 39.4 A<sup>0</sup> in PMMA/C30B (5wt%) nanocomposites, thus confirming intercalated nanomorphology. The dispersion characteristics of organoclay within PMMA matrix was also investigated using transmission electron microscopy (TEM). Further, dynamic mechanical analysis (DMA) shows a substantial increase in storage modulus of PMMA matrix with the incorporation of organoclays. Additionally, an improved fire retardancy of PMMA was also observed in PMMA/Bentonite (5wt %) nanocomposites with an evidence of reduced horizontal rate of burning.

Key words: PMMA, Cloisite 30B, Bentonite, Nanocomposites, DMA, WAXD



#### Reinforcement studies – Effect of thiophene-plasma coating of silica on the performance in EPDM, SBR and NBR

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The filler surface chemistry is a crucial factor for the level of dispersion and fillerpolymer interaction in rubber, thus determining the vulcanizate properties. Plasmapolymerization allows tailoring the surface chemistry without influence on the bulk properties. Thiophene was used as monomer in this study for its sulfur moiety, and the plasma-thiophene (PTh) coated silica was blended with EPDM, SBR and NBR, as these polymers differ in polarity and unsaturation. As reference, untreated and silanized silica were used.

In EPDM, plasma-polymerization onto silica results in a lowering of the filler-filler interaction compared to untreated silica due to a better match of the surface energy between filler and polymer. The PTh-silica shows the best dispersion compared to untreated and silanized silica. The final properties of the PTh-silica reinforced material are improved compared to untreated silica reinforced EPDM.

In SBR and NBR, the plasma-treatment again results in a better dispersion as well as a higher bound rubber content. In terms of mechanical properties, the PTh-silica results in a better performance compared to untreated and even to silanized silica.

This study shows that thiophene plasma-polymerized silica can act as a replacement for the silica-silane system; and in some cases it performs even better than the silanized silica.

**Key words:** plasma polymerization, thiophene plasma coated silica, rubber reinforcement, silanized silica filler dispersion

# Electrical studies on silver subsurface particulate films on blends of polystyrene and poly (4-vinylpyridine)

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Vacuum deposition of metals on softened polymers offers a technique to prepare subsurface particulate films. Morphology of such films depends on deposition as well as thermodynamic parameters. In addition, the polymer metal interaction plays an important role in deciding the morphology. The electrical properties of particulate films are strongly dependent on their morphology. Blending of polymers can be used to control the morphology of such films and thereby, tailor their electrical properties. Blends of polystyrene (PS) and poly (4-vinylpyridine) (P4VP) prepared by mixing in common solvent, dimethyl formamide (DMF), are solution cast on to clean glass substrates. The substrates were held at 457 K, much above the glass transition temperature of both the polymers, to ensure sufficient polymer fluidity during deposition, to obtain a subsurface particulate film. A constant deposition rate of 0.4 nm/s was used throughout the study. The particle sizes were estimated from the line width broadening of the X-ray diffraction (XRD) peaks and the mean particle sizes are in the range 30-50 nm. Films on softened PS give rise to a very high room temperature resistance due to the formation of a highly agglomerated structure. On the other hand, films on softened P4VP gives rise to a room temperature resistance in the range of a few tens to a few hundred M $\Omega/\Box$ , which is desirable for device applications. Blends of PS and P4VP show room temperature resistances in the desirable range, even at a PS/ P4VP ratio of 75:25. The film resistances in the desired range could be obtained on PS by blending it with P4VP.

**Key words:** softened polymers, vacuum deposition of metals, electrical resistance, XRD, PS/ P4VP blends

#### Design of experiments for optimizing NBR nanocomposite formulations

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Design of experiments (DoE) is a structured statistical technique used for analyzing the behaviour of a product, process, or simulation by changing multiple design parameters in a specific manner and recording the response. The output of a DoE is a set of design parameters and responses that are turned into a mathematical model by using curve-fitting methods. Applications of DoE include choosing between alternatives, selecting the key factors affecting a response, response surface modelling, regression modeling, etc. The interpretation of results consists of determining the set of factors that are statistically significant for each response measured in the experiment, quantifying the relationship between each measured response and the statistically significant factors and determining the ranges of the statistically significant factors (or "process windows" or "process set points") that lead to certain optimal/desired ranges for the measured responses.

In the present work we used DoE to optimize the formulation of NBR [nitrile rubber] based nanocomposites. A Box-Benken Design with three factors and three levels was used to quantify the relationship between mechanical properties and levels of ingredients. The variables chosen are silica content, nanoclay loading and vulcanization system. A masterbatch of NBR and nanoclay was made in a Haake Rheocord followed by compounding on a two roll mill. The compounds were compression moulded and evaluated for tensile strength, modulus, elongation at break and hardness. The effect of heat ageing on mechanical properties was also studied. Based on regression analysis, data from the experiments were used to fit mathematical models of the general form

$$\begin{split} Y &= b_1 + b_2 x_1 + b_3 x_2 + b_4 x_3 + b_5 x_4 + b_6 {x_1}^2 + b_7 {x_2}^2 + b_8 {x_3}^2 + b_9 {x_4}^2 + b_{10} x_1 x_2 + b_{11} x_1 x_3 + b_{12} x_1 x_4 + b_{13} x_2 x_3 \\ &+ b_{14} x_2 x_4 + b_{15} x_3 x_4 \end{split}$$

The sign and magnitude of the coefficients were different for different ingredients and properties. The predictions based on the design were confirmed by verification experiment. MINITAB was used for generating contour plots to study the interaction between the three factors. The nature of contour plots obtained can be categorized as mound shaped and rising ridge indicating different types of interactions. The contour plots were overlaid to find the optimal formulation.

Key words: design of experiments, NBR, nanocomposites, contour plots, optimal formulation

#### Blends of unsaturated polyester resin with maleated HTPB

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Unsaturated polyester resin is widely used in the fibre reinforced plastics industry. The widespread use of the resin is due to its low cost, ease of processing, ease of combination with reinforcements, rapid cure, excellent dimensional stability and ease of colouring and modification for special purpose. UPR is a blend of unsaturated polyester with unsaturated co-reactant diluent like styrene. The fracture toughness and impact resistance of rigid unsaturated polyester can be improved by the incorporation of functional elastomers like hydroxy terminated polybutadiene (HTPB). HTPB is further functionalised by maleic anhydride grafting. The maleated HTPB is characterised by IR spectral studies. The maleated HTPB is then blended with polyester resin and the properties are compared with neat resin. Maleic anhydride graft HTPB is found to increase toughness substantially without seriously affecting tensile and flexural properties.

Key words: FRP, unsaturated polyester resin, fracture toughness, HTPB

## All-PP composites based on β and α polymorphic forms: mechanical properties

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Nowadays considerable efforts are being made to improve the properties of Poly(propylene) (PP) (versatile thermoplastic) matrices by reinforcing it with fibres. Although excellent mechanical properties have been achieved in this way, life cycle assessment does not yield favourable results for PP composites when they are "traditionally" reinforced with glass fibres. Self-reinforced composites represent an effective alternative to the traditional fibre reinforced composites where the matrix and the reinforcement are from the same polymer, thereby supporting the ease of recyclability. This topic has gained interest since the production of "single polymer composite" from polyethylene fibres and polyethylene matrix. Later on another group succeeded to convert a part of such fibres into matrix in which the residual fibres were embedded via "hot compaction". This material is nowadays commercially available as Curve®. The creation of highly oriented, co-extruded PP tapes allows the production of recyclable "all-polypropylene" (all-PP) composites, with a large temperature processing window (20-40°C) and a high volume fraction of highly oriented PP. This concept explored by researchers in the last years and was commercialised under the trade name PURE®. The most recent development with all-PP composites is to exploit the polymorphism- related difference in the melting range of  $beta(\beta)$ -(matrix) and alpha( $\alpha$ ) -phase (reinforcement) PPs carried out in the author's laboratory. Note that the  $\beta$ -PP has a markedly lower melting point than the alpha version. In this work, all polypropylene (all-PP) composites were manufactured from  $\alpha$ -PP tapes and  $\beta$ -PP matrix. The mechanical performance of the composite was investigated in a range of frequencies and temperatures using dynamic mechanical thermal analysis (DMTA). The volume fractions of matrix and reinforcement were estimated using optical microscopic images. Both the DMTA and the static flexural bending tests revealed that the  $\alpha$ -PP tapes act as an effective reinforcement for the  $\beta$ -PP matrix. Time temperature superposition (TTS) was applied to estimate the stiffness of the composites as a function of frequency ( $f = 10^{-9....}10^{20}$ ) in the form of a master curve. The Williams-Landel-Ferry (WLF) model described properly change in the experimental shift factors used to create the storage modulus vs. frequency master curve.

Key words: all-PP composites,  $\alpha$  and  $\beta$  polymorphic forms, mechanical properties, DMTA, timetemperature superposition

#### Studies on processing of styrene butadiene rubber-CaCO<sub>3</sub> nanocomposites by different mixing techniques and their performance properties

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Nano particles of CaCO<sub>3</sub> were synthesized by matrix mediated growth under controlled conditions and was used as filler in styrene butadiene rubber (SBR). The particle size of the synthesized nano CaCO<sub>3</sub> (35-60 nm) was determined by XRD and transmission electron microscope (TEM). The confirmed by SBR-CaCO<sub>3</sub> nanocomposites were prepared by using a Brabender Plastograph. The mechanical and physical properties of the nanocomposites were determined .The fracture surface of the nanocomposites was observed on a scanning electron microscope (SEM). The properties of the Brabender processed SBR-CaCO<sub>3</sub> nanocomposites were compared with two-roll mill processed SBR-CaCO<sub>3</sub> nanocomposites. The results showed that CaCO<sub>3</sub> nano-filler enhanced the properties of SBR as compared to pristine  $CaCO_3$ - SBR composites in both the techniques. Substantial improvement in properties was observed in the case of Brabender processed SBR-CaCO<sub>3</sub> nanocomposites as compared to pristineCaCo<sub>3</sub> based and two-roll mill processed SBR-CaCO<sub>3</sub> nanocomposites. The enhancement in properties was observed in Brabender processing technique owing to the higher shear rates which resulted in proper dispersion and mixing of nano CaCO<sub>3</sub> in SBR polymer matrix and to proper wettability of the inorganic particles by the polymer matrix.

**Key words:** - styrene butadiene rubber (SBR), nanocomposites, Brabender Plastograph, scanning electron microscopy (SEM)

## Studies on pressure sensitive adhesives based on blends of natural rubber and polychloroprene rubber modified with phosphorylated cashew nut shell liquid prepolymer

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Effect of variations in composition and processing on the T-peel adhesion strength of rexin specimens bonded with phosphorylated cashew nut shell liquid prepolymer (PCNSL) based pressure sensitive adhesives (PSAs) containing natural rubber (NR) and polychloroprene rubber (CR) has been studied. Increase in adhesion strength above that of a commercial sample of PSA has been observed with the increase in solids content of the PCNSL based PSA from 15% to 25%. Also, considerable increase in adhesion strength has been obtained with the increase in storage time prior to testing of the specimens from 1 to 7 days which indicates the time dependent diffusion behavior of PCNSL based PSA facilitating wetting and bond formation with the substrates. Irrespective of the solids content and the type of PCNSL, a maximum in T-peel adhesion strength is obtained at a CR dosage of 90 phr in the blend. Typical cohesive failure along-with high strength is obtained with PSAs based on PCNSL having a higher degree of phosphorylation / oligomerization. Uniform and almost complete wetting of the substrate has been confirmed by the optical stereo micrographs of the failure surfaces of the test specimens and the results of viscosity obtained from rheometry.

**Key words :-** pressure sensitive adhesives, natural rubber / polychloroprene rubber blends, phosphorylated cashew nut shell liquid prepolymer, peel adhesion, cohesive failure

## Aromatic-aliphatic co-polyester poly (butylene adipate-coterephthalate) bio-nanocomposite: Influence of organic modification on structure and properties

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Bio-nanocomposite hybrids based on poly (butylene adipate-co-terephthalate) (PBAT) and layered silicates were prepared by melt interaction technique using co-rotating twin screw extruder having blown film unit. Sodium montmorillonite (Na<sup>+</sup>MMT) along with three different commercially available nanoclays i.e., Cloisite30B (C30B), Cloisite20A (C20A), Bentonite (B109) was used. Wide Angle X-Ray Diffraction (WAXD) studies indicated an increase in d-spacing of the nanoclays in the biohybrids revealing formation of intercalated morphology. nanocomposites Morphological studies using transmission electron microscopy (TEM) also confirmed that nanoclays were finely dispersed in the PBAT matrix and there was presence of partially exfoliated clay galleries along with intercalated structures in the bionanocomposite hybrids. Mechanical tests showed that the bio-nanocomposite hybrids prepared using Bentonite nanoclay exhibited higher tensile modulus. Functionalization of PBAT matrix upon grafting with maleic anhydride (MA) resulted in further improvement in mechanical properties. The existence of interfacial bonds in grafted bio-nanocomposite hybrids is substantiated using FTIR spectroscopy. Thermal properties of bio-nanocomposite hybrids employing DSC and TGA also revealed improved Tg, Tc and thermal stability over the virgin polymer. Dynamic Mechanical Analysis (DMA) indicated an increase of storage modulus (E') of PBAT biopolymer with incorporation of nanofiller. The biodegradability of PBAT bio-nanocomposite hybrids showed an increase in the rate of biodegradability with addition of Na<sup>+</sup> MMT due to hydrophilic nature of the nanoclay.

**Key words:** poly(butylene adipate-co-terephthalate), TEM, DMA, MA-g-PBAT, bionanocomposites

#### Uncompatibilized and reactively compatibilized ternary polymer blends of PA6/PP/ABS: Morphological investigation

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Morphological investigation was carried out with melt mixed ternary polymer blends of polyamide 6 (PA6)/ polypropylene (PP)/ acrylobutadiene styrene (ABS) in order to understand the role of compatibilization in morphology developments. Uncompatibilized 80/10/10 PA6/PP/ABS blends exhibited matrix- dispersed droplet type morphology in which the dispersed phases (PP & ABS) found to exhibit core-shell type of morphology. The difference in morphology type may be due to a difference in surface energy between the matrix and one of the dispersed phases. Eventually it was found that "core-shell" type of morphology changed to "co-continuous" type on increasing the concentration of the PP and ABS in the ternary blends. In this context styrene maleic anhydride (SMA) co-polymer was found to act as a compatibilizer in PA6/PP/ABS ternary blends manifested in finer domain size or smaller ligament size in the respective ternary blends. Dynamic mechanical characterization has been carried out in order to understand the relationship between morphology and mechanical properties of PA6/PP/ABS ternary blends.

Key words: ternary polymer blends, core-shell morphology, styrene maleic anhydride copolymer, DMA, compatibilizer

#### Thermal and mechanical properties of poly (vinyl chloride)/ microscale and nanoscale calcium carbonate composites via melt intercalation

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Calcium carbonate was synthesized by *in situ* deposition technique and its nano size (35 to 60 nm) was confirmed by transmission electron microscopy (TEM). Composites of the filler CaCO<sub>3</sub> (micro and nano) and the matrix poly (vinyl chloride) (PVC) were prepared with different filler loading (0-5 wt. %) by melt intercalation. Brabender torque rheometer equipped with an internal mixer was used for preparation of composites. The effect of filler content, both nano and micro level on the nanostructure and properties is reported here. The nanostructures were studied by wide angle X-ray diffraction (WAXD) and scanning electron microscopy (SEM). The mechanical, thermal and dynamic mechanical properties of PVC/ micro and nano CaCO<sub>3</sub> composites were characterized using universal testing machine (UTM), thermo gravimetric analyzer (TGA) and dynamic mechanical analyzer (DMA). The results of thermal analysis indicated that the thermal stability of PVC/nano-CaCO<sub>3</sub> composites was better as compared with the corresponding microcomposites and that of pristine PVC and maximum improvement was obtained at 1 and 3 phr loadings. However, tensile strength decreased significantly with increasing loading of both nano and micro CaCO<sub>3</sub> while storage modulus and glass transition temperature increased significantly.

Keywords: poly (vinyl chloride), nanoparticles, TEM, WAXD, thermal stability, DMA

#### Effect of nano TiO<sub>2</sub> in conducting polyaniline composites for smart corrosion prevention coatings

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Among various inherently conducting polymers, polyaniline (PANI) has been the most widely studied due to its acceptable chemical stability together with relatively high electrical conductivity, environmental stability, ease of synthesis, handling and processing. In recent developments, PANI especially is expected to impart self healing properties in corrosion resistant coatings due to its redox behaviour. The passivation of metal surface responsible for corrosion protection by PANI has been reported recently. The use of PANI in nano size and incorporation of nano metal oxides would lead to improved barrier and corrosion protection properties. This paper reports the synthesis, characterization and corrosion resistance properties of this combination of materials viz. PANI with nano TiO<sub>2</sub>. The composite coating dispersion were made containing medium doped PANI and rutile grade nanoTiO<sub>2</sub> additives in the concentration range of 0 to 4.2 wt% in PVB with total solids content of 10 %. These were coated by dip coating method on steel substrate and dried at room temperature followed by baking in air circulated oven at 50°C for 4 h. The corrosion resistance of the coatings was studied by accelerated test in hot saline (3.5% NaCl solution at  $(65^{\circ}C)$  followed by electrochemical impedance analysis such as Tafel Plot and electrochemical impedance spectroscopy recorded periodically after exposure. The shift in open circuit potential (OCP) and low frequency impedance with time was noted for each composition. These results show that the corrosion resistance of coating is tremendously enhanced by the addition of nano-TiO<sub>2</sub>. This has been explained on the basis of improved barrier properties as well as formation of nano-TiO<sub>2</sub> layer which acts as noble metal. The n-type nano-TiO<sub>2</sub> and p-type PANI also forms p-n junction which gives potential barrier to charge transport. The role of PANI in the corrosion protection is seen in self healing effect even after the initiation of corrosion due to dopant release and ion capture process thus making these 'smart' coatings.

Key words: nano TiO<sub>2</sub>, PANI, corrosion protection, electrochemical impedance analysis, smart coatings

# Swelling behaviour of hydrogels based on crosslinked NR/PEG block copolymers.

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Hydrogels are multi-component hydrophilic polymeric networks that imbibe enough water to cause macroscopic changes in the sample dimension. A striking feature of hydrogel is its swelling degree that can be controlled by modifying the polymer backbone structure or crosslink density. Similarly volume phase transitions can be achieved in hydrogels by varying the crosslink density or by changing the surrounding conditions such as pH etc.

Focusing on these points, we zeroed in on swelling studies using a series of block copolymers based on non-polar natural rubber (NR) and polar polyethylene glycol (PEG) of molecular masses 4000. The synthesis was carried out by solution polymerization. Varying crosslink density in the block copolymer was attained by varying the NCO/OH ratio. The synthesised block copolymers were then subjected to swelling studies in water and at varying pH, viz., pH 4, pH 7 and pH 9. The swelling experiments have been used to determine the equilibrium uptake values, the transport coefficients, mechanism of sorption and sorption kinetics.

The results indicated that the hydrogels gave maximum equilibrium uptake in the sample with NCO/OH ratio 1.1 due to the increase in polymer mobility, free volume and existence of better interactions. Ample support for this observation could be provided by considering the sorption coefficient values, which was especially high in sample with NCO/OH ratio 1.1. The equilibrium uptake of water by the samples was found to be high at pH 4 compared to pH 7 and pH 9. Dynamic swelling curves of copolymer hydrogels with higher NCO/OH ratios and under acidic, neutral and basic media exhibited remarkable overshoot. This can be attributed to the relaxation-controlled (anomalous) transport. The transport of water in the hydrogels followed first order kinetics. Thus noticeable changes were brought in hydrogels by varying the crosslink density and pH, which, in itself, is an indication that if fine tuned, these sensitive hydrogels can find applications in drug delivery systems, separation systems etc.

Key words: hydrogels, swelling behaviour, NR/PEG block copolymers, sorption coefficient, transport of water

#### Synthesis, curing and characterization of tetraglycidyl epoxy resin

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Epoxies generally out-perform most other resin types in terms of mechanical properties and resistance to environmental degradation, which leads to their large scale use in aircraft components. It has outstanding thermal and adhesion properties. Some of these resins can be cured at room temperature, but heat can be used to accelerate the cure of the epoxies. Among the high temperature epoxy resins, tetraglycidyl diamino diphenyl methane can provide high crosslinking density, so that hardened bodies obtained from the known composition exhibits both high modulus and high heat resistance which are inevitable for matrix materials for the advanced composites used in aerospace, electronics, automotive and other industries. In the present investigation, tetraglycidyl diamino diphenyl methane was synthesized through glycidation of 4, 4'-diamino diphenyl methane with a large excess of epichlorohydrin under controlled reaction conditions. Diamino diphenyl methane (specifically increases temperature and chemical resistance), diamino diphenyl sulphone and triethylene tetramine were used for curing. The formulated curing mixture was cured as per the curing schedule described. The molecular structure of tetraglycidyl diamino diphenyl methane was confirmed by nuclear magnetic resonance spectroscopic technique. The degradation behavior of cured samples was studied by thermogravimetric analysis. The resin was cured with the above mentioned three amine curatives and their properties were compared using differential scanning calorimetry (DSC).

**Key words:** tetraglycidyl epoxy; curing; nuclear magnetic resonance spectroscopy; fourier transform infrared spectroscopy; thermogravimetry; differntial scanning calorimetry

#### Development of epoxy based material for rapid tooling applications

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For minimizing the mould making cost for plastic parts production, epoxy modified tooling material was developed. In epoxy resin we added different proportions of aluminium powder, sphericglass and liquid silicone rubber. This study first analyzed the best material which is good in properties such as thermal conductivity, tensile, compressive and flexural strength. Then the best proportion of the above mentioned materials with all such properties is analyzed for thermal fatigue. If the material is to be used as a substitute for tooling applications, thermal fatigue is very much desired. Hence this was studied with temperature higher than 200°C. This study also focuses on the machinability behavior for the best proportions.

Key words: rapid tooling, epoxy composite, tooling material, thermal fatigue, machinability

## Preparation of polyvinylalcohol based thin film composite nanofiltration membranes: Application in the removal of hardness from brackish water

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Pressure driven membranes have acquired a significant position in the area of separation science and technology. Nanofiltration (NF) membranes are relatively new class of charged pressure driven membranes. Due to preferential selectivity towards ions, lower operating pressure and higher flux, NF membranes have wide scope of applications in water and waste-water treatment. Hard water is probably the most common water problem found not only at home but also in the industries causing scaling in boilers, cooling towers, pipelines and other industrial equipments. Treatment of hard water with nanofiltration membranes may be a unique solution to produce soft water. Polyvinyl alcohol (PVA) being a water soluble biodegradable polymer has immense potential as a membrane material because of its high water permeation and film forming characteristics. Additionally presence of innumerable number of hydroxyl groups in this polymer may impart a charge effect in the closer vicinity and make the membrane suitable to act as nanofiltration membranes with preferential rejection towards multivalent ions than the monovalent ones.

In this work PVA (degree of hydrolysis 86-87%) crosslinked with maleic acid (MA) has been used successfully as barrier layer of polysulphone (PSF) based thin film composite membranes. The crosslinking of PVA and its presence in PSF matrix has been established by FTIR and contact angle study. The effect of variation of crosslinker (MA) dose, cure time and temperature on membrane performance (flux and rejection of inorganic salts) have been studied and the optimum membrane compositions were evaluated. Such membranes show differential rejection among the sulphate and chloride salts. On an average 65% difference exists between the rejection of MgSO<sub>4</sub> (70-90%) and NaCl (15-35%). The overall trend of rejection by such membranes is  $R_{Na_2SO_4} > R_{MgSO_4} > R_{NaCl} > R_{MgCl_2} \cong R_{CaCl_2}$  (R = Rejection). The average molecular weight cutoff (MWCO) of such membranes varies between 250-450 Dalton. These membranes may be useful for the removal of dissolved sulphates (salts) and partial desalination of brackish water.

Key words: nanofiltration membranes, PVA based thin film, FTIR, contact angle, desalination

## *In-situ* generation of silica in epoxy matrix and modified epoxy matrix via sol-gel process

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Epoxy resin /silica organic-inorganic hybrid materials were prepared by using sol-gel technique. Tetraethoxysilane was used as the precursor for the in-situ generation of silica. The choice of epoxy resin as a matrix was made because of its highly reactive nature which can interact with the *in-situ* generated silica. The sol-gel reaction was carried out at room temperature by using ethanol as mutual solvent. Epoxy resin modified with amine containing polydimethylsiloxane also taken as matrix for *in-situ* generation of silica. An aliphatic amine was used as a curing agent. The resultant hybrid material was characterized by using fourier transform infra-red spectroscopy (FTIR), differential scanning calorimetry (DSC), thermo gravimetric analyzer (TGA) and atomic force microscopy (AFM). Infra-red spectroscopic studies were used to indicate the occurrence of chemical interaction within epoxy resin/silica organic-inorganic hybrid material. The shift in glass transition temperature (Tg) was determined by using DSC. The filler content and thermal stability were studied using TGA. Particle size and its distribution were determined by using AFM. The mechanical reinforcement within the hybrid material was demonstrated through the flexural behavior of the material.

**Key words:** *in-situ* generated of silica, modified epoxy matrix, organic-inorganic hybrid, sol-gel technique, amine curing

### Use of deproteinized and normal skim rubbers for property improvement in natural rubber

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Skim natural rubber latex is a protein rich by-product obtained during the centrifugal concentration of natural rubber latex. Skim latex has very low dry rubber content (4-8 %) and rubber particles are smaller in size. It has higher proportion of non-rubber solids which is mostly proteinaceous in nature. The proteins in skim latex can be decomposed by proteolytic enzymes. The proteolytic enzyme, stabilized liquid papain, was used for deproteinization followed by creaming. This results in quick and easy coagulation of skim latex. The type and level of non-rubbers present in the same give rise to rather slow and often scorchy cure resulting in high modulus vulcanizates. The latter can be considered to arise at least in part due to the protein present in the rubber acting as a reinforcing filler and participation in the curing process. Despite these adverse features, skim rubber has low dirt content, often accompanied by light colour and relatively low cost. Blending natural rubber with skim rubber is a method of taking advantage of the relatively low price of skim rubber while minimizing its disadvantages. In addition, it seems possible that in such blends the fast curing characteristics of the skim can be utilized.

In this paper we have examined the cure behaviour and technological properties on adding 20 phr (parts per hundred rubber) each of deproteinized skim rubber (DPSR) and skim rubber to ISNR 20 mix without further addition of curatives and comparing the properties to that of a similar ISNR 20 mix. Two cure systems, one which contains the usual dosage of accelerator and antioxidant and the other system which contains comparatively lower level of accelerator without any antioxidant were studied. In the former case, the cure characteristics showed that there is attainment of good level of cure and cure rate even after addition of 20 phr skim rubber or DPSR to ISNR 20 with no extra curatives, compared to the conventional ISNR 20 mix. Also ISNR 20 vulcanizate and the vulcanizate containing additional 20 parts of skim rubber showed comparable values of moduli, tensile strength, tear strength and abrasion resistance and these values were higher than that observed for ISNR 20 vulcanizate containing 20 parts DPSR. Skim rubber incorporated mix showed a slightly higher resistance to crack initiation and crack failure when compared to ISNR 20 mix. However, comparable flex resistance was obtained for ISNR 20 mix and 20 parts DPSR incorporated mix. Comparatively lower values of resilience and higher heat build-up and compression set were recorded for the mix containing 20 parts of skim rubber.

The blend which contains 20 parts DPSR showed slightly better dynamic properties and improved air ageing characteristics as compared to normal skim rubber. For the mixes which contain lower level of curatives, cure characteristics were comparable but the values were lower than that which contains the usual dosage. The same trend was observed for the mechanical properties and ageing characteristics. The study has shown that incorporation of 20 parts skim rubber or deproteinized skim rubber to ISNR 20 imparts cure characteristics and mechanical properties similar to that attained by ISNR 20 without the incorporation of additional curatives.

**Key words:** deproteinized skim rubber, natural rubber, enzymatic deproteinisation, cure rate, mechanical properties

#### Photodegradable polypropylene film – Natural weathering studies

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Polypropylene (PP) is an attractive and widely used material for packaging due to its low cost, higher tensile strength, gloss and versatility and hence, their consumption increases thereby littering, which leads to environmental pollution. To solve these problems, out of the various technologies available, photodegradation seems to be a better choice due to the freely available sunlight. The polymers that degrade by peroxidation followed by bioassimilation of the oxidation products are more environmentally acceptable than the biopolymers. In the present work, in order to enhance the photodegrabbility of PP, transition metal salt of stearic acid was synthesized as prodegradant (MF01) and incorporated in PP. The virgin polypropylene and its blend with 0.2 % MF01 were extruded into films of 60 micron thickness. The films were exposed to natural weathering from December 2006 to March 2007 (winter season) and May 2007 to July 2007 (summer season). The photodegradation behaviour was studied using fourier transform infrared spectrometry (FTIR), universal testing machine (UTM) and scanning electron microscope (SEM). A steep increase in the various indices like hydroperoxide, hydroxyl, carbonyl, vinylidene, lactones, ester, carboxylic acid and crystallinity were noted for virgin PP after 50 days of exposure whereas these values increased after 15 days of exposure for the prodegradant added PP. The sudden decrease in the elongation at break (%) for the materials signifies chain scission. PP films having higher carbonyl index values showed surface cracks in the scanning electron micrographs, indicating the degradation of the material.

Key words: photodegradation, polypropylene, natural weathering, FTIR, SEM, photodegradant

## Effect of organic modification on the compatibilisation efficiency of Poly (trimethylene terephthalate) PTT/m-LLDPE blend nanocomposites

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Poly (trimethylene terephthalate)(PTT) and metallocene linear low density polyethylene (m-LLDPE) blends and its nanocomposites were prepared using melt blending technique in a batch mixer. Organically modified nanoclays; Cloisite 20A(C20A), Cloisite 30B(C30B) and Bentone 109(B109) have been used as nanoscale reinforcement to prepare blend nanocomposites. The blend composition of PTT/m-LLDPE of 70:30 has been optimized based on the mechanical performance. Further, characterization studies such as DMA, DSC/TGA, TEM and WAXD have been made to evaluate the effect of incorporation of nanoclays into the blend matrix. WAXD studies revealed a significant increase in  $d_{001}$  spacing of clay galleries in the blend nanocomposites indicating intercalated morphology. From DSC, it was observed that Cloisite 30B with 5 wt. % shows higher crystallization temperature as compared with PTT Virgin and other modified clay systems. Further, with the increase in the scanning rate, crystallization temperature of PTT virgin polymer as well as nanocomposites decreases. TGA thermograms indicated that the thermal stability of the blend increases with the incorporation of Cloisite 20A. DMA measurements reveal that the Cloisite 30B nanocomposite has maximum modulus as compared to the other nanocomposites. It is interpreted from DMA results that PTT/m-LLDPE blend is immiscible due to observation of two peaks and shifting of Tg outward. Nanocomposites show higher tensile strength and modulus as well as flexural strength and modulus as compared to the optimized blend. The effect of m-LLDPE content on the mechanical properties of PTT has also been investigated. It is found that m-LLDPE functions as impact modifier to enhance the impact properties of neat PTT and prepare rubber-toughened blend.

**Keywords**-: poly (trimethylene terephthalate), polymer blend and nanocomposites, compatibilisation efficiency, modified nanoclays, mechanical properties

### Intercalated poly (methyl methacrylate) layered silicate nanocomposites: Effect of organoclay structure

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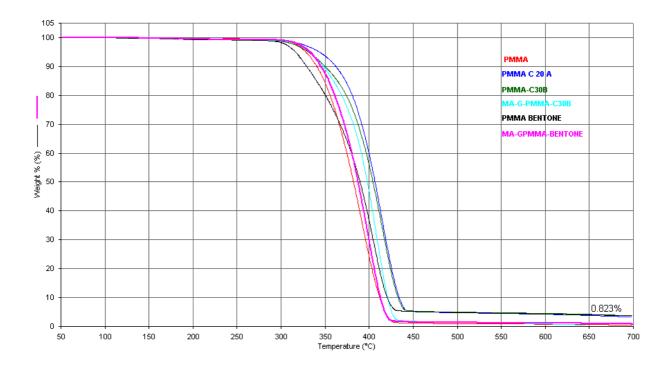
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Poly (methyl methacrylate) / layered silicates nanocomposites were prepared using melt intercalation technique. Commercially modified nanoclays such as Cloisite 30B, Cloisite 20A and Bentonite have been used as organoclays for the preparation of nanocomposites. Maleic anhydride (MA) has been used as a compatibilizing agent for improving the interfacial adhesion between organoclays and PMMA matrix. PMMA matrix with 5wt % of Cloisite 30B nanoclay exhibited optimum tensile properties. The tensile modulus of PMMA/Cloisite 30B 5% nanocomposite increases to about 35% as compared to virgin PMMA matrix. Thermal measurements employing differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) also showed improved thermal stability and marginal increase in glass transition temperature of PMMA matrix with the incorporation of nanoclays. The morphological studies concerning wide-angle x-ray diffraction (WAXD) revealed an increase in d-spacing from 18.5 A<sup>0</sup> in C30B nanoclay to 39.4 A<sup>0</sup> in PMMA/C30B (5wt%) nanocomposites, thus confirming intercalated nanomorphology. The dispersion characteristics of organoclay within PMMA matrix was also investigated using transmission electron microscopy (TEM). Further, dynamic mechanical analysis (DMA) shows a substantial increase in storage modulus of PMMA matrix with the incorporation of organoclays. Additionally, an improved fire retardancy of PMMA was also observed in PMMA/Bentonite (5wt %) nanocomposites with an evidence of reduced horizontal rate of burning.

Key words: PMMA, Cloisite 30B, Bentonite, Nanocomposites, DMA, WAXD



### Reinforcement studies – Effect of thiophene-plasma coating of silica on the performance in EPDM, SBR and NBR

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The filler surface chemistry is a crucial factor for the level of dispersion and fillerpolymer interaction in rubber, thus determining the vulcanizate properties. Plasmapolymerization allows tailoring the surface chemistry without influence on the bulk properties. Thiophene was used as monomer in this study for its sulfur moiety, and the plasma-thiophene (PTh) coated silica was blended with EPDM, SBR and NBR, as these polymers differ in polarity and unsaturation. As reference, untreated and silanized silica were used.

In EPDM, plasma-polymerization onto silica results in a lowering of the filler-filler interaction compared to untreated silica due to a better match of the surface energy between filler and polymer. The PTh-silica shows the best dispersion compared to untreated and silanized silica. The final properties of the PTh-silica reinforced material are improved compared to untreated silica reinforced EPDM.

In SBR and NBR, the plasma-treatment again results in a better dispersion as well as a higher bound rubber content. In terms of mechanical properties, the PTh-silica results in a better performance compared to untreated and even to silanized silica.

This study shows that thiophene plasma-polymerized silica can act as a replacement for the silica-silane system; and in some cases it performs even better than the silanized silica.

**Key words:** plasma polymerization, thiophene plasma coated silica, rubber reinforcement, silanized silica filler dispersion

# Electrical studies on silver subsurface particulate films on blends of polystyrene and poly (4-vinylpyridine)

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Vacuum deposition of metals on softened polymers offers a technique to prepare subsurface particulate films. Morphology of such films depends on deposition as well as thermodynamic parameters. In addition, the polymer metal interaction plays an important role in deciding the morphology. The electrical properties of particulate films are strongly dependent on their morphology. Blending of polymers can be used to control the morphology of such films and thereby, tailor their electrical properties. Blends of polystyrene (PS) and poly (4-vinylpyridine) (P4VP) prepared by mixing in common solvent, dimethyl formamide (DMF), are solution cast on to clean glass substrates. The substrates were held at 457 K, much above the glass transition temperature of both the polymers, to ensure sufficient polymer fluidity during deposition, to obtain a subsurface particulate film. A constant deposition rate of 0.4 nm/s was used throughout the study. The particle sizes were estimated from the line width broadening of the X-ray diffraction (XRD) peaks and the mean particle sizes are in the range 30-50 nm. Films on softened PS give rise to a very high room temperature resistance due to the formation of a highly agglomerated structure. On the other hand, films on softened P4VP gives rise to a room temperature resistance in the range of a few tens to a few hundred M $\Omega/\Box$ , which is desirable for device applications. Blends of PS and P4VP show room temperature resistances in the desirable range, even at a PS/ P4VP ratio of 75:25. The film resistances in the desired range could be obtained on PS by blending it with P4VP.

**Key words:** softened polymers, vacuum deposition of metals, electrical resistance, XRD, PS/ P4VP blends

#### Design of experiments for optimizing NBR nanocomposite formulations

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Design of experiments (DoE) is a structured statistical technique used for analyzing the behaviour of a product, process, or simulation by changing multiple design parameters in a specific manner and recording the response. The output of a DoE is a set of design parameters and responses that are turned into a mathematical model by using curve-fitting methods. Applications of DoE include choosing between alternatives, selecting the key factors affecting a response, response surface modelling, regression modeling, etc. The interpretation of results consists of determining the set of factors that are statistically significant for each response measured in the experiment, quantifying the relationship between each measured response and the statistically significant factors and determining the ranges of the statistically significant factors (or "process windows" or "process set points") that lead to certain optimal/desired ranges for the measured responses.

In the present work we used DoE to optimize the formulation of NBR [nitrile rubber] based nanocomposites. A Box-Benken Design with three factors and three levels was used to quantify the relationship between mechanical properties and levels of ingredients. The variables chosen are silica content, nanoclay loading and vulcanization system. A masterbatch of NBR and nanoclay was made in a Haake Rheocord followed by compounding on a two roll mill. The compounds were compression moulded and evaluated for tensile strength, modulus, elongation at break and hardness. The effect of heat ageing on mechanical properties was also studied. Based on regression analysis, data from the experiments were used to fit mathematical models of the general form

$$\begin{split} Y &= b_1 + b_2 x_1 + b_3 x_2 + b_4 x_3 + b_5 x_4 + b_6 {x_1}^2 + b_7 {x_2}^2 + b_8 {x_3}^2 + b_9 {x_4}^2 + b_{10} x_1 x_2 + b_{11} x_1 x_3 + b_{12} x_1 x_4 + b_{13} x_2 x_3 \\ &+ b_{14} x_2 x_4 + b_{15} x_3 x_4 \end{split}$$

The sign and magnitude of the coefficients were different for different ingredients and properties. The predictions based on the design were confirmed by verification experiment. MINITAB was used for generating contour plots to study the interaction between the three factors. The nature of contour plots obtained can be categorized as mound shaped and rising ridge indicating different types of interactions. The contour plots were overlaid to find the optimal formulation.

Key words: design of experiments, NBR, nanocomposites, contour plots, optimal formulation

#### Blends of unsaturated polyester resin with maleated HTPB

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Unsaturated polyester resin is widely used in the fibre reinforced plastics industry. The widespread use of the resin is due to its low cost, ease of processing, ease of combination with reinforcements, rapid cure, excellent dimensional stability and ease of colouring and modification for special purpose. UPR is a blend of unsaturated polyester with unsaturated co-reactant diluent like styrene. The fracture toughness and impact resistance of rigid unsaturated polyester can be improved by the incorporation of functional elastomers like hydroxy terminated polybutadiene (HTPB). HTPB is further functionalised by maleic anhydride grafting. The maleated HTPB is characterised by IR spectral studies. The maleated HTPB is then blended with polyester resin and the properties are compared with neat resin. Maleic anhydride graft HTPB is found to increase toughness substantially without seriously affecting tensile and flexural properties.

Key words: FRP, unsaturated polyester resin, fracture toughness, HTPB

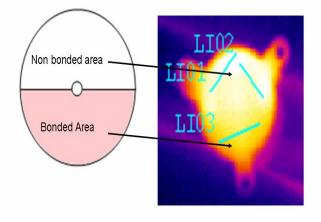
## Nondestructive testing of defects in adhesive joints

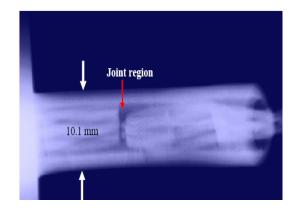
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Reliability aspects of underwater components are important when considering their durability and performance. These components are deployed underwater for long period of time and have no option for monitoring the health and functionality. Rubber materials are generally used for encapsulating underwater components to prevent moisture ingress. During the encapsulation stage, surface and subsurface defects and discontinuities such as micro-cracks, voids, porosity and delamination occur in the components. These defects are due to service stress, process inconsistency, stringent environmental conditions and inconsistent workmanship. Failure analysis of the components shows that adhesive failure, either by mechanical failure or water ingress through the interface, is the major cause of the component failure. Hence, it is essential to determine the integrity of the adhesive joints of the underwater components. For detecting and localizing the defects without destroying the components, special techniques such as non destructive testing is required.

In the present study, the defects in the adhesive joints have been detected and characterized using the micro-focal x-ray radiography and infrared thermal imaging techniques. The infrared thermographic image of the component with known defects is given below. From the thermal gradient as shown below, defects like non-bonded area can be detected. Also, the defects in the embedded components in micro-level can be detected using the microfocal x-ray radiography as shown below.





IR thermal image

Microfocal x-ray radiographic image

**Key words:** nondestructive testinf, adhesive joints, under water rubber components, X-ray radiography, infrared thermal imaging

## Structure property relationship studies of melt spun carbon nanotubes filled polypropylene fiber

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Polypropylene (PP) is one of the major polymeric fiber materials of future in view of its impressive consumption in the past decade. However, PP fibre needs reinforcement in order to achieve high stiffness and strength for engineering applications. Since the discovery of carbon nanotubes (CNT) by Iijima, CNT have emerged as a potential candidate as reinforcing filler in polymer based composites due to their unparallel mechanical, electrical and thermal properties. Multiwalled carbon nanotubes (MWNT) were varied (0.5-3 wt%) in PP/MWNT composites which were melt-mixed by using twin screw microcompounder. The resulting composites were subsequently melt–spun into fibers and were post drawn at 120°C with a draw ratio of 8. Two different types of MWNT were utilized in order to understand the effect of different types of MWNT in enhancing mechanical properties of the composite fibers. It was found that MWNT obtained from DMSRDE were found to be superior over Nanocyl NC 3100 in achieving high modulus of PP/MWNT composite fibers. Herman's orientation factor of (110) PP plane and MWNT along the fiber axis was determined using wide angle X-ray diffraction and Raman spectroscopy respectively. Structure property relationship studies were performed in PP/MWNT composite fibers.

Key words: Polypropylene (PP), Multiwalled carbon nanotube (MWNT), melt spinning

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### Novel nanocomposite polymer electrolytes based on electrospun poly(vinylidene fluoride-co-hexafluoropropylene) for lithium batteries

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Rechargeable batteries using polymer electrolytes (PEs) instead of traditional liquid electrolytes are well adapted to various geometries because of their advantages in providing lighter and safer batteries with longer shelf life, leak proof construction and easy fabrication into desired shape and size. Electrospinning technique has attracted immense attention recently as a versatile and easy method to prepare polymer membranes, that are made up of thin fibers of micron and sub-micron diameters. The high crystallinity of polymer membranes is one of the major causes of the low ionic conductivity of polymer electrolytes, and it thus limits their use in lithium batteries. This problem can be addressed to a certain extent by the addition of nano-sized ceramic fillers to polymer electrolytes. The size of the fillers is an important characteristic as nano size of a particle apart from providing large surface area for interactions between polymer and electrolyte.

A series of nanocomposite polymer electrolytes (NCPE) based on poly(vinylidene fluoride-cohexafluoropropylene) [P(VdF-HEP)] incorporated with nanoparticles of BaTiO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub> were prepared by electrospinning technique. The addition of the ceramic fillers barely influenced the thermal properties and % crystallinity of the polymer matrix. The melting temperature of pristine P(VdF-HFP) is 159 °C, while the polymers with fillers have lower melting points in a close range of 153.4, 153.8 and 154.9 °C for membranes with BaTiO<sub>3</sub>, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, respectively and the % crystallinity values obtained from the DSC data follows the order BaTiO<sub>3</sub> (47.1%) < SiO<sub>2</sub> (47.9) < Al<sub>2</sub>O<sub>3</sub> (49.2) < membrane without filler (74.5%). The composite membranes exhibit a porous morphology formed by interlaying of fibers of AFD ~ 1-2.5 µm. The porosity varies in the narrow range of 84-87% for the membranes, showing a slight increasing trend with ceramic content. With a high porosity ~ 90%, the membranes exhibit electrolyte uptake of > 425%. The resultant porous membranes also exhibit electrolyte retention capacity. The presence of the ceramic nanoparticles has positive effect on the mechanical properties of the membranes. The ionic conductivity and the electrochemical properties of the PE based on electrospun PVdF-HFP is enhanced by the presence of the nano sized ceramic fillers. The PE based on the membrane with ceramic fillers which shows better ionic conductivity of  $10^{-3}$  S/cm at 25 °C and have anodic stability > 4.6 V versus Li/Li<sup>+</sup> and show good compatibility with lithium metal electrode. The suitability in Li/LiFePO<sub>4</sub> cell is demonstrated by exhibiting about 100% utilization of the cathode material (165 mAh/g) at 1 C-rate at 25 °C. In comparison with BaTiO<sub>3</sub>, the performance of the Li/LiFePO<sub>4</sub> cells with NCPEs containing Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> was observed to be lower discharge capacities of 153 mAh/g and 156 mAh/g respectively. The enhanced performance of the BaTiO<sub>3</sub> based NCPE is attributed mainly to its better interactions with the host polymer and compatibility with the lithium metal. Incorporation of the ceramic filler is more a useful efficient in improving the properties of the PEs.

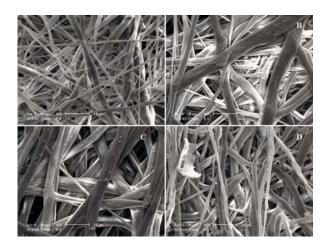


Fig. 1. SEM images of electrospun P(VdF-HFP) membranes with (A) 0% filler, (B) SiO<sub>2</sub>, (C) Al<sub>2</sub>O<sub>3</sub>, and (D) BaTiO<sub>3</sub>.

**Key words:** nanocomposite polymer electrolytes, P(VdF-HEP), electrospinning, lithium batteries, nanofillers

## Biomimetic synthesis of nanohybrids based on calcium hydroxyapatite and carboxymethyl cellulose

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Over the past decade, the main goal of bone tissue engineering has been to develop biodegradable materials as bone graft substitutes for filling large defects in bones. Bone and teeth consist of a small amount of organic matrix, which manipulates the formation of apatite into distinct microstructures suitable for the mechanical forces which they encounter *in-vivo*. The processes and materials that control such crystal nucleation and growth are of great interest to materials scientists to learn about the architecture, morphology, and patterning of inorganic materials at all dimensions from the nanoscale to macroscopic scale by mimicking the process of biomineralization. In the present paper we report biomimetic synthesis of nanohybrids based on carboxymethyl cellulose (CMC) and hydroxyapatite (HA) nanoparticles by a co-precipitation method. The physico-chemical characterizations were done before and after calcination using fourier transform infrared spectroscopy, solid state <sup>31</sup>P nuclear magnetic resonance (NMR) spectroscopy and thermogravimetric analysis (TGA). The formation of nanohybrid was observed by wide angle X-ray diffraction (WAXD), scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX) and transmission electron microscopy (TEM). The nanohybrid was formed as aggregates of nanoparticles adsorbed on CMC. With increasing content of CMC, the crystallite size of hydroxyapatite particles decreased (with 2 wt. % 18±3 nm). The morphological aspects of calcined samples have shown the sintering ability of HA nanoparticles. The possible mechanism for interaction between CMC and HA, nucleation and growth of nanocrystals of HA is discussed. It is summarized that nanohybrids of hydroxyapatite nanoparticles can be prepared for mimicking the process of nucleation and growth in nature using biodegradable and biocompatible macromolecules like CMC.

Key words: biopolymer; hydroxyapatite; cellulose; nanoparticles; X-ray diffraction; particle size

### Mechanical properties of natural rubber / poly butadiene rubber blends prepared using fatty acid incorporated natural rubber

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Blends based on natural rubber (NR) and polybutadiene rubber (BR) are extensively used in tire sector due to the enhanced mechanical properties like heat build-up, and abrasion resistance realized in the vulcanizates. In such blends homogeneous dispersion of carbon black is a problem as the latter has a tendency to migrate to the BR phase. Generally plasticizers are used to enhance filler dispersion in rubbers. In NR/BR blends it is possible to improve carbon black dispersion by prior incorporation of suitable plasticizers in NR before preparation of rubber blends. Fatty acids which are good plastisizers can be preferentially incorporated in the NR phase by the addition as surfactants in latex stage before coagulation. In this paper an investigation on the preparation, cure characteristics and mechanical properties of NR/BR blends prepared using fatty acid incorporated NR is carried out.

Natural rubber latex is treated with the required quantity of fatty acid soap and then coagulated by addition of suitable acids. The coagulation of fatty acid incorporated latex depends on the type of coagulants. 0.8 % sulphuric acid is shown to be a better coagulant than formic or acetic acids. The coagulum is washed well to remove acids and then dried at 70  $^{0}$  C in an air oven to get dry rubber. Rubber compounds based on pure NR, 80/20 and 60/40 NR/BR blends are prepared using conventional mixing methods. The compounds are vulcanized and tested as per standard test methods.

When soap is added to latex, the fatty acid ions displace a part of the protein molecules and strongly get adsorbed on the rubber particles. This surface bound fatty acid anions get converted to the corresponding fatty acids by reaction with acids during the process of coagulation. The fatty acids retained on rubber during coagulation play a major role on the cure characteristics, filler dispersion, mechanical properties and ageing characteristics of the recovered rubber and hence in blends prepared using such rubber.

Due to the presence of fatty acids, the pure and NR/BR blends show better cure characteristics as revealed from a higher level of vulcanization even though the cure time is comparatively longer. The presence of fatty acids also helps in a better dispersion of filler. Due to the higher level of crosslinking and better filler dispersion pure and blend vulcanizates show a higher modulus, tensile strength, and hardness along with comparable dynamic properties like heat build-up and compression set. in relation to conventional rubber vulcanizates. It is expected

that for fatty acid incorporated rubber there can be weak interactions involving the carboxyl group and the active sites on the surface of carbon black. A noticeably higher solvent resistance and abrasion resistance is also observed for NR prepared by the new process due to the presence of better interaction of filler with rubber.

Key words: NR/BR blends, fatty acids, filler dispersion, filler-rubber interaction

## Effect of electron beam curing on mechanical and electrical properties of silica filled silicone and FKM rubber and its comparison with chemical curing

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The effects of electron beam (EB) irradiation on mechanical and electrical properties of Silicone rubber (MQ), and Fluro rubber (FKM) compounds filled with Precipitated and Fumed Silica filler have been reported in this paper. The effect of different degree of radiation dosage on both electrical and mechanical properties was investigated. Some comparison has been made between properties of EB cured vulanizates of theses two rubbers with Peroxide cured Silicon rubber and Calcium hydroxide cured FKM rubber. The type of silica filler used affects both electrical and mechanical properties of EB cured vulcanizates. The tensile strength of silicone rubber is marginally affected by irradiation dosage up to 15 MRads, but further increase in irradiation dosage shows some fall in properties. But for FKM rubber strength properties increases progressively with irradiation dosage up to 15 Mrads there after some drop is observed. Almost similar trend is noted for tear strength properties of these rubbers. However elongation at break for both MQ and FKM continuously decreases with the increase in radiation dosage. This is in line with the change in gel fraction with radiation dosage. The reinforcement by ppt silica is better during chemical cure compared to EB cure for both rubbers whereas in the presence of fumed silica EB curing gives higher tensile strength compared to chemical cure.

The radiation dosage has marginal effect on electrical conductivity, and dissipation factor. However loss factors for chemically crosslinked rubbers are higher than that of EB cured ones. Compared to ppt silica filled systems, fumed silica filled ones exhibit less electrical loss.

## Mechanical and rheological behavior of peroxide cured polypropylene (PP)/ethylene octene copolymer (EOC) thermoplastic vulcanizates (TPVS)

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Technologically compatible binary blends of polypropylene (PP) and ethylene octene copolymer (EOC) were dynamically vulcanized by coagent assisted peroxide crosslinking system. Addition of peroxide in PP/EOC blend involves two major competing reactions: EOC cross-linking and PP degradation by  $\beta$ -scission. Final product properties are thus dependent on the balance among those two competing reactions. As the concentration of peroxide increases, particle size decreases. However, mechanical properties of these TPVs are not good enough, which is due to severe degradation in the PP phase in the presence of peroxide.

Principally, coagent incorporation increases the crosslinking efficiency in the EOC phase and decreases the degradation in the PP phase. The present study focuses on the influence of the three structurally different coagents namely triallyl cyanurate (TAC), trimethyl propane triacrylate(TMPTA) and N,N'-m-phenylene dimalemide(HVA-2) on the mechanical and rheological properties of the PP/EOC thermoplastic vulcanizates (TPVs). Depending on the structure and reactivity, different coagents show different performance. All the compositions were prepared by melt mixing method in the Haake rheomix at 180°C and rheological properties also have been evaluated at the same temperature. Viscoelastic behaviour of the TPVs prepared were analysed by a dynamic oscillatory rheometer in the melt state in Rubber Process Analyzer (RPA 2000). Morphologically TPVs consist of dense crosslinked rubber domains in the thermoplastic phase and their rheological behavior can be compared to that of highly filled polymers. The crosslinked particles tend to agglomerate and build local cluster which tends to disintegrate by shearing. A variety of rheological observations such as Payne effect, modulus recovery and shear rate sensitivity were studied by carrying out frequency sweep, strain sweep, and stress relaxation tests in sequence.

**Key words:** PP/EOC blends, dynamic peroxide curing, coagents, rheological properties, viscoelastic properties

#### Finite element analysis of hyperelastic material

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Due to the increasing demands of the rubber components used in the automotive and aerospace industries, the development of computational methods for elastomer analysis has attracted extensive research attention. This work is focused on developing a finite element programme code for the analysis of hyperelastic materials restricted to plane stress case.

Hyperelastic refers to materials which can experience large elastic strain that is recoverable. Rubber like materials falls in this category. The behavior of hyperelastic material is described based on Mooney-Rivilin and Neo-Heokean material models. The constitutive theories for a large elastic deformation is based on the strain energy density function which is coupled with finite element method, can be used effectively to analyze and design elastomer.

Due to non-linear stress-strain relation, the hyperelastic materials will cause a structure stiffness to change at different load levels. In finite element formulation, the modeling of hyperelastic material should incorporate both geometric non-linearity due to large deformation as well as material non-linearity. Because of nonlinear relationship the finite element equations are nonlinear in terms of displacement. An iterative Newton-Raphson method was employed for the solution of non-linear governing equations. At each finite element solution step we obtained strain or strain increment, used to compute the stress which is needed to evaluate the internal force as well as the tangent stiffness matrix. The computed stress and deformation results obtained from finite element programme code shows good agreement with simple benchmark problem and as well as with FEA package (MARC).

**Key words:** finite element analysis, hyperelastic material, Mooney-Rivilin model, Neo-Heokean material model, Newton-Raphson method

## Graft-copolymerization of cellulose-based filter paper and its development as antibacterial food-packaging material

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With the growing public health awareness of disease transmissions and cross-infection caused by microorganisms, use of antimicrobial materials has increased in many application areas like protective clothing for medical and chemical works, other health related products, antibacterial packaging material that can improve product quality and keep it free from microbial adhesion, etc. Such antimicrobial packaging materials may be produced by introducing silver, gold or copper nanoparticles into polymer film. The reason is that these metals are highly toxic to microorganisms, showing strong biocidal effects on as many as 16 species of bacteria including *E.Coli*.

However, silver nanoparticles loaded synthetic polymeric films are not used as packaging material because of the non-degradable nature of these synthetic polymers which have put a great challenge before environmental scientists and chemists. We have developed ordinary filter papers as antibacterial packaging material by grafting it with vinyl monomers like acrylamide followed by loading of silver nanoparticles, utilizing our recently developed approach. The degradable nature of filter paper makes it an attractive alternative for use as packaging material.

The present work describes preparation of a silver nanoparticles loaded grafted filter paper for the purpose of using as antibacterial packaging material. The paper shows fair biocidal action against *E.Coli* and it can be used as a packaging material for food stuff.

**Key words:** grafted filter paper, silver nanoparticles, antibacterial packaging material, biodegradable packaging material

## A Review on thermally stable organic modifiers for montmorillonite nanoclays

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Among nanomaterials, polymeric nanocomposites have emerged as one of the most important classes of materials and hence, a field of active research. A number of products enabled with nanofillers are already put in the market, mainly in automotive and packaging industries. One of the most important classes of nanocomposites is based on silicate nanoclays. Montmorillonite clay, modified with different ammonium cations have been studied most extensively for fundamental understanding as well as for commercial applications. However, the application space for polymer nanocomposites remained restricted to low temperature resins such as polyolefins and polyamides, limited mainly by relatively low thermal stability of the alkyl ammonium ions (below 200 °C), used for modification of the nanoclays. This restricts exploitation of the potentials of this technology into the arena of high performance polymers such as engineering thermoplastics, which are most often compounded at high temperatures. Hence, recently, a number of research groups have taken up the challenge of extending the applicability of nanoclays to high-temperature resins. In this presentation, recent trends in compatibilization of nanoclays using thermally stable modifiers will be reviewed. Recent results published in literature on nanoclays modified with organic modifiers such as phosphonium or imidazolium cations, that have thermal stability up to about 300 °C, will be discussed. Different applications proposed for this new class of high-temperature polymeric nanocomposite will also be discussed.

**Key words:** montmorillonite nanoclays, organic modifiers, thermal stability, phosphonium cations, imidazolium cations

#### **Transducer using Terfenol-D/epoxy composite**

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Terfenol-D (alloy of iron, dyesprosium and terbium rare-earth materials) has received considerable attention as a material for magnetostrictive transducers and actuators due to its giant magnetostriction. Nevertheless, device development using this material has always been hampered by problems related to eddy currents and high brittleness of the material. Both of these problems can be effectively addressed by developing composites of magnetostrictive materials in epoxy matrices. A study has been carried out on a Terfenol-D /epoxy composite to assess its suitability for use in low frequency underwater transducers. Samples with different percentages of volume filling of Terfenol-D powder of 0- 300 micron sizes were prepared and their, magnetic properties such as magnetostriction, magnetization and permeability were studied. The maximum attainable magnetostriction for a composite of 60% volume filling of Terfenol-D powder was found to be 450 ppm. The saturation magnetisation of the composite for this volume filling was obtained as 1.2 Tesla. Further, mechanical and dynamic mechanical properties of the composite and its relation with the volume percentage of Terfenol-D powder in the composite were also studied. A linear analytical approach using the rule of mixtures was employed to calculate the effect of volume fraction of the Terfenol-D powder on the magnetic and mechanical properties of the composite. The measured values were found to be comparable with the theoretical values.

In order to assess the feasibility of the material for use in low frequency underwater transducers, the composite material was formed into rods (8 mm diameter X 28 mm length) and were employed in a Class IV Flextensional Transducer, as a transduction material. Underwater acoustic measurements were carried out and the results are compared with those of a similar transducer using monolithic Terfenol-D material, in the same geometries.

Key words: Underwater transducer, Terfenol-D, magnetostriction, magnetization, mechanical poperties

### A comprehensive study on degradation of nano-silica filled model TPE blend systems

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The effect of nano-silica on the thermal degradation behaviors of LDPE-EVA based thermoplastic elastomeric blends were monitored in nitrogen as well as in oxygen atmospheres using thermo gravimetric analyses (TGA). The pristine silica nano-particles were melt-blended with the LDPE-EVA system at 1.5, 3 and 5 wt% loadings, respectively, by varying the sequence of addition. In one of the compositions, coupling agent Bis-[3-(triethoxysilyl)propyl] tetrasulphide (Si-69) was used to improve the interaction of hydrophilic silica fillers with polymer matrices. In anaerobic condition, no significant changes were observed in terms of thermal stability of such blend systems. However, in oxygen atmosphere, the TGA plots reflected a dramatic change. A three staged degradation of all the filled samples were observed. The changes in the decomposition onset ( $T_i$ ) and maximum degradation temperatures ( $T_{max}$ ) were correlated well with the morphology of the filled TPE systems as observed by transmission and scanning electron microscopes. The kinetic rate constants and activation energies were calculated using non-isothermal kinetic analysis. A comparison between non-isothermal and isothermal kinetic parameters revealed the approximate degradation mechanisms of nano-silica filled and unfilled TPE blend systems.

The initial part of degradation was probably controlled by oxygen diffusion, decomposition of LDPE and acetic acid elimination from EVA. The next stage of degradation was found to be a strong function of mutual interactions between EVA and nano-silica. Si-69 provided a significant stabilization at the initial stages of degradation (first two). However, the final stages of degradation were remarkably unaffected by the presence of nano-silica fillers. On the whole, it was observed that the thermal stability of TPE blends was a strong function of morphology which in turn was decided by the sequence of addition of ingredients during blend preparation, amount of silica nano-fillers added and presence of coupling agent. The mutual interaction of the polymer matrices with nano-silica fillers strongly influenced the kinetic parameters.

## **Key Words:** Non-isothermal degradation, Silica nano-Filler, Coupling Agent, Activation Energy, Thermoplastic Elastomer, Morphology, Degradation

## Synthesis and characterization of polypropylene/ionomer/ organoclay nanocomposites

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The compatibilization effects provided by ionomer-g-polypropylenes versus those of a maleated polypropylene, PPMA, for forming polypropylene-based nanocomposites were compared. We have prepared a novel compatibilizer by grafting ionic functional groups on to the PP and evaluated its efficiency as compatibilizer in the preparation of PP/clay nanocomposites. The PP/ionomer/organoclay nanocomposites were prepared by two different routes, namely, direct melt mixing and by masterbatch. The structure and morphology of the nanocomposites were characterized by WAXD and TEM. Mechanical properties such as flexural and tensile modulus of the nanocomposites prepared were studied using INSTRON and the crystallization behavior was studied using differential scanning calorimetry (DSC) and polarized optical microscopy (POM). Thermal stabilities were characterized using TGA. The dispersion of clay was found to be dependent on the method of preparation, type of compatibilizer used and the amount of compatibilizer used. The dispersion of the organoclay was better with the ionomer than PPMA and the dispersion was better when the nanocomposites were prepared by two step masterbatch route than the single step direct mixing method. The dispersion of the organoclay improved with increase in the amount of compatibilizer. The nanocomposites obtained with ionomer as compatibilizer showed improved nucleation, thermal stability and mechanical properties compared to the nanocomposites obtained using PPMA as compatibilizer.

Key words: PP-based nanocomposites, WAXD, TEM, ionomer-g-polypropylenes, compatibilization

#### Effect of plasticizer, filler and solvent swell on polyurethane elastomers

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Polyurethane elastomers are developed using different types of isocyanate terminated polyether based prepolymers (A, B and C) with four types of multifunctional hydroxy derivated curatives (X1, X2, X3 and X4) and selected processing additives namely plasticizer and filler. The polyurethane elastomers are developed with a view to utilize them in high performance print roller applications, with improved strength and solvent resistance characteristics. The properties like pot life, hardness, tensile strength, modulus, tear strength, compression set, density and solvent resistance of these polyurethane elastomers are studied in the absence of additives and in the presence of additives.

Among the polyurethane elastomers prepared, the product obtained from prepolymer C with curative X3 exhibits better strength properties and solvent resistance characteristics than those from other products. High percentage of reactive functional groups present in the prepolymers and curatives enhance the crosslink density, which in turn enhances the mechanical properties and solvent resistance characteristics. Incorporation of additives (plasticizer and filler) improve the performance characteristics of polyurethane elastomers, the enhancement of strength properties and solvent resistance behaviour are observed in all cases of filled polyurethane elastomer irrespective of prepolymers and curatives. However, degree of improvement varies based on the nature of reactants involved.

#### Keywords

polyurethane elastomers, plasticizers, solvent swell, mechanical properties, print rollers

## Studies on EPDM based compositions for underwater acoustic applications

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Polymeric compositions are widely employed in various underwater acoustic applications. The major uses of these composites are for packaging underwater electronic gadgets which cannot function if directly exposed to sea water environments. These composites have to function as acoustic windows, reflectors, absorbers or a combination of these, depending on the frequency of interest. In this paper, the acoustic properties of EPDM rubber formulations are studied for its window application. A series of compositions are made by incorporating different ingredients at various loading levels and evaluated for their acoustic parameters. All compositions are studied for their cure characteristics at various temperatures and time using MDR2000 rheometer. The compounds developed are found to be reversion resistant beyond their cure conditions. Compositions ranging from 150-250 pphr reinforcement loading are found to be transmitting acoustic energy with negligible loss. Circular discs of diameters 50mm and 200mm with 20mm thickness are used for acoustic studies. The insertion loss and echo reduction behaviour are studied in a vertical water filled pulse tube using standard acoustic projector-cum-receiver. Dynamic mechanical properties are also studied at various frequencies and temperatures. Physical and mechanical properties are evaluated as per ASTM standards. Results showed that the material can be a good candidate for acoustic window application. The negligible water absorption and high underwater environmental stability make this material suitable for sub-sea application. Studies showed that insertion loss of the material is 0.2dB in the range of 2 kHz to 15 kHz. The water absorption of the material is 0.002% when immersed in both fresh and saline for 24 hours at room temperature. The weight gain due to water absorption, when submerged in water for more than 40days is negligible.

**Key words:** underwater acoustic applications, EPDM, acoustic window, insertion loss, echo reduction

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#### Stress analysis of air borne polymeric composite structure

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Composite structures are extensively used in air borne applications in civilian and military field owing to inherent advantages of high strength to weight ratio, ability to withstand high loads, slow failure rates, tailorability of mechanical and chemical properties and better directional properties. The most common types of composites employed in air borne applications are carbon fiber reinforced epoxy and glass fiber reinforced epoxy. One of the FRP structures developed for airborne application is in the shape of 'C' with various geometrical discontinuities for weight reduction and mounting of sensors and hinges for integrating to main assembly. Presence of such deviations from regular geometries leads to build up of stress concentrations at such irregularities, which could be fatal and lead to catastrophic failures. In order to understand the actual stress distribution, predict and prevent any failure of the structure, proper theoretical analysis is required.



Section of the "C" channel structure showing geometrical discontinuities

A finite element analysis software ANSYS was used to evaluate the stress response of the composite structure. As the structure is intended to operate underwater, analysis was carried out to simulate the effect of hydrostatic pressure loads. Airworthiness requirements also demands that the structure to withstand high inertial acceleration loads coming on the system during various maneuvering. Analysis was also carried out to ensure that the structure is capable of withstanding these inertial acceleration loads. The structure is mounted with sensor elements and the effect of these sensor elements were modelled using lumped masses method. 20-node hexahedral element was used to mesh the structure. As the structure is fabricated with fiber reinforced plastics having orthotropic properties, properties such as elastic modulus, shear modulus and Poisson's ratio were considered for all the three directions for the analysis. The analysis was carried out for 30% glass filled polycarbonate, Glass fiber reinforced epoxy composites and carbon fiber reinforced epoxy composites. The von-Mises stress distribution obtained

showed the maximum stress near the top hinges and the corresponding displacement distribution showed maximum displacements at the top of the structure.

Key words: stress analysis, fiber reinforced epoxy composites, underwater applications

## Effect of post drawing parameters of melt spinning of carbon nanotube filled polypropylene fiber

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Isotactic polypropylene (PP) utilized as a commercial polymeric fiber exhibits a wide range of mechanical properties. However PP fiber needs reinforcement in order to achieve high stiffness and strength for engineering applications. Since the discovery of carbon nanotubes (CNT) by Iijima, CNT have emerged as a potential candidate as reinforcing filler in polymer based composite fibers due to their unique mechanical, electrical and thermal properties. Multiwalled carbon nanotubes (MWNT) were varied (0.5-3 wt %) in melt mixed PP/MWNT composites which were prepared by using twin screw microcompounder. The resulting composites were subsequently melt spun into fiber. The melt spun fibers were drawn at draw ratio of 8 with varying post drawing parameters (temperature and speed of drawing the composite fibers) in order to understand the effect of post drawing parameters on mechanical properties of composite fibers. The effect of post drawing parameters on crystalline chain orientation (Herman's orientation factor for (110) PP plane) and crystal size of (110) PP plane were studied using wide angle X-Ray diffraction. Structure property relationship studies were performed in PP/MWNT composite fibers.

**Key words:** carbon nanotube filled PP fiber, melt spinning, post drawing parameters, mechanical properties, WAXD

# Competitive extraction of Na, K, Ba, Ca, Mg by NR/PEO-1000, NR/PEO-4000 block copolymers

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The ionophoric property of NR/PEO block copolymers is due to the presence of PEO segments in the block copolymer backbone. Amphiphilic compounds such as PEO exhibit complexation ability towards many metal salts of uni and divalent metals comparable to crown ethers. In general more flexible PEO are able to wrap the metal ions in helical fashion and thus can act as carriers/extractants with properties parallel to that of crown ethers. But because of their common selectivity, they are not widely used as such as crown ethers.

A series of NR/PEO block copolymers were prepared from TDI, PEO with molecular weights 1000, 4000 and liquid natural rubber by solution polymerization. Because of the above stated pseudohelical property and common selectivity, complexation studies with different metal salt solutions like NaCl, KCl, BaCl<sub>2</sub>, CaCl<sub>2</sub>, MgSO<sub>4</sub> were undertaken to find the competitive extraction order. The results have been analysed by comparing the overall metal complexation values.

Table1. Ion uptake by the polymer samples

Polymer sample	Uptake of metal ions (mM/g)						
	Na <sup>+</sup>	$\mathbf{K}^+$	Ba <sup>++</sup>	Ca <sup>++</sup>	Mg <sup>++</sup>		
NR/PEO-1000	1.995	3.78	2.80	2.2362	0.88		
NR/PEO-4000	2.1158	4.408	3.196	2.8556	0.4229		

The order of competitive extraction of the two block polymers is same.i.e,

K>Ba>Ca>Na>Mg, which almost coincides with the PEO complexation. The order of PEO complexation in alkali metals is K>Rb>Cs>Na>Li and that of alkaline earth metals is Ba>Sr>Ca>Mg.

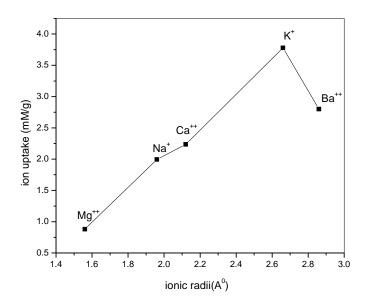


Figure 1. Plot of ion uptake versus ionic radii

From fig (1) it is clear that, as the ionic radii increases, complexation ability also increases; except for barium. The reason for maximum extraction of  $K^+$  is that, its ionic radius is almost similar to the cavity size of 18-crown-6. But in the case of  $Ba^{2+}$ , its ionic radius is slightly greater than the cavity size of 18-crown-6. Therefore, the helical structure has to expand a little which leads to the lower absorption compared to  $K^+$ .

For alkali and alkaline earth metals, co-ordination is from 6-8.i.e, the ligand should have at least 6 donor atoms (5-CH<sub>2</sub>-CH<sub>2</sub>-O-)- units in the molecule to satisfy all the coordination sites. In this case, the PEO segments can accommodate the ions by forming a helical structure of suitable cavity size, depending upon the size of the ion, i.e., either by size comparable to that of 15-crown-5 or 18-crown-6 where the number of

-CH<sub>2</sub>-CH<sub>2</sub>-O- units are 5 and 6.

Hence, here the maximum competitive extraction is for potassium, which shows that PEO chains prefer to take a helical structure similar to that of 18-crown-6.

The situation can be schematically represented as

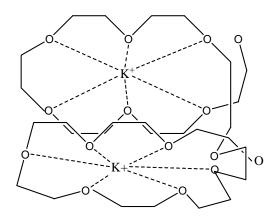


Figure 2. Pseudocavity binding of  $K^+$ 

**Key words:** competitive ion extraction, block copolymers, PEO, coordination sites, helical structure

# A Study of mechanical properties of flax-g-poly(MA) reinforced phenol-

# formaldehyde composites

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In the present paper, we report the preparation of graft copolymers of flax fibers with methyl acrylate (MA) using Fenton's reagent (FAS-H<sub>2</sub>O<sub>2</sub>) as redox system. Synthesized flax-g-poly(MA) was characterized with FTIR, TGA/DTA, scanning electron microscopy (SEM), and X-ray diffraction (XRD) techniques. Composites were prepared using flax-g-poly(MA) as a reinforcement and phenol-formaldehyde (PF) as the binding material. Mechanical properties of phenol-formaldehyde composites were compared and it has been found that composites reinforced with flax-g-poly(MA) showed improvement in mechanical properties. Composites reinforced with flax-g-poly(MA) showed better tensile strength (235 N) and compressive strength (814 N) in comparison to composites reinforced with original flax fiber which showed lower tensile strength (162 N) and compressive strength (372 N). Composites reinforced with flax-g-poly(MA) shows the improved MOR, MOE, and SP.

Key words: flax fiber, MA grafting, PF-flax composites, mechanical properties, XRD, SEM

# Protein functionalized polysaccharide nano particles for novel applications

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There has been growing interest in the use of natural polysaccharides for biomedical applications, drug delivery vehicles, as minimally invasive scaffolds for tissue engineering, because of their non toxicity, biocompatibility, biodegradability, low interfacial tension and high molecular and oxygen permeability. By exploiting these features it may be possible to mimic features of the natural extracellular matrix, and control tissue structure and cellular functions. Consequently, hydrogels have been investigated for cell gene therapy, enzyme and cell encapsulation, drug delivery, joint cushioning and lubrication and as environmental shape memory materials. Protein/peptide oral drug delivery is a complicated process mainly due to poor intrinsic protein permeability as a result of large molecular weight, degradation by proteolytic enzymes in the stomach and in the small intestine, and chemical instability. Protein functionalized micro and nano particles are very versatile and were made to overcome this problem. Low molecular weight chitosan, guar gum, starch were used for the preparation of nano particles using precipitation and ionic crosslinking method and was then linked to the enzyme (subtilisin) protein or BSA by glutaraldehyde coupling. Polysaccharides having a molecular weight of 8 to 36 KDa gave high-quality nano composite spherical particles of 70-612 nm size, with a good poly dispersity index of 0.1- 0.7. Molecular weight greater than 50 KDa gave micro particles and vesicles of more than 1 microns as indicated by dynamic laser light scattering, SEM, and TEM studies. The optimum pH of the polysaccharide nanoparticle immobilized enzyme was shifted to 8.0 from 7.0, whereas there was no change in the optimum temperature. The immobilized enzyme shows better affinity to the substrate (casein) with a lower  $K_{M}$  value of  $4.097 \times 10^{-5}$  than the native subtilisin which is  $3.30 \times 10^{-4}$ . These composite catalytic nano particles are having excellent activity, pH sensitivity and stability which make them suitable for oral drug delivery, tissue scaffolds, microreactors or for cosmetic applications.

**Key words:** polysaccharide nano particles, protein functionalization, precipitation method, ionic crosslinking method, biomedical applications

# Preparation and Characterization of ethylene co-vinyl acetate based drug delivery system for cardiovascular applications

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Major complications of cardiovascular lesions are often accompanied by inflammatory reactions and smooth muscle cell proliferation. Curcumin has been shown to possess antiinflammatory and anti-proliferative properties. As a solution to above cardiovascular problems, sustained drug delivery system releasing curcumin from ethylene-co-vinyl acetate (EVA) matrices is proposed.

Various grades of EVA having 40%, 28%, 18% and 12% vinyl acetate content were evaluated for the selection of a suitable grade. The EVA grades were characterized by fourier transform infrared (FT-IR) spectroscopy, dynamic mechanical analysis (DMA), testing solubility in organic solvents and determining mechanical properties. Curcumin is incorporated into the matrices by dissolving both matrix and curcumin separately in solvents, mixing together and later evaporating the solvent from the system. Curcumin loaded systems were characterized by FT-IR, contact angle measurements, water absorption, mechanical testing and checking the drug release profile from the matrix.

FT-IR data confirms that there was no chemical reaction between EVA and the drug. Increased drug content in the matrices results significant increase in tensile strength and modulus whereas fracture strain records substantial decrease. The results of contact angle indicated that loading curcumin in EVA does not alter surface properties of the matrix significantly. DMA revealed that addition of curcumin does not alter glass transition temperature either. It also shows that when the vinyl acetate content increases the storage modulus decreases. Water absorption studies show an increase in water uptake by matrices with increase in drug loading.

From the results obtained EVA with 40% vinyl acetate content was found to be the most suitable system as a matrix. The selection was based on the low modulus, high elongation, solubility in the organic solvents and film forming properties. Drug elution profiles up to a period 15 days were monitored. From the results it is expected that curcumin loaded EVA-40 system would be suitable for drug release applications in cardiovascular system.

**Key words:** EVA, drug delivery system, cardiovascular applications, curcumin, drug elution profiles

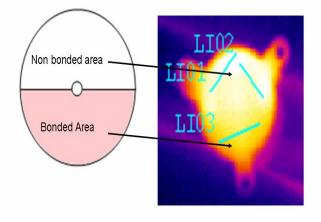
# Nondestructive testing of defects in adhesive joints

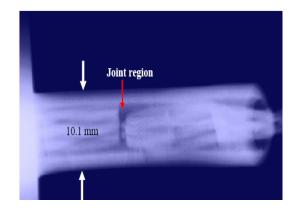
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Reliability aspects of underwater components are important when considering their durability and performance. These components are deployed underwater for long period of time and have no option for monitoring the health and functionality. Rubber materials are generally used for encapsulating underwater components to prevent moisture ingress. During the encapsulation stage, surface and subsurface defects and discontinuities such as micro-cracks, voids, porosity and delamination occur in the components. These defects are due to service stress, process inconsistency, stringent environmental conditions and inconsistent workmanship. Failure analysis of the components shows that adhesive failure, either by mechanical failure or water ingress through the interface, is the major cause of the component failure. Hence, it is essential to determine the integrity of the adhesive joints of the underwater components. For detecting and localizing the defects without destroying the components, special techniques such as non destructive testing is required.

In the present study, the defects in the adhesive joints have been detected and characterized using the micro-focal x-ray radiography and infrared thermal imaging techniques. The infrared thermographic image of the component with known defects is given below. From the thermal gradient as shown below, defects like non-bonded area can be detected. Also, the defects in the embedded components in micro-level can be detected using the microfocal x-ray radiography as shown below.





IR thermal image

Microfocal x-ray radiographic image

**Key words:** nondestructive testinf, adhesive joints, under water rubber components, X-ray radiography, infrared thermal imaging

# Structure property relationship studies of melt spun carbon nanotubes filled polypropylene fiber

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Polypropylene (PP) is one of the major polymeric fiber materials of future in view of its impressive consumption in the past decade. However, PP fibre needs reinforcement in order to achieve high stiffness and strength for engineering applications. Since the discovery of carbon nanotubes (CNT) by Iijima, CNT have emerged as a potential candidate as reinforcing filler in polymer based composites due to their unparallel mechanical, electrical and thermal properties. Multiwalled carbon nanotubes (MWNT) were varied (0.5-3 wt%) in PP/MWNT composites which were melt-mixed by using twin screw microcompounder. The resulting composites were subsequently melt–spun into fibers and were post drawn at 120°C with a draw ratio of 8. Two different types of MWNT were utilized in order to understand the effect of different types of MWNT in enhancing mechanical properties of the composite fibers. It was found that MWNT obtained from DMSRDE were found to be superior over Nanocyl NC 3100 in achieving high modulus of PP/MWNT composite fibers. Herman's orientation factor of (110) PP plane and MWNT along the fiber axis was determined using wide angle X-ray diffraction and Raman spectroscopy respectively. Structure property relationship studies were performed in PP/MWNT composite fibers.

Key words: Polypropylene (PP), Multiwalled carbon nanotube (MWNT), melt spinning

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# Novel nanocomposite polymer electrolytes based on electrospun poly(vinylidene fluoride-co-hexafluoropropylene) for lithium batteries

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Rechargeable batteries using polymer electrolytes (PEs) instead of traditional liquid electrolytes are well adapted to various geometries because of their advantages in providing lighter and safer batteries with longer shelf life, leak proof construction and easy fabrication into desired shape and size. Electrospinning technique has attracted immense attention recently as a versatile and easy method to prepare polymer membranes, that are made up of thin fibers of micron and sub-micron diameters. The high crystallinity of polymer membranes is one of the major causes of the low ionic conductivity of polymer electrolytes, and it thus limits their use in lithium batteries. This problem can be addressed to a certain extent by the addition of nano-sized ceramic fillers to polymer electrolytes. The size of the fillers is an important characteristic as nano size of a particle apart from providing large surface area for interactions between polymer and electrolyte.

A series of nanocomposite polymer electrolytes (NCPE) based on poly(vinylidene fluoride-cohexafluoropropylene) [P(VdF-HEP)] incorporated with nanoparticles of BaTiO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub> were prepared by electrospinning technique. The addition of the ceramic fillers barely influenced the thermal properties and % crystallinity of the polymer matrix. The melting temperature of pristine P(VdF-HFP) is 159 °C, while the polymers with fillers have lower melting points in a close range of 153.4, 153.8 and 154.9 °C for membranes with BaTiO<sub>3</sub>, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, respectively and the % crystallinity values obtained from the DSC data follows the order BaTiO<sub>3</sub> (47.1%) < SiO<sub>2</sub> (47.9) < Al<sub>2</sub>O<sub>3</sub> (49.2) < membrane without filler (74.5%). The composite membranes exhibit a porous morphology formed by interlaying of fibers of AFD ~ 1-2.5 µm. The porosity varies in the narrow range of 84-87% for the membranes, showing a slight increasing trend with ceramic content. With a high porosity ~ 90%, the membranes exhibit electrolyte uptake of > 425%. The resultant porous membranes also exhibit electrolyte retention capacity. The presence of the ceramic nanoparticles has positive effect on the mechanical properties of the membranes. The ionic conductivity and the electrochemical properties of the PE based on electrospun PVdF-HFP is enhanced by the presence of the nano sized ceramic fillers. The PE based on the membrane with ceramic fillers which shows better ionic conductivity of  $10^{-3}$  S/cm at 25 °C and have anodic stability > 4.6 V versus Li/Li<sup>+</sup> and show good compatibility with lithium metal electrode. The suitability in Li/LiFePO<sub>4</sub> cell is demonstrated by exhibiting about 100% utilization of the cathode material (165 mAh/g) at 1 C-rate at 25 °C. In comparison with BaTiO<sub>3</sub>, the performance of the Li/LiFePO<sub>4</sub> cells with NCPEs containing Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> was observed to be lower discharge capacities of 153 mAh/g and 156 mAh/g respectively. The enhanced performance of the BaTiO<sub>3</sub> based NCPE is attributed mainly to its better interactions with the host polymer and compatibility with the lithium metal. Incorporation of the ceramic filler is more a useful efficient in improving the properties of the PEs.

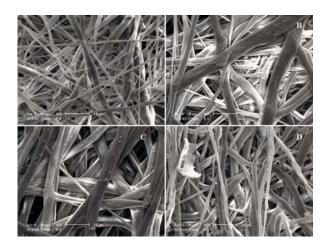


Fig. 1. SEM images of electrospun P(VdF-HFP) membranes with (A) 0% filler, (B) SiO<sub>2</sub>, (C) Al<sub>2</sub>O<sub>3</sub>, and (D) BaTiO<sub>3</sub>.

**Key words:** nanocomposite polymer electrolytes, P(VdF-HEP), electrospinning, lithium batteries, nanofillers

# Biomimetic synthesis of nanohybrids based on calcium hydroxyapatite and carboxymethyl cellulose

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Over the past decade, the main goal of bone tissue engineering has been to develop biodegradable materials as bone graft substitutes for filling large defects in bones. Bone and teeth consist of a small amount of organic matrix, which manipulates the formation of apatite into distinct microstructures suitable for the mechanical forces which they encounter *in-vivo*. The processes and materials that control such crystal nucleation and growth are of great interest to materials scientists to learn about the architecture, morphology, and patterning of inorganic materials at all dimensions from the nanoscale to macroscopic scale by mimicking the process of biomineralization. In the present paper we report biomimetic synthesis of nanohybrids based on carboxymethyl cellulose (CMC) and hydroxyapatite (HA) nanoparticles by a co-precipitation method. The physico-chemical characterizations were done before and after calcination using fourier transform infrared spectroscopy, solid state <sup>31</sup>P nuclear magnetic resonance (NMR) spectroscopy and thermogravimetric analysis (TGA). The formation of nanohybrid was observed by wide angle X-ray diffraction (WAXD), scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX) and transmission electron microscopy (TEM). The nanohybrid was formed as aggregates of nanoparticles adsorbed on CMC. With increasing content of CMC, the crystallite size of hydroxyapatite particles decreased (with 2 wt. % 18±3 nm). The morphological aspects of calcined samples have shown the sintering ability of HA nanoparticles. The possible mechanism for interaction between CMC and HA, nucleation and growth of nanocrystals of HA is discussed. It is summarized that nanohybrids of hydroxyapatite nanoparticles can be prepared for mimicking the process of nucleation and growth in nature using biodegradable and biocompatible macromolecules like CMC.

Key words: biopolymer; hydroxyapatite; cellulose; nanoparticles; X-ray diffraction; particle size

# Mechanical properties of natural rubber / poly butadiene rubber blends prepared using fatty acid incorporated natural rubber

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Blends based on natural rubber (NR) and polybutadiene rubber (BR) are extensively used in tire sector due to the enhanced mechanical properties like heat build-up, and abrasion resistance realized in the vulcanizates. In such blends homogeneous dispersion of carbon black is a problem as the latter has a tendency to migrate to the BR phase. Generally plasticizers are used to enhance filler dispersion in rubbers. In NR/BR blends it is possible to improve carbon black dispersion by prior incorporation of suitable plasticizers in NR before preparation of rubber blends. Fatty acids which are good plastisizers can be preferentially incorporated in the NR phase by the addition as surfactants in latex stage before coagulation. In this paper an investigation on the preparation, cure characteristics and mechanical properties of NR/BR blends prepared using fatty acid incorporated NR is carried out.

Natural rubber latex is treated with the required quantity of fatty acid soap and then coagulated by addition of suitable acids. The coagulation of fatty acid incorporated latex depends on the type of coagulants. 0.8 % sulphuric acid is shown to be a better coagulant than formic or acetic acids. The coagulum is washed well to remove acids and then dried at 70  $^{0}$  C in an air oven to get dry rubber. Rubber compounds based on pure NR, 80/20 and 60/40 NR/BR blends are prepared using conventional mixing methods. The compounds are vulcanized and tested as per standard test methods.

When soap is added to latex, the fatty acid ions displace a part of the protein molecules and strongly get adsorbed on the rubber particles. This surface bound fatty acid anions get converted to the corresponding fatty acids by reaction with acids during the process of coagulation. The fatty acids retained on rubber during coagulation play a major role on the cure characteristics, filler dispersion, mechanical properties and ageing characteristics of the recovered rubber and hence in blends prepared using such rubber.

Due to the presence of fatty acids, the pure and NR/BR blends show better cure characteristics as revealed from a higher level of vulcanization even though the cure time is comparatively longer. The presence of fatty acids also helps in a better dispersion of filler. Due to the higher level of crosslinking and better filler dispersion pure and blend vulcanizates show a higher modulus, tensile strength, and hardness along with comparable dynamic properties like heat build-up and compression set. in relation to conventional rubber vulcanizates. It is expected

that for fatty acid incorporated rubber there can be weak interactions involving the carboxyl group and the active sites on the surface of carbon black. A noticeably higher solvent resistance and abrasion resistance is also observed for NR prepared by the new process due to the presence of better interaction of filler with rubber.

Key words: NR/BR blends, fatty acids, filler dispersion, filler-rubber interaction

# Effect of electron beam curing on mechanical and electrical properties of silica filled silicone and FKM rubber and its comparison with chemical curing

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The effects of electron beam (EB) irradiation on mechanical and electrical properties of Silicone rubber (MQ), and Fluro rubber (FKM) compounds filled with Precipitated and Fumed Silica filler have been reported in this paper. The effect of different degree of radiation dosage on both electrical and mechanical properties was investigated. Some comparison has been made between properties of EB cured vulanizates of theses two rubbers with Peroxide cured Silicon rubber and Calcium hydroxide cured FKM rubber. The type of silica filler used affects both electrical and mechanical properties of EB cured vulcanizates. The tensile strength of silicone rubber is marginally affected by irradiation dosage up to 15 MRads, but further increase in irradiation dosage shows some fall in properties. But for FKM rubber strength properties increases progressively with irradiation dosage up to 15 Mrads there after some drop is observed. Almost similar trend is noted for tear strength properties of these rubbers. However elongation at break for both MQ and FKM continuously decreases with the increase in radiation dosage. This is in line with the change in gel fraction with radiation dosage. The reinforcement by ppt silica is better during chemical cure compared to EB cure for both rubbers whereas in the presence of fumed silica EB curing gives higher tensile strength compared to chemical cure.

The radiation dosage has marginal effect on electrical conductivity, and dissipation factor. However loss factors for chemically crosslinked rubbers are higher than that of EB cured ones. Compared to ppt silica filled systems, fumed silica filled ones exhibit less electrical loss.

# Mechanical and rheological behavior of peroxide cured polypropylene (PP)/ethylene octene copolymer (EOC) thermoplastic vulcanizates (TPVS)

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Technologically compatible binary blends of polypropylene (PP) and ethylene octene copolymer (EOC) were dynamically vulcanized by coagent assisted peroxide crosslinking system. Addition of peroxide in PP/EOC blend involves two major competing reactions: EOC cross-linking and PP degradation by  $\beta$ -scission. Final product properties are thus dependent on the balance among those two competing reactions. As the concentration of peroxide increases, particle size decreases. However, mechanical properties of these TPVs are not good enough, which is due to severe degradation in the PP phase in the presence of peroxide.

Principally, coagent incorporation increases the crosslinking efficiency in the EOC phase and decreases the degradation in the PP phase. The present study focuses on the influence of the three structurally different coagents namely triallyl cyanurate (TAC), trimethyl propane triacrylate(TMPTA) and N,N'-m-phenylene dimalemide(HVA-2) on the mechanical and rheological properties of the PP/EOC thermoplastic vulcanizates (TPVs). Depending on the structure and reactivity, different coagents show different performance. All the compositions were prepared by melt mixing method in the Haake rheomix at 180°C and rheological properties also have been evaluated at the same temperature. Viscoelastic behaviour of the TPVs prepared were analysed by a dynamic oscillatory rheometer in the melt state in Rubber Process Analyzer (RPA 2000). Morphologically TPVs consist of dense crosslinked rubber domains in the thermoplastic phase and their rheological behavior can be compared to that of highly filled polymers. The crosslinked particles tend to agglomerate and build local cluster which tends to disintegrate by shearing. A variety of rheological observations such as Payne effect, modulus recovery and shear rate sensitivity were studied by carrying out frequency sweep, strain sweep, and stress relaxation tests in sequence.

**Key words:** PP/EOC blends, dynamic peroxide curing, coagents, rheological properties, viscoelastic properties

### Finite element analysis of hyperelastic material

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Due to the increasing demands of the rubber components used in the automotive and aerospace industries, the development of computational methods for elastomer analysis has attracted extensive research attention. This work is focused on developing a finite element programme code for the analysis of hyperelastic materials restricted to plane stress case.

Hyperelastic refers to materials which can experience large elastic strain that is recoverable. Rubber like materials falls in this category. The behavior of hyperelastic material is described based on Mooney-Rivilin and Neo-Heokean material models. The constitutive theories for a large elastic deformation is based on the strain energy density function which is coupled with finite element method, can be used effectively to analyze and design elastomer.

Due to non-linear stress-strain relation, the hyperelastic materials will cause a structure stiffness to change at different load levels. In finite element formulation, the modeling of hyperelastic material should incorporate both geometric non-linearity due to large deformation as well as material non-linearity. Because of nonlinear relationship the finite element equations are nonlinear in terms of displacement. An iterative Newton-Raphson method was employed for the solution of non-linear governing equations. At each finite element solution step we obtained strain or strain increment, used to compute the stress which is needed to evaluate the internal force as well as the tangent stiffness matrix. The computed stress and deformation results obtained from finite element programme code shows good agreement with simple benchmark problem and as well as with FEA package (MARC).

**Key words:** finite element analysis, hyperelastic material, Mooney-Rivilin model, Neo-Heokean material model, Newton-Raphson method

# Graft-copolymerization of cellulose-based filter paper and its development as antibacterial food-packaging material

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With the growing public health awareness of disease transmissions and cross-infection caused by microorganisms, use of antimicrobial materials has increased in many application areas like protective clothing for medical and chemical works, other health related products, antibacterial packaging material that can improve product quality and keep it free from microbial adhesion, etc. Such antimicrobial packaging materials may be produced by introducing silver, gold or copper nanoparticles into polymer film. The reason is that these metals are highly toxic to microorganisms, showing strong biocidal effects on as many as 16 species of bacteria including *E.Coli*.

However, silver nanoparticles loaded synthetic polymeric films are not used as packaging material because of the non-degradable nature of these synthetic polymers which have put a great challenge before environmental scientists and chemists. We have developed ordinary filter papers as antibacterial packaging material by grafting it with vinyl monomers like acrylamide followed by loading of silver nanoparticles, utilizing our recently developed approach. The degradable nature of filter paper makes it an attractive alternative for use as packaging material.

The present work describes preparation of a silver nanoparticles loaded grafted filter paper for the purpose of using as antibacterial packaging material. The paper shows fair biocidal action against *E.Coli* and it can be used as a packaging material for food stuff.

**Key words:** grafted filter paper, silver nanoparticles, antibacterial packaging material, biodegradable packaging material

# A Review on thermally stable organic modifiers for montmorillonite nanoclays

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Among nanomaterials, polymeric nanocomposites have emerged as one of the most important classes of materials and hence, a field of active research. A number of products enabled with nanofillers are already put in the market, mainly in automotive and packaging industries. One of the most important classes of nanocomposites is based on silicate nanoclays. Montmorillonite clay, modified with different ammonium cations have been studied most extensively for fundamental understanding as well as for commercial applications. However, the application space for polymer nanocomposites remained restricted to low temperature resins such as polyolefins and polyamides, limited mainly by relatively low thermal stability of the alkyl ammonium ions (below 200 °C), used for modification of the nanoclays. This restricts exploitation of the potentials of this technology into the arena of high performance polymers such as engineering thermoplastics, which are most often compounded at high temperatures. Hence, recently, a number of research groups have taken up the challenge of extending the applicability of nanoclays to high-temperature resins. In this presentation, recent trends in compatibilization of nanoclays using thermally stable modifiers will be reviewed. Recent results published in literature on nanoclays modified with organic modifiers such as phosphonium or imidazolium cations, that have thermal stability up to about 300 °C, will be discussed. Different applications proposed for this new class of high-temperature polymeric nanocomposite will also be discussed.

**Key words:** montmorillonite nanoclays, organic modifiers, thermal stability, phosphonium cations, imidazolium cations

### **Transducer using Terfenol-D/epoxy composite**

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Terfenol-D (alloy of iron, dyesprosium and terbium rare-earth materials) has received considerable attention as a material for magnetostrictive transducers and actuators due to its giant magnetostriction. Nevertheless, device development using this material has always been hampered by problems related to eddy currents and high brittleness of the material. Both of these problems can be effectively addressed by developing composites of magnetostrictive materials in epoxy matrices. A study has been carried out on a Terfenol-D /epoxy composite to assess its suitability for use in low frequency underwater transducers. Samples with different percentages of volume filling of Terfenol-D powder of 0- 300 micron sizes were prepared and their, magnetic properties such as magnetostriction, magnetization and permeability were studied. The maximum attainable magnetostriction for a composite of 60% volume filling of Terfenol-D powder was found to be 450 ppm. The saturation magnetisation of the composite for this volume filling was obtained as 1.2 Tesla. Further, mechanical and dynamic mechanical properties of the composite and its relation with the volume percentage of Terfenol-D powder in the composite were also studied. A linear analytical approach using the rule of mixtures was employed to calculate the effect of volume fraction of the Terfenol-D powder on the magnetic and mechanical properties of the composite. The measured values were found to be comparable with the theoretical values.

In order to assess the feasibility of the material for use in low frequency underwater transducers, the composite material was formed into rods (8 mm diameter X 28 mm length) and were employed in a Class IV Flextensional Transducer, as a transduction material. Underwater acoustic measurements were carried out and the results are compared with those of a similar transducer using monolithic Terfenol-D material, in the same geometries.

Key words: Underwater transducer, Terfenol-D, magnetostriction, magnetization, mechanical poperties

# A comprehensive study on degradation of nano-silica filled model TPE blend systems

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The effect of nano-silica on the thermal degradation behaviors of LDPE-EVA based thermoplastic elastomeric blends were monitored in nitrogen as well as in oxygen atmospheres using thermo gravimetric analyses (TGA). The pristine silica nano-particles were melt-blended with the LDPE-EVA system at 1.5, 3 and 5 wt% loadings, respectively, by varying the sequence of addition. In one of the compositions, coupling agent Bis-[3-(triethoxysilyl)propyl] tetrasulphide (Si-69) was used to improve the interaction of hydrophilic silica fillers with polymer matrices. In anaerobic condition, no significant changes were observed in terms of thermal stability of such blend systems. However, in oxygen atmosphere, the TGA plots reflected a dramatic change. A three staged degradation of all the filled samples were observed. The changes in the decomposition onset ( $T_i$ ) and maximum degradation temperatures ( $T_{max}$ ) were correlated well with the morphology of the filled TPE systems as observed by transmission and scanning electron microscopes. The kinetic rate constants and activation energies were calculated using non-isothermal kinetic analysis. A comparison between non-isothermal and isothermal kinetic parameters revealed the approximate degradation mechanisms of nano-silica filled and unfilled TPE blend systems.

The initial part of degradation was probably controlled by oxygen diffusion, decomposition of LDPE and acetic acid elimination from EVA. The next stage of degradation was found to be a strong function of mutual interactions between EVA and nano-silica. Si-69 provided a significant stabilization at the initial stages of degradation (first two). However, the final stages of degradation were remarkably unaffected by the presence of nano-silica fillers. On the whole, it was observed that the thermal stability of TPE blends was a strong function of morphology which in turn was decided by the sequence of addition of ingredients during blend preparation, amount of silica nano-fillers added and presence of coupling agent. The mutual interaction of the polymer matrices with nano-silica fillers strongly influenced the kinetic parameters.

#### Key Words: Non-isothermal degradation, Silica nano-Filler, Coupling Agent, Activation Energy, Thermoplastic Elastomer, Morphology, Degradation

# Synthesis and characterization of polypropylene/ionomer/ organoclay nanocomposites

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The compatibilization effects provided by ionomer-g-polypropylenes versus those of a maleated polypropylene, PPMA, for forming polypropylene-based nanocomposites were compared. We have prepared a novel compatibilizer by grafting ionic functional groups on to the PP and evaluated its efficiency as compatibilizer in the preparation of PP/clay nanocomposites. The PP/ionomer/organoclay nanocomposites were prepared by two different routes, namely, direct melt mixing and by masterbatch. The structure and morphology of the nanocomposites were characterized by WAXD and TEM. Mechanical properties such as flexural and tensile modulus of the nanocomposites prepared were studied using INSTRON and the crystallization behavior was studied using differential scanning calorimetry (DSC) and polarized optical microscopy (POM). Thermal stabilities were characterized using TGA. The dispersion of clay was found to be dependent on the method of preparation, type of compatibilizer used and the amount of compatibilizer used. The dispersion of the organoclay was better with the ionomer than PPMA and the dispersion was better when the nanocomposites were prepared by two step masterbatch route than the single step direct mixing method. The dispersion of the organoclay improved with increase in the amount of compatibilizer. The nanocomposites obtained with ionomer as compatibilizer showed improved nucleation, thermal stability and mechanical properties compared to the nanocomposites obtained using PPMA as compatibilizer.

Key words: PP-based nanocomposites, WAXD, TEM, ionomer-g-polypropylenes, compatibilization

#### Effect of plasticizer, filler and solvent swell on polyurethane elastomers

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Polyurethane elastomers are developed using different types of isocyanate terminated polyether based prepolymers (A, B and C) with four types of multifunctional hydroxy derivated curatives (X1, X2, X3 and X4) and selected processing additives namely plasticizer and filler. The polyurethane elastomers are developed with a view to utilize them in high performance print roller applications, with improved strength and solvent resistance characteristics. The properties like pot life, hardness, tensile strength, modulus, tear strength, compression set, density and solvent resistance of these polyurethane elastomers are studied in the absence of additives and in the presence of additives.

Among the polyurethane elastomers prepared, the product obtained from prepolymer C with curative X3 exhibits better strength properties and solvent resistance characteristics than those from other products. High percentage of reactive functional groups present in the prepolymers and curatives enhance the crosslink density, which in turn enhances the mechanical properties and solvent resistance characteristics. Incorporation of additives (plasticizer and filler) improve the performance characteristics of polyurethane elastomers, the enhancement of strength properties and solvent resistance behaviour are observed in all cases of filled polyurethane elastomer irrespective of prepolymers and curatives. However, degree of improvement varies based on the nature of reactants involved.

#### Keywords

polyurethane elastomers, plasticizers, solvent swell, mechanical properties, print rollers

# Studies on EPDM based compositions for underwater acoustic applications

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Polymeric compositions are widely employed in various underwater acoustic applications. The major uses of these composites are for packaging underwater electronic gadgets which cannot function if directly exposed to sea water environments. These composites have to function as acoustic windows, reflectors, absorbers or a combination of these, depending on the frequency of interest. In this paper, the acoustic properties of EPDM rubber formulations are studied for its window application. A series of compositions are made by incorporating different ingredients at various loading levels and evaluated for their acoustic parameters. All compositions are studied for their cure characteristics at various temperatures and time using MDR2000 rheometer. The compounds developed are found to be reversion resistant beyond their cure conditions. Compositions ranging from 150-250 pphr reinforcement loading are found to be transmitting acoustic energy with negligible loss. Circular discs of diameters 50mm and 200mm with 20mm thickness are used for acoustic studies. The insertion loss and echo reduction behaviour are studied in a vertical water filled pulse tube using standard acoustic projector-cum-receiver. Dynamic mechanical properties are also studied at various frequencies and temperatures. Physical and mechanical properties are evaluated as per ASTM standards. Results showed that the material can be a good candidate for acoustic window application. The negligible water absorption and high underwater environmental stability make this material suitable for sub-sea application. Studies showed that insertion loss of the material is 0.2dB in the range of 2 kHz to 15 kHz. The water absorption of the material is 0.002% when immersed in both fresh and saline for 24 hours at room temperature. The weight gain due to water absorption, when submerged in water for more than 40days is negligible.

**Key words:** underwater acoustic applications, EPDM, acoustic window, insertion loss, echo reduction

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### Stress analysis of air borne polymeric composite structure

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Composite structures are extensively used in air borne applications in civilian and military field owing to inherent advantages of high strength to weight ratio, ability to withstand high loads, slow failure rates, tailorability of mechanical and chemical properties and better directional properties. The most common types of composites employed in air borne applications are carbon fiber reinforced epoxy and glass fiber reinforced epoxy. One of the FRP structures developed for airborne application is in the shape of 'C' with various geometrical discontinuities for weight reduction and mounting of sensors and hinges for integrating to main assembly. Presence of such deviations from regular geometries leads to build up of stress concentrations at such irregularities, which could be fatal and lead to catastrophic failures. In order to understand the actual stress distribution, predict and prevent any failure of the structure, proper theoretical analysis is required.



Section of the "C" channel structure showing geometrical discontinuities

A finite element analysis software ANSYS was used to evaluate the stress response of the composite structure. As the structure is intended to operate underwater, analysis was carried out to simulate the effect of hydrostatic pressure loads. Airworthiness requirements also demands that the structure to withstand high inertial acceleration loads coming on the system during various maneuvering. Analysis was also carried out to ensure that the structure is capable of withstanding these inertial acceleration loads. The structure is mounted with sensor elements and the effect of these sensor elements were modelled using lumped masses method. 20-node hexahedral element was used to mesh the structure. As the structure is fabricated with fiber reinforced plastics having orthotropic properties, properties such as elastic modulus, shear modulus and Poisson's ratio were considered for all the three directions for the analysis. The analysis was carried out for 30% glass filled polycarbonate, Glass fiber reinforced epoxy composites and carbon fiber reinforced epoxy composites. The von-Mises stress distribution obtained

showed the maximum stress near the top hinges and the corresponding displacement distribution showed maximum displacements at the top of the structure.

Key words: stress analysis, fiber reinforced epoxy composites, underwater applications

# Effect of post drawing parameters of melt spinning of carbon nanotube filled polypropylene fiber

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Isotactic polypropylene (PP) utilized as a commercial polymeric fiber exhibits a wide range of mechanical properties. However PP fiber needs reinforcement in order to achieve high stiffness and strength for engineering applications. Since the discovery of carbon nanotubes (CNT) by Iijima, CNT have emerged as a potential candidate as reinforcing filler in polymer based composite fibers due to their unique mechanical, electrical and thermal properties. Multiwalled carbon nanotubes (MWNT) were varied (0.5-3 wt %) in melt mixed PP/MWNT composites which were prepared by using twin screw microcompounder. The resulting composites were subsequently melt spun into fiber. The melt spun fibers were drawn at draw ratio of 8 with varying post drawing parameters (temperature and speed of drawing the composite fibers) in order to understand the effect of post drawing parameters on mechanical properties of composite fibers. The effect of post drawing parameters on crystalline chain orientation (Herman's orientation factor for (110) PP plane) and crystal size of (110) PP plane were studied using wide angle X-Ray diffraction. Structure property relationship studies were performed in PP/MWNT composite fibers.

**Key words:** carbon nanotube filled PP fiber, melt spinning, post drawing parameters, mechanical properties, WAXD

# Competitive extraction of Na, K, Ba, Ca, Mg by NR/PEO-1000, NR/PEO-4000 block copolymers

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The ionophoric property of NR/PEO block copolymers is due to the presence of PEO segments in the block copolymer backbone. Amphiphilic compounds such as PEO exhibit complexation ability towards many metal salts of uni and divalent metals comparable to crown ethers. In general more flexible PEO are able to wrap the metal ions in helical fashion and thus can act as carriers/extractants with properties parallel to that of crown ethers. But because of their common selectivity, they are not widely used as such as crown ethers.

A series of NR/PEO block copolymers were prepared from TDI, PEO with molecular weights 1000, 4000 and liquid natural rubber by solution polymerization. Because of the above stated pseudohelical property and common selectivity, complexation studies with different metal salt solutions like NaCl, KCl, BaCl<sub>2</sub>, CaCl<sub>2</sub>, MgSO<sub>4</sub> were undertaken to find the competitive extraction order. The results have been analysed by comparing the overall metal complexation values.

Table1. Ion uptake by the polymer samples

Polymer sample	Uptake of metal ions (mM/g)						
	Na <sup>+</sup>	$\mathbf{K}^+$	Ba <sup>++</sup>	Ca <sup>++</sup>	Mg <sup>++</sup>		
NR/PEO-1000	1.995	3.78	2.80	2.2362	0.88		
NR/PEO-4000	2.1158	4.408	3.196	2.8556	0.4229		

The order of competitive extraction of the two block polymers is same.i.e,

K>Ba>Ca>Na>Mg, which almost coincides with the PEO complexation. The order of PEO complexation in alkali metals is K>Rb>Cs>Na>Li and that of alkaline earth metals is Ba>Sr>Ca>Mg.

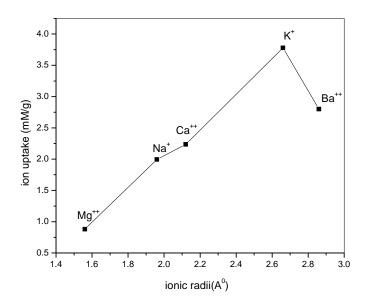


Figure 1. Plot of ion uptake versus ionic radii

From fig (1) it is clear that, as the ionic radii increases, complexation ability also increases; except for barium. The reason for maximum extraction of  $K^+$  is that, its ionic radius is almost similar to the cavity size of 18-crown-6. But in the case of  $Ba^{2+}$ , its ionic radius is slightly greater than the cavity size of 18-crown-6. Therefore, the helical structure has to expand a little which leads to the lower absorption compared to  $K^+$ .

For alkali and alkaline earth metals, co-ordination is from 6-8.i.e, the ligand should have at least 6 donor atoms (5-CH<sub>2</sub>-CH<sub>2</sub>-O-)- units in the molecule to satisfy all the coordination sites. In this case, the PEO segments can accommodate the ions by forming a helical structure of suitable cavity size, depending upon the size of the ion, i.e., either by size comparable to that of 15-crown-5 or 18-crown-6 where the number of

-CH<sub>2</sub>-CH<sub>2</sub>-O- units are 5 and 6.

Hence, here the maximum competitive extraction is for potassium, which shows that PEO chains prefer to take a helical structure similar to that of 18-crown-6.

The situation can be schematically represented as

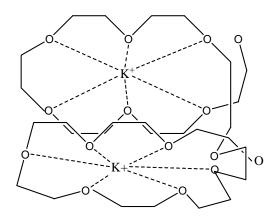


Figure 2. Pseudocavity binding of  $K^+$ 

**Key words:** competitive ion extraction, block copolymers, PEO, coordination sites, helical structure

# A Study of mechanical properties of flax-g-poly(MA) reinforced phenol-

# formaldehyde composites

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In the present paper, we report the preparation of graft copolymers of flax fibers with methyl acrylate (MA) using Fenton's reagent (FAS-H<sub>2</sub>O<sub>2</sub>) as redox system. Synthesized flax-g-poly(MA) was characterized with FTIR, TGA/DTA, scanning electron microscopy (SEM), and X-ray diffraction (XRD) techniques. Composites were prepared using flax-g-poly(MA) as a reinforcement and phenol-formaldehyde (PF) as the binding material. Mechanical properties of phenol-formaldehyde composites were compared and it has been found that composites reinforced with flax-g-poly(MA) showed improvement in mechanical properties. Composites reinforced with flax-g-poly(MA) showed better tensile strength (235 N) and compressive strength (814 N) in comparison to composites reinforced with original flax fiber which showed lower tensile strength (162 N) and compressive strength (372 N). Composites reinforced with flax-g-poly(MA) shows the improved MOR, MOE, and SP.

Key words: flax fiber, MA grafting, PF-flax composites, mechanical properties, XRD, SEM

# Protein functionalized polysaccharide nano particles for novel applications

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There has been growing interest in the use of natural polysaccharides for biomedical applications, drug delivery vehicles, as minimally invasive scaffolds for tissue engineering, because of their non toxicity, biocompatibility, biodegradability, low interfacial tension and high molecular and oxygen permeability. By exploiting these features it may be possible to mimic features of the natural extracellular matrix, and control tissue structure and cellular functions. Consequently, hydrogels have been investigated for cell gene therapy, enzyme and cell encapsulation, drug delivery, joint cushioning and lubrication and as environmental shape memory materials. Protein/peptide oral drug delivery is a complicated process mainly due to poor intrinsic protein permeability as a result of large molecular weight, degradation by proteolytic enzymes in the stomach and in the small intestine, and chemical instability. Protein functionalized micro and nano particles are very versatile and were made to overcome this problem. Low molecular weight chitosan, guar gum, starch were used for the preparation of nano particles using precipitation and ionic crosslinking method and was then linked to the enzyme (subtilisin) protein or BSA by glutaraldehyde coupling. Polysaccharides having a molecular weight of 8 to 36 KDa gave high-quality nano composite spherical particles of 70-612 nm size, with a good poly dispersity index of 0.1- 0.7. Molecular weight greater than 50 KDa gave micro particles and vesicles of more than 1 microns as indicated by dynamic laser light scattering, SEM, and TEM studies. The optimum pH of the polysaccharide nanoparticle immobilized enzyme was shifted to 8.0 from 7.0, whereas there was no change in the optimum temperature. The immobilized enzyme shows better affinity to the substrate (casein) with a lower  $K_{M}$  value of  $4.097 \times 10^{-5}$  than the native subtilisin which is  $3.30 \times 10^{-4}$ . These composite catalytic nano particles are having excellent activity, pH sensitivity and stability which make them suitable for oral drug delivery, tissue scaffolds, microreactors or for cosmetic applications.

**Key words:** polysaccharide nano particles, protein functionalization, precipitation method, ionic crosslinking method, biomedical applications

# Preparation and Characterization of ethylene co-vinyl acetate based drug delivery system for cardiovascular applications

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Major complications of cardiovascular lesions are often accompanied by inflammatory reactions and smooth muscle cell proliferation. Curcumin has been shown to possess antiinflammatory and anti-proliferative properties. As a solution to above cardiovascular problems, sustained drug delivery system releasing curcumin from ethylene-co-vinyl acetate (EVA) matrices is proposed.

Various grades of EVA having 40%, 28%, 18% and 12% vinyl acetate content were evaluated for the selection of a suitable grade. The EVA grades were characterized by fourier transform infrared (FT-IR) spectroscopy, dynamic mechanical analysis (DMA), testing solubility in organic solvents and determining mechanical properties. Curcumin is incorporated into the matrices by dissolving both matrix and curcumin separately in solvents, mixing together and later evaporating the solvent from the system. Curcumin loaded systems were characterized by FT-IR, contact angle measurements, water absorption, mechanical testing and checking the drug release profile from the matrix.

FT-IR data confirms that there was no chemical reaction between EVA and the drug. Increased drug content in the matrices results significant increase in tensile strength and modulus whereas fracture strain records substantial decrease. The results of contact angle indicated that loading curcumin in EVA does not alter surface properties of the matrix significantly. DMA revealed that addition of curcumin does not alter glass transition temperature either. It also shows that when the vinyl acetate content increases the storage modulus decreases. Water absorption studies show an increase in water uptake by matrices with increase in drug loading.

From the results obtained EVA with 40% vinyl acetate content was found to be the most suitable system as a matrix. The selection was based on the low modulus, high elongation, solubility in the organic solvents and film forming properties. Drug elution profiles up to a period 15 days were monitored. From the results it is expected that curcumin loaded EVA-40 system would be suitable for drug release applications in cardiovascular system.

**Key words:** EVA, drug delivery system, cardiovascular applications, curcumin, drug elution profiles