

SESSIONE 4 | MATERIALI COMPOSITI E NANOSTRUTTURATI

OC 4.1

'CLICK' CHEMISTRY AND ATOM TRANSFER RADICAL POLIMERIZATION (ATRP): A VERSATILE TOOL TO PREPARE NANOCOMPOSITES

M. Hoyos, O. Monticelli, S. Russo

The 'Click' Chemistry has been employed in many polymer functionalizations and new materials synthesis, especially in conjunction with controlled radical polymerization methods, such as ATRP. The 'Click' concept, introduced by K. B. Sharpless in 2001, has emerged as a powerful synthetic methodology that can help solving many technological challenges. One of the most important features of the 'Click' concept is the extraordinary selective nature of these reactions. For instance, the Cu(I) catalyzed azide-alkyne cycloaddition (CuAAC) can coexist with other reactive groups without competitive interference. As a result, the preparation of a wide range of functional polymeric materials has been realized in the recent years; however, only a limited number of works has been reported so far on polymer/clay nanocomposites prepared by 'Click' reaction. We report on the use of 'Click' reactions as a novel route for coupling of alkyne-organophilic montmorillonite (MMT) with azide end-group polystyrene (N₃-PS), synthesized by ATRP.

OC 4.2

RADIATION INDUCED CROSSLINKING OF SBR BASED BLENDS CONTAINING A MODIFIED SiO₂ FILLER WITH ENHANCED FREE RADICAL REACTIVITY

A. Buttafava, D. Dondi, C. Palamini, F. Pepori, A. Faucitano, L. Giannini, A. Lostritto, M. Nahmias, L. Conzatti

Ionizing radiations from a ⁶⁰Co source have been employed for inducing radical reactions finally leading to the grafting of unsaturated oligomers and vinyl monomers onto the surface and micropores of precipitated silica. The target was to obtain modified silica with enhanced polar compatibility with respect to polybutadiene and styrene-butadiene copolymers rubber matrices and suited to favour the formation of chemically bound rubber in a vulcanization process. The latter property was expected to follow from the characteristics of free radical reactivity arising from the unsaturations present in the organic coating. The picture obtained from the EPR experiments is that of the grafting reactions being initiated by SiO₂ species leading to crosslinking of the polybutadiene substrate.

OC 4.3

POLYMERIZATION OF NORBORNENE CATALYZED BY GRUBBS FUNCTIONALIZED CARBON NANOTUBES

C. Costabile, P. Longo, F. Grisi, G. Siniscalchi, P. Ciambelli, M. Sarno, C. Leone, D. Sannino

The synthesis of polynorbornene by ring opening metathesis polymerization (ROMP) in the presence of 1st and 2nd generation Grubbs catalyst-functionalized nanotubes, is reported. The activities of the catalyst-functionalized nanotubes in ROMP of 2-norbornene were compared with those of bare 1st and 2nd generation Grubbs catalysts and the obtained materials were characterized by DSC (Differential Scanning Calorimetry), Infrared, TG-DTA-MS (Thermogravimetric analysis coupled with a mass spectrometer) analysis, and Scanning Electron Microscopy (SEM).

OC 4.4

PBT-BASED NANOCOMPOSITES BY *IN SITU* ENTROPICALLY-DRIVEN RING-OPENING POLYMERIZATION OF MACROCYCLIC OLIGOMERS

L. Conzatti, M. Alessi, P. Stagnaro, M. Canetti, P. Hodge

Pristine montmorillonite (MMT) modified with a new synthesized imidazolium salt bearing a functional moiety able to catalyze transesterification reactions was prepared and characterized. This modified MMT was used for obtaining PBT-based nanocomposites through *in situ* entropically-driven ring-opening polymerization (ED-ROP) of the corresponding macrocyclic oligomers (PBT-MCOs) previously intercalated in between the layers of the clay. TGA analysis of the imidazolium-modified clay indicates enhanced decomposition temperatures with respect to those of organoclay modified with ammonium salts. PBT-based nanocomposites with 3 wt% of pristine and imidazolium-modified MMT were prepared. WAXD results indicate the intercalation in between clay layers of PBT-MCOs before and of PBT polymer chains after ED-ROP.

OC 4.5

NANOSTRUCTURED TITANIA FILMS BY SELF-ASSEMBLING BLOCK COPOLYMER TEMPLATES

D. Scalarone, J. Tata, F. Caldera, M. Lazzari, O. Chiantore

Micellar systems prepared by addition of titanium dioxide precursors to PS-*b*-PEO solutions have been used as templates for the preparation of nanostructured titania films. By varying self-assembly influencing parameters different morphologies have been obtained, ranging from mesoporous films to TiO₂ nanodots.

OC 4.6

NANOSTRUCTURED HYBRID NETWORKS BASED ON HIGHLY FLUORINATED ACRYLATES

R. Bongiovanni, M. Sangermano, A. Medici, C. Tonelli, G. Rizza

A dual-curing process is described for obtaining highly fluorinated acrylic networks containing nanosilica. The new materials showed better thermal resistance and improved hardness, while maintaining the hydrophobicity of the fluorinated polymer. They were obtained by UV-curing a suitable mixture of a newly synthesized perfluoropolyetherurethanediacrylate and alkoxy silanes, followed by a thermal treatment during which the sol-gel process took place. The obtained crosslinked networks had a complex morphology: nanometric silica particles were formed, as observed by TEM, and embedded in a biphasic crosslinked matrix made of perfluoropolyether domains and of copolymeric crosslinked domains containing the polyurethane acrylic units and silicic chains formed by the alkoxydes condensation.

OC 4.7

SELECTIVE GOLD DEPOSITION ONTO A NANOSTRUCTURED BLOCK COPOLYMER FILM CRYSTALLIZED BY EPITAXY

C. De Rosa, F. Auriemma, G. Talarico, R. Di Girolamo, R. Aprea

Selective deposition of gold nanoparticles onto rubbery nanodomains of semicrystalline diblock copolymer films, achieved through self-assembly coupled with epitaxial crystallization of one block (for the preparation of the block copolymer nanostructure) and successive metal evaporation, provides a simple method for the obtainment of block-copolymer based hybrid nanocomposites ordered over large area.

OC4.8

EVIDENCE OF POLYOLEFINS/CLAY MOLECULAR INTERACTION AT THE INTERFACE OF NANOCOMPOSITES

E. Passaglia, E. Taburoni, M. Bertoldo, L. Conzatti, S. Coiai, N. Muksing, F. Ciardelli

Polyolefin nanocomposites by varying the nature and structure of the polymer matrix (from EPM to PP), the type of polymer compatibilizer (grafted functionality and molecular weight) and the amount of layered silicate were prepared and characterized by XRD, TEM, DSC, TGA and dielectric measurements. The selective extraction of these materials was carried out to remove the nonbonded polymer and to isolate the composite with the sole polymer strongly interacting with the inorganic surface that was accurately characterized with respect, in particular, to morphology development and thermal characteristics. All the collected results were discussed by considering the role of interface between functionalized polyolefin chains and silicate layers and also in relation to resulting organoclay dispersion state and stability.

OC 4.9

COUPLING AGENT SILICE – SILANO PER UNA MESCOLA A BASE SILICE A RIDOTTO IMPATTO AMBIENTALE

P. Riccio, S. Dello Iacono, A. Citterio, D. Cozzi, M. Galimberti

This work investigates elastomeric composites with silica as the reinforcing filler, suitable for a large scale application such as the one in tyre. In particular, three silica-elastomer coupling agents were studied, with the aim to promote a lower energy dissipation of the composite material as well as a minor ethanol emission from the silica-silane condensation reaction. A *vis a vis* comparison in sulphur cured compounds demonstrated that a mercaptosilane (MS) brings about an improvement in the compatibilization of the polar filler with the elastomer, as shown by better reinforcement parameters, a lower hysteresis and a higher abrasion resistance. The lower amount of MS required to promote the compatibilization allows to reduce the ethanol emission.

OC 4.10

GRAFTING OF POLYBUTADIENES CONTAINING TRIALKOXSILANE GROUPS ON SILICA SURFACE

G. Colucci, A. Di Gianni, A. Priola, F. Torello, S. Bracco, P. Sozzani

The present work describes a method to modify the surface of silica, reducing its polar character and making it compatible and dispersible into hydrocarbon based elastomers. Low molar mass polybutadienes (PB) were added of mercaptopropyltrimethoxysilane (MPTS) in the presence of a radical initiator [1]. MPTS was added quantitatively in the range of 1 to 3 moles per polymer chain. The silanised PBs were reacted with silica via thermal condensation with its silanol groups: typically a 2:1 w/w ratio between silica and silanised PB was used [2]. The condensation reaction of a trifunctional silane allows to obtain the condensation of one or two alkoxy groups. The condensation of all three alkoxy groups on the silica does not occur, probably for steric reasons.

OC 4.11

NOVEL CELLULAR MATERIALS SHOWING AUXETIC BEHAVIOR: RTM PROCESSING AND PROPERTIES

G. Cicala, G. Recca, F. Scarpa, A. Lorato

The present work is focused on a novel technology for the production of composite cellular materials showing auxetic behavior. Auxetic means that the material gets fatter when stretched rather than become thinner. This means that the auxetic materials present a negative Poisson Ratio. The processing technology and the mechanical properties of the developed materials will be presented.

OC 4.12

STUDIO DELL'EVOLUZIONE DELLA REAZIONE DI RETICOLAZIONE DI UNA RESINA TERMOINDURENTE MEDIANTE ANALISI TERMOGRAFICA

P. Cianciafara, N. Campo, R. Montanini, A.M. Visco

In this work we successfully applied a non destructive technique (the Infrared Thermography) for the study of an exothermic cure reaction development. The investigated materials were based on polyester resin reinforced with a fibre glass (MAT300). They were cured without any energetic source or by a microwave source (doses of 0.8 s/g and 1.3 s/g). The Infrared Thermography technique highlighted the thermal distribution during the exothermic cure reaction development of all the studied samples. This indicated which samples contains different crosslink degrees, visualizing the not homogeneous areas.

OC 4.13

MECHANICAL CHARACTERIZATION OF E-GLASS SINGLE FIBRES AFTER HIGH TEMPERATURE EXPOSURE

E. Boiocchi, R. Frassine, S. Feih

Composite materials fire resistance is of paramount importance for many structural applications. Tensile properties in the fibre direction are influenced by the fibre strength and a better understanding of single fibre properties after high temperature exposure is required. In this work the strength loss of E-glass single fibres after high temperature exposure is evaluated by performing tensile tests on single fibres. A significant variation in fibre strength is observed and a Weibull statistical distribution analysis is applied in order to calculate the characteristic values. It was concluded that the high temperature exposure increases the size of the flaw that are present in the fibres.

OC 4.14

COMPOSITES MADE OF LLDPE AND EICHHORNIA CRASSIPES WOOD (WATER HYACINTH): PREPARATION AND PROPERTIES

M.P. Luda, L.M. Sani

Dispersed polyethylene bags and water hyacinth proliferation both have severe environmental impact in African country, in particular in those in the Sahel area. For this reason locally sustainable technologies of recycling and reusing of such items are of relevant interest for these countries. In this paper we explore the possibility of preparing composites made by polyethylene plastic bags, mostly LLDPE, and water hyacinth fibers. Composites containing up to 50% w/w of fibers have been prepared and the introduction of fibers increases some of the mechanical properties of LLDPE. The fibers interferes with PE crystallization leading to a different dependence of modulus on temperature. Processing conditions influence the final properties of the composites. These composites are resistant to termites attack, and therefore are potentially applicable for use in Niger as substitute for traditional wood items such as under roof panel and small furniture etc.

OC 4.15

STRUCTURAL AND ELECTRICAL ANISOTROPY OF SOLUTION-CAST POLY(3-HEXYLTHIOPHENE) FILMS

M. Cardinali, L. Valentini, J.M. Kenny

We found that the utilization of the dip-coating technique for the deposition of regioregular poly(3-hexylthiophene) films can facilitate their self-assembly into nanofibrillar lamellar structure after the evaporation of the solvent. The condition for the formation of the nanofibrillar structures leads to an improved electrical conductivity by using only this approach without further thermal treatment.

OC 4.16

CONTROLLO DELLA STRUTTURA DI UN "ORGANOCLAY" ALL'INTERNO DI POLIMERI IDROCARBURICI

V. Cipolletti, S. Giudice, M. Galimberti, G. Guerra

Two different kinds of organoclays of montmorillonite with a double-chain ammonium salt were obtained in the presence of many different thermoplastic or elastomeric polymers. Independently of the chemical nature of the polymer, all the obtained organoclays present a basal spacing of 4.0 nm or of 6.0 nm (possibly corresponding to paraffin-type perpendicular mono-layer and bi-layer intercalates), when the mixing occurs in the absence and in the presence of a small amount of stearic acid, respectively. This gives an easy way to control the structure (and properties) of the organoclay in polymer composites.

OC 4.17

A NEW APPROACH FOR OBTAINING INTERCALATED/EXFOLIATED RUBBER/ORGANO-MONTMORILLONITE NANOCOMPOSITES

L. Conzatti, M. Alessi, P. Stagnaro, A. Di Gianni, G. Colucci, A. Priola, L. Giannini

A new and efficient approach for the preparation of rubber-based nanocomposites with polymer chains effectively intercalated in between the clay layers is described. A commercial organophilic montmorillonite containing a hydroxylated ammonium ion is reacted with liquid maleinized polybutadienes, leading to a strongly increased organophilicity of the clay. SAXS analysis evidences a remarkable change of the clay interlayer distance, suggesting the attainment of an almost exfoliated structure. The interlayer distance thus obtained is maintained when the modified clay is dispersed into a rubber matrix (BR and SBR). TEM analyses are in good agreement with the SAXS results indicating an overall good dispersion of the modified clay into the rubber matrices with isolated lamellae and intercalated stacks of a few layers.

OC 4.18

EFFECTS OF ORGANO-LAYERED DOUBLE HYDROXIDE STRUCTURE ON MORPHOLOGY AND THERMAL PROPERTIES OF LDPE BASED NANOCOMPOSITES

S. Coiai, E. Passaglia, N. Muksing, L. Conzatti, M. Sisani, U. Costantino

In this work, the ability of organo-layered hydroxides (organo-LDHs), modified with different kinds of surfactants, to undergo intercalation/exfoliation in LDPE was investigated. It was found that the local ordering and the rearrangement between the layers of the surfactant strongly influences the dispersion degree of organo-LDHs in the LDPE matrix, with and without the addition of a compatibilizer. In particular, the intercalation of polymer chains seems to be hindered when surfactant molecules form a bilayer structure, whereas mono layered organo-LDHs were successfully dispersed. Data collected about morphological and thermal properties of nanocomposites will be discussed to provide new insights about the dispersion of organo-LDHs in LDPE.

OC 4.19

CRYSTALLIZATION BEHAVIOUR OF NANOCOMPOSITES BASED ON CLAY AND LDPE

G. Spagnoli, G. Ramorino, M. Penco, E. Passaglia, S. Coiai, F. Ciardelli

In this work, the morphology, thermal properties, and crystallization kinetic of nanocomposites of blends based on LDPE and organically modified montmorillonite have been studied. In particular, LDPE binary blends containing as second component a grafted maleic anhydride-LDPE copolymer (LDPE-g-MA was used as matrices). This copolymer was prepared by reactive melt mixing of the anhydride and LDPE in presence of a free radical generator. The morphological analysis, performed by X-ray diffraction and TEM, showed materials with completely exfoliated structure. The blends compatibility was studied using DMTA and DSC analysis. The crystallization kinetic for prepared sample, was studied using non-isothermal Avrami method.

OC 4.20

ORDERED NANOCOMPOSITES FROM PTFE/PMMA CORE-SHELL NANOPARTICLES

K. Sparnacci, D. Antonioli, S. Deregibus, M. Laus, T. Poggio, V. Kapeliouchko, G. Palamone, G. Zuccheri, R. Passeri

OC 4.21

PMMA/SILICA NANOCOMPOSITES: PREPARATION, SOLID STATE NMR AND STRUCTURE/PROPERTIES RELATIONSHIP

M. Avella, R. Avolio, D. Capitani, M.E. Errico, G. Gentile

PMMA based nanocomposites filled with properly functionalized silica nanoparticles have been prepared by in situ polymerization. In particular, silica nanoparticles have been modified by grafting a coupling agent, methacryloylpropyl trimethoxysilane (MPTMS), characterized by unsaturated end-capped groups. Solid state NMR has permitted to analyse the interphase and to highlight interactions occurred between growing PMMA macroradicals and functional groups of the silica coupling agent during the preparation. These interactions have promoted a strong nanoparticle/PMMA interfacial adhesion responsible for a homogeneous dispersion of the filler as well as the property enhancement of nanocomposites.

OC 4.22

CARATTERIZZAZIONE AFM DI RIVESTIMENTI IBRIDI E NANOCOMPOSITI A MATRICE EPOSSIDICA

L. Torlaj, F. Piccinini, S. Turri, M. Levi

Epoxy two component nanocomposite coatings were prepared through both "top-down" (mechanical dispersion of nano-oxides or clays) and "bottom-up" procedures (sol-gel syntheses). The nanocomposites were characterized in terms of nanoscratch behaviour through AFM techniques. The products can be proposed as thick coatings or finishings for civil and industrial floorings.

OC 4.23

RECYCLED MULTILAYER CARTONS AS CELLULOSE SOURCE IN HDPE BASED COMPOSITES: IMPROVEMENT OF INTERFACIAL ADHESION AND PHYSICAL PROPERTIES

M. Avella, R. Avolio, I. Bonadies, C. Carfagna, M. E. Errico, G. Gentile

In this communication, a mechanical recycling of multilayer carton scraps (MC), consisting in the use of MC without the physical separation of its different fractions (cellulose fibers and LDPE, 80/20 wt/wt) is proposed. In particular, MC was considered as a source of cellulose fibers to realize HDPE based composites. Composites containing up to 60 wt% of milled MC were prepared by reactive blending consisting into the addition of different amount (5 and 10 wt%) of a linear low density polyethylene grafted with maleic anhydride (coupling agent, MAPE) during HDPE/MC processing. Then, structure/properties relationships were deeply investigated as a function of MC and coupling agent content. The coupling agent was able to induce a complete polymeric covering of cellulose fraction as well as a strong HDPE/cellulose interfacial adhesion and significant improvements of material final properties.

OC 4.24

BLOCK-COPOLYMERS BASED HYBRID NANOCOMPOSITES FORMING NANOSTRUCTURES FOR APPLICATIONS IN MICROELECTRONICS

C. De Rosa, R. Di Girolamo, F. Auriemma, R. Avallone, T. Napolitano, G. P. Pepe

The possibility of realizing integrated memory devices and circuits in low-cost plastic electronics applications with a simple and easy processing is demonstrated. Our approach consists in obtaining highly ordered and well oriented nanostructured thin films of block-copolymers (BCP), acting as structure guiding hosts of surface coated gold nanoparticles (AuNp) with memory functions.

OC 4.25

LAVORAZIONE E CARATTERIZZAZIONI DI FILM TWIST NANOCOMPOSITI

R. Marino, N. Tz. Dintcheva, F.P. La Mantia

In this work mechanical behavior of nano composite films based on polyethylene was studied; the films were prepared by film blowing process and they were cold drawn to make them suitable for twist-wrapping. Experimental results have shown that cold drawing enhances significantly the orientation; it was found that when increasing the draw ratio, elastic modulus and tensile strength of polyethylene films increase, particularly in presence of organo-clay. The elongation at break and the yield-deformation sharply decrease with orientation, mainly in films subjected to a draw ratio equal to 6. According to mechanical behavior, the maintenance angle increases with increasing draw ratio and particularly by adding nano-clay, probably owing to the applied draw ratio that reduces nanoparticle size and, as a consequence, hinders the applied torsional elastic recovery.

OC 4.26

DAL CONTROLLO DELLE NANOSTRUTTURE ALLE PROPRIETA' DI NANOCOMPOSITI ELASTOMERICI

S. Giudice, P. Riccio, A. Lostritto, L. Giannini, M. Galimberti, V. Cipolletti

This work discusses the correlation between nanostructures and properties for nanocomposite materials based on hydrocarbon polymers and cationic clays modified in situ with ammonium cations. The hydrocarbon polymer is thus shown first as the reaction medium for the clay modification reaction and then as the matrix of the composite material. Nanostructures were investigated through X-ray diffraction and their

thermodynamic transitions were studied with calorimetric analysis. In the case of rubber-clay nanocomposites: rheological and vulcanization behaviour, physical-mechanical properties, with particular attention to their evolution in a wide temperature range are discussed. Clays are shown to deeply affect the material properties, bringing to better rheology and higher reinforcement with respect to traditional fillers.

OC 4.27

T-PEEL TEARING RESISTANCE OF NATURAL RUBBER / ORGANOCLAY NANOCOMPOSITES

G. Ramorino, S. Agnelli, R. De Santis, C. Andreana, T. Riccò

OC 4.28

RHEOLOGICAL BEHAVIOUR OF LINEAR LOW DENSITY POLYETHYLENE (LLDPE)-SILICA MICRO AND NANOCOMPOSITES

A. Dorigato, A. Pegoretti, A. Penati

LLDPE-silica composites were prepared by melt compounding, using various types of SiO₂ micro and nanoparticles, in order to study their rheological behaviour. Dynamic shear moduli and shear viscosity were strongly increased by the introduction of high surface area fillers, while glass microbeads only marginally affected rheological properties of the material. A new model was successfully proposed to fit viscosity data.

OC 4.29

STUDIES ON DYNAMIC MECHANICAL AND RHEOLOGICAL PROPERTIES OF NANOCOMPOSITES OF RECYCLED PBT FROM AUTOMOTIVE PARTS

F. Zanata, N. B. Quispe, D. H. Souza, J.R. Bartoli, E.N. Ito

In this work, recycled PBT nanocomposites were prepared by melt intercalation at two extrusion rates, 150 and 90 rpm, and reinforced with two different organoclays, Cloisite 20A and 25A (less organophylic). The relative influence of each factor could be seen from rheological and dynamic-mechanical properties and are related to nanocomposite intercalation or exfoliation. Nanocomposites presented improved storage modulus and stiffness compared to recycled and virgin net PBT. Incorporation of nanoclays by melt intercalation tends to reduce the melt viscosity of the nanocomposites at the usual range of polymer processing shear rates.

OC 4.30

EFFECT OF NANOFILLER ON THE THERMAL STABILITY AND ON THE SPINNABILITY OF POLYPROPYLENE

L. Fambri, D. Lorenzi, G. Sartori, G. Ferrara

Two different nanofillers, an organic modified cationic clay (Cloisite 15A) and synthetic hydrotalcite (Perkalite F100), were added to polypropylene at 0.3% by wt. in order to study the effect on the thermoxidation stability and to evaluate the spinnability. Thermogravimetric analysis in air was performed at various heating rates (from 0.5 to 30 °C/min), and the following kinetics study confirmed the beneficial effect of nanofillers. Moreover, various monofilaments were spun with diameter ranging between 50 and 200 micron, by using a lab-scale extruder at various collecting rates. All fibers of polypropylene with or without nanofiller at various draw ratios exhibited the typical stress-strain curve, and an interpretation model of mechanical testing is also presented. A maximum strength of 1.0±0.1 GPa was estimated for all the tested materials.

OC 4.31

IONIC POLYMER POLYMER COMPOSITES (IP²C)_s WITH AN IONIC LIQUID AS STABLE SOLVENT

G. Di Pasquale, S. Graziani, M. La Rosa, A. Pollicino, E. Umana

Electroactive polymers can be utilized for modern intelligent integrated electronic and optoelectronic devices and are playing an increasing role in science and technology. Ionic Polymer Polymer Composites (IP²C) with sensing and acting capabilities have been manufactured and tested. These all organic electroactive composites have been prepared by covering Nafion®117 membranes with the conducting polymer PEDOT:PSS as electrode element and using an ionic liquid as solvent (1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EmI-Tf)) instead of water. These devices have been electrically analyzed. The results show that it is feasible to adopt the selected solvent to produce all-organic devices based on Nafion® 117 with considerable electromechanical transduction capacities.

OC 4.32

PREPARAZIONE E CARATTERIZZAZIONE DI NANOCOMPOSITI POLIMERO/CNT_s SOTTOPOSTI A STIRO ELONGAZIONALE

N. Tz. Dintcheva, R. Arrigo, M. Morreale, M.C. Mistretta, F.P. La Mantia

La preparazione di nanocompositi Polimero/CNTs a base di PA, PS ed EVA è stata effettuata utilizzando un estrusore bivate e i compositi così formulati sono stati sottoposti successivamente ad uno stiro elongazionale. Principalmente sono state monitorate le proprietà meccaniche dei filamenti in funzione del rapporto di stiro, il comportamento reologico e la morfologia dei sistemi a diversi contenuti di CNTs.

OC 4.33

RELAZIONI PROPRIETÀ-MORFOLOGIA-PARAMETRI DI PROCESSO IN MATERIALI NANOCOMPOSITI A MATRICE POLIMERICA

R. Scaffaro, M. Ceraulo, F.P. La Mantia

Recently, there has been a growing interest for a new class of polymer-based materials called nanocomposites. In these materials, low amounts of a filler are dispersed at a nanometric scale and they may present unique properties without significant changes in processability and transparency. Aim of this work is to study the relationships between the morphology and the rheological properties of polymer based nanocomposites, prepared in the melt, considering the silicate nanofillers as a deformable component in the blend. For this purpose, was investigated the validity of Wu's equation to find a relationship between processing conditions and the final morphology of the nanocomposite. The results indicate that the clay shear deformability changes on changing the polarity of medium where it is dispersed.

Poster

P 4.1

THERMO-MECHANICAL CHARACTERIZATION OF EPOXY NANOCOMPOSITES WITH DIFFERENT INORGANIC FILLERS

E. Amendola, A.M. Scamardella, D. Acierno

Herein we describe the synthesis and properties of a new class of polymers based on thiazole units. Thiazole systems are obtained for condensation of acetophenone with urea in presence of bromine as mild oxidant. The subsequent copolymerization with N,N-diethanolamine brought to the chromophoric system. The recorded large solvatochromic effect is indicative of great nonlinear response of molecular systems. Polymers were obtained for condensation with 2,4-tolylendiisocyanate. Polymers show high glass transition and decomposition temperature, respectively 220°C and higher than 300°C

P 4.2

STUDIO PRELIMINARE SULL'OTTENIMENTO DI GRAFENE ATTRAVERSO ESFOZIAZIONE DELLA GRAFITE CON LIQUIDI IONICI E SUO UTILIZZO PER LA PREPARAZIONE DI NANOCOMPOSITI POLIMERICI

A. Mariani, V. Alzari, D. Nuvoli, S. Scognamillo

In this preliminary work we demonstrated the feasibility of graphene obtainment by graphite exfoliation with ionic liquids and its use in polymer nanocomposites. TEM analysis showed the presence of single layer graphene. An increase of glass transition temperature for polymers containing graphene was also found.

P 4.3

POLY(ETHYLENE-CO-NORBORNENE)/MWNTS BY IN SITU COPOLYMERIZATION WITH SCANDIUM HALF-SANDWICH CATALYST

L. Boggioni, A. Ravasio, I. Tritto, C. D'Arrigo, A. Perico, and J. Okuda

The in situ synthesis of P(E-co-N)/MWNT composites by rare-earth half-sandwich scandium precursor $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\eta^1\text{-CH}_2\text{SiMe}_3)_2(\text{THF})]$ activated by $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ is reported. A very active catalytic system for E-co-N copolymerization was combined with a brief sonication of MWNTs in toluene for disaggregating the native nanotube bundles. This strategy allows for obtaining P(E-co-N)/MWNT composites with high yields and with minimum aluminium residue. The P(E-co-N)/MWNT masterbatches were melt blended with commercial TOPAS to produce cyclic olefin copolymer nanocomposites with excellent dispersion of the MWNTs in the matrix.

P 4.4

MECHANISM OF FORMATION OF CHAR COATING IN LDPE/ORGANOCLAY NANOCOMPOSITES

L. Botta, R. Scaffaro, F. P. La Mantia

In this work a complete characterization of the char-like coating formed during annealing treatment of polyethylene-clay nanocomposite was performed. Moreover, it was monitored the concentration of the silicate from the surface to the bulk of the sample in order to understand the mechanism of formation of this char coating. It was shown, by ATR- FTIR analysis, TEM microscopy and TGA measurements that a great number of tactoids or silicate layers accumulated on the surface of the sample during the annealing treatment. Moreover the concentration of silicate quickly decreases along the thickness of the sample and at 120 μm in-depth the morphology of the material is very similar to that of the untreated sample.

P 4.5

MESCOLE SBR/SILICE PER L'INDUSTRIA DEGLI PNEUMATICI: UN NUOVO MODIFICANTE DELLA SILICE

A. Bertora, M. Castellano, L. Marini, E. Marsano, A. Turturro

P 4.6

ANALISI DEL PROCESSO DI RETICOLAZIONE A MICROONDE DI LAMINATI IN VETRORESINA

P. Cianciafara, A.M. Visco, N. Campo

In this work we studied the cure reaction development and so, the related mechanical and physical properties, of polyester resin reinforced with fibreglass composites. The composites were cured without any energetic source or by a microwave source, at different exposures doses. The cure reaction development, with or without the microwave source employment, was monitored by measuring its exothermal heat. Experimental flexural tests results highlighted the threshold value of exposition dose in order to stiffen the material without induces defects. Non destructive vibrational tests were also applied to the materials in order to check their damping properties and their stiffness. These tests matched the results obtained with the flexural one.

P 4.7

SYNTHESIS AND CHARACTERIZATION OF TiO₂/PMMA BULK NANOCOMPOSITES

L. De Trizio, A. Colombo, R. Simonutti

In-situ radical bulk polymerization was performed in order to achieve optically transparent composites of polymethyl methacrylate (PMMA) and TiO₂ nanoparticles. The inorganic particles were surface functionalized by 3-(trimethoxysilyl)propyl methacrylate (MPS) and trimethoxy(octyl)silane (MOS) to make them dispersible in the monomer. After ultrasonication the stable colloidal dispersions obtained were polymerized at low temperatures, using benzoyl peroxide as the initiator, to avoid formation of bubbles. The optical, mechanical and chemical properties of the nanocomposites were characterized focusing on the effect of inorganic particles on the radical polymerization. In the case of MPS modified particles we obtained insoluble crosslinked objects. Using MOS as a coupling agent, a controlled polymerization was observed with a decrease in the polydispersity index by increasing the amount of TiO₂.

P 4.8

SYNTHESIS AND CHARACTERISATION OF PET MODIFIED WITH MINERAL NANOPARTICLES

D. Di Franco, T. Lugato, G. Di Silvestro, M.A. Ortenzi, H. Farina, C.M. Yuan

PET samples containing different kinds of Cloisites were synthesized in situ and thermal, molecular and rheological data were obtained. Cloisites had both organic quaternary ammonium salts (Cloisite 10A and Cloisite 15A) and sodium ions (Cloisite Na+) in order to verify if the exfoliation process of the lamellae was superior with Cloisite 10A and Cloisite 15A (having an ammonium salt more compatible with the polymeric matrix) than with Na+. Data indicate that the presence of the organically modified cloisites catalyzes the formation of diethyleneglycol (DEG) in the polymeric chains, a side-reaction product leading to lower T_m but that, on the other side, a good molecular weight can be achieved together with a very low melt viscosity.

P 4.9

MELT COMPOUNDING DI NANOCOMPOSITI POLIMERICI: EFFETTO DEL PROCESSO E DELLA TIPOLOGIA DI CARICA

E. Garofalo, L. Di Maio, S. Montesano, L. Incarnato

This study focuses on the possibility to improve performances of polyamide nanocomposites through conveniently tuning materials and processing conditions in melt compounding. The polymer-silicate nanocomposites were prepared by means of a twin screw extruder using a commercial polyamide 6-based copolymer, as thermoplastic matrix, and two different organoclay as filler. Hybrids were submitted to rheological, structural and thermal analysis in order to point out the effects of both extrusion rates and polymer-clay affinity on morphology and properties of the nanocomposite systems.

P 4.10

THE ROLE OF ORGANOCCLAY IN THE MORPHOLOGY MODIFICATION AND IN THE PROPERTIES OF POLYETHYLENE/POLYAMIDE BLEND SYSTEMS

N.Tz. Dintcheva, G. Filippone, F. P. La Mantia, D. Acierno

The opportune choice of the blend constituents and the control of microstructure can lead to multiphase systems with enhanced performances. The objective of the present study is focused on the analysis of technologically relevant properties, such as rheological and mechanical properties, of a nanocomposite polymer blends: LDPE/PA11, LDPE/PA6 and HDPE/PA6 (all blends PE/PA=75/25 parts) filled with small amounts (5 parts) of an organomodified montmorillonite.

P 4.11

CARATTERIZZAZIONE DI COMPOSITI A MATRICE EPOSSIDICA RINFORZATI CON FIBRE DI VETRO E DI OPUNTIA-FICUS INDICA

V. Fiore, G. Di Bella, A. Valenza

Nowadays, increasing awareness of replacing synthetic fiber such as glass fiber with natural one has emerged due to environmental problems and pollutions. Aim of this work is to replace one or more layers of glass mat in GFRP laminates with natural fiber obtained from natural dehydration of cladodes of *Opuntia ficus-indica*, a plant widespread in dry regions of the world like Sicily, and evaluate the influence of this replacing on the mechanical performances of hybrid structures. Flexural and tensile tests are carried out in order to evaluate the specific properties of the hybrid composite.

P 4.12

PREPARAZIONE E CARATTERIZZAZIONE DI NANOCOMPOSITI A BASE DI FERRITI DI MANGANESE PER IL RILASCIO MIRATO DI FARMACI ANTITUMORALI

L. D'Ilario, L. Francolini, A. Martinelli, V. Rinaldelli, M. Bellusci, A. Piozzi

A novel drug targeting release system was developed by the preparation of albumin coated-magnetic nanoparticles based on mixed manganese-iron oxides. This system was employed to study the adsorption and the release kinetics of methotrexate, an antitumor drug.

The characterization of the nanocomposites evidenced that the albumin coating did not affect nanoparticle magnetic properties, in terms of superparamagnetic behavior, and allowed the adsorption of high drug amounts. Moreover, the nanocomposites showed a faster drug release with respect to the uncoated nanoparticles.

P 4.13

PREPARATION OF UV-CURED NANOCOMPOSITE EPOXY COATINGS FOR THE PROTECTION OF METAL SUBSTRATES AGAINST CORROSION

G. Malucelli, A. Di Gianni, F. Deflorian, M. Fedel, R. Bongiovanni

In this work we prepared UV-cured coatings, based on a cycloaliphatic di-epoxy monomer, in the presence of montmorillonites, either commercially available, or modified on purpose (Cloisite Na⁺, Cloisite 30B), dispersed at two different concentrations (5 and 10% w/w). The addition of the nanofillers improved the thermo-oxidative stability of the nanocomposites, due to the formation of either intercalated or exfoliated nanoclays morphologies. The corrosion resistance of the cured films coated on a metal substrate was investigated with electrochemical techniques and compared to the behavior of the neat UV-cured epoxy resin films. In particular, the measurement of the barrier properties revealed that the different stability of the coatings depends on the type of nanoclay used and its intercalated or exfoliated morphology.

P 4.14

POLYETHYLENE/CLAY NANOCOMPOSITE: MORPHOLOGY AND MECHANICAL PROPERTIES MODIFICATION UNDER CONVERGENT FLOW

R. Marino, N. T. Dintcheva, F.P. La Mantia

The elongational flow, typical flow involved in spinning and film-blowing processing operations, significantly increases with the reduction of the capillary diameter. The morphology of a polyethylene/clay nanocomposite sample, subjected to convergent flow whose intensity varies by using capillary with different diameter and length-to-diameter ratio was studied. The applied convergent flow, at the entrance of the capillary, is able to change the clay morphology and consequently the final material properties on polyethylene/clay system with limited affinity between the matrix and organo-modified clay particles.

P 4.15

ELECTROSPUN POLYAMIDE 6 NANO-FIBERS CONTAINING SILVER NANO PARTICLES

E. Marsano, E. Giunco, L. Francis

Electrospun nano-fibers are typically collected in the form of non-woven mats, which are of interest for a variety of applications including semi-permeable membranes, filters, composite reinforcement, and scaffolding used in tissue engineering. The electrospinning process has received a great deal of attention in the last decade because of its ability to consistently generate polymer nano-fibers that range from 5 to 1000 nm in diameter. Recently, the incorporation of Ag nano particles into ultrafine nano-fibers has attracted a great deal of attention, because the presence of metallic nano particles could enormously increase their properties. In this communication the preparation of novel nano polymeric nano-fibers using Polyamide 6 (PA6) containing silver nano particles capped with Poly Vinyl Pyrrolidone (PVP) will be reported.

P 4.16

NANOCOMPOSITES OF SULFONATED TELECHELIC POLYCARBONATE WITH ORGANICALLY MODIFIED CLAYS

M. Colonna, D. J. Brunelle, C. Berti, M. Fiorini, E. Binassi

P 4.17

PHASE INTERACTIONS IN ORGANIC-INORGANIC HYBRIDS CONTAINING TITANIA AND AN ALIPHATIC POLYESTER OR POLYCARBONATE

E. Cortecchia, L. Mazzocchetti, M. Scandola

New organic-inorganic hybrids were synthesised by sol-gel process. The inorganic phase was composed of titania while the organic matrix is made of either aliphatic polyester or polycarbonate. Attention was paid to investigation of interactions between organic and inorganic domains. It was found that transesterification reactions occur during the synthesis. Although transesterification proceeds with different mechanisms in polyester- and in polycarbonate-containing hybrids, in both cases it provides strong interactions between phases, as assessed by FT-IR and XPS analyses. The obtained hybrids are transparent to visible light and, when applied as thin layer coatings, they provide substrates with radiopacity and barrier effect to ultraviolet radiation.

P 4.18

HYBRID EPOXY COATINGS CONTAINING ALUMINA: CHARACTERISATION AND OXYGEN PERMEABILITY

A. Medici, M. Sangermano, P. Palmero, A. Priola

A new class of hybrid coatings were prepared by mixing two selected powders of alumina with a commercial UV-curable epoxy resin. The obtained coatings were characterized with respect to the oxygen permeability. The results showed a fast formation of the networks which have been coated upon a commercial PET thin film. The presence of the filler induces an increase of the surface hardness of the epoxy matrix, while the bulk properties do not have been sensitively changed. It has been clearly demonstrated a correlation between the permeability measurements and the morphology investigations obtained by SEM analysis. The barrier effect of the fillers is appreciable preventing the coalescence of the powder in the matrix after curing. The 5% w/w of filler dispersed in the epoxy resin reduced of the 60% the oxygen permeability of the matrix.

P 4.19

SYNTHESIS AND CHARACTERIZATION OF UV-CURED ACRYLIC NANOCOMPOSITES BASED ON MODIFIED MONTMORILLONITES

R. Peila, G. Malucelli, A. Priola

UV-cured nanocomposites were prepared through the photopolymerization of an acrylic resin added of organophilic montmorillonites, further modified with organic compatibilizers. Such modification determined an increase of the interlayer distance, as revealed by XRD analysis. The different types of the modified nanoclays were then dispersed in the acrylic monomer at 5% wt. and UV-cured. XRD measurements showed a slight increase of the interlayer distance indicating the formation of intercalated structures. The photopolymerization reaction was monitored through real-time FT-IR. The nanocomposites were investigated by DSC and TGA analyses. TGA analysis evidenced an increase of the thermal stability in air of the nanocomposites with respect to the neat UV-cured acrylic resin.

P 4.20

NANOCOMPOSITE BASED ON BLOCK COPOLYMER MATRIX AND DIMENSIONALLY DIFFERENT NANOPARTICLES

L. Peponi, A. Tercjak, R. Verdejo, M. A. Lopez-Manchado, L. Valentini, I. Mondragon, J. M. Kenny

In this work we present a morphological change in the block copolymer matrix when dimensionally different nanoparticles have been added to the block copolymer matrix. In particular, silver nanoparticles, O-D, carbon nanotubes, 1-D and graphene nanosheets, 2-D have been selective incorporated in the PS domains of the poly(styrene-*b*-isoprene-styrene) block copolymer matrix.

P 4.21

SYNTHESIS OF SPIN LABELED SILICA AND ORGANOCILY: EPR MOLECULAR DYNAMIC STUDY AT POLYMER/FILLER INTERFACES

F. Pepori, D. Dondi, A. Buttafava, A. Faucitano, G. Ricci, G. Leone, L. Conzatti

The rubber-filler interactions in SBR/SiO₂ and organically modified clays were investigated by EPR analysis of the motional states. Different synthetic techniques were used for the two systems: spin labels of different length were bound to the silica surface and spin labels bearing nitroxyl radicals were intercalated within the clays lamellae. Exfoliation processes for the latter were followed by EPR coupled with TEM analysis. The results have been interpreted in terms of polymer-filler interactions and the kinetics of the intercalation and exfoliation processes.

P 4.22

STEREO AND CHEMOSELECTIVE POLYMERIZATION OF 1,3-BUTADIENE PROMOTED BY (AMIDOMETHYL)PYRIDINE TITANIUM(IV) AND ZIRCONIUM(IV) COMPLEXES

L. Annunziata, S. Pragliola, D. Pappalardo, C. Pellicchia

A new family of (amidomethyl)pyridine ligands and of the corresponding titanium (IV) and zirconium (IV) were synthesized and characterized. All the complexes were tested in the 1,3-butadiene polymerization. While zirconium complexes produced highly cis 1,4-polybutadiene, titanium complexes resulted less stereospecific producing prevailing cis 1,4-polybutadiene with randomly distributed trans 1,4-units (4-6%) and 1,2 units (10-12%). In particular, Titanium complexes showed a behaviour similar to CpTiCl₃, for which a Ti(III) species, formed by *in situ* reduction of the Ti(IV) catalyst precursor, has been hypothesized to be the true active catalyst.

P 4.23

CHARACTERIZATION OF POLYETHYLENE/CALCIUM CARBONATE NANOCOMPOSITES

R. Scaffaro, F.P. La Mantia, M. Morreale

Polymer nanocomposites are particularly interesting in the view of industrial applications. They can lead to significantly higher elastic modulus, tensile strength and barrier properties in comparison to the neat polymer matrix. In the present work, different types of nano-scale and micro-scale calcium carbonates were added to a polyethylene matrix. Rheological and mechanical characterization was carried out on the obtained materials, with particular focusing on the effect of filler size and filler load.

P 4.24

MATERIALI NANOSTRUTTURATI PER IL RIVESTIMENTO DI SUBSTRATI POLIMERICI

S. Senatore, N. Contiello, A. Citterio, V. Beretti, L. Conzatti, M. Galimberti

Alcoholic nanosilica dispersions were prepared through sol-gel synthesis, in the frame of experimental conditions suitable for an industrial development. Solvents traditionally used in the coating world were used, the product stability was verified over months and gravure as well as flexographic inks were prepared. Silica nanoparticles were observed by transmission electron microscopy to maintain their nano-size also in the presence of polymers used as binders in the coating products. Abrasion and scratch resistance were found to be remarkably improved by a coating product containing silica nanoparticles from sol-gel synthesis.

P 4.25

NANOCOMPOSITE ELASTOMERS WITH In Situ FORMED SILICA FOR LOW ENERGY DISSIPATION

M. Sestito, G. Lampignano, D. Cozzi, A. Citterio, F. Negroni, M. Arimondi, L. Conzatti, M. Galimberti

Well defined and evenly distributed silica nanoparticles were generated *in situ* in an elastomeric matrix, by applying sol-gel reactions in the frame of experimental conditions suitable for an industrial scale up. The condensation of tetraethoxysilane (TEOS) in a carbon black/rubber composite brought to a nice dispersion of *in situ* nanosilica, as shown by TEM analysis, particularly when TEOS was used in the presence of a sulphur containing silane (TESPT). In a sulphur cured isoprene rubber based compound, with carbon black as the main filler, with respect to precipitated silica, *in situ* nanosilica affords: slightly lower dynamic moduli at high temperature, better modulus stability with temperature, remarkably lower dissipation of energy. So prepared nanocomposite elastomeric materials could be suitable for large scale applications such as those in tyres.

P 4.26

SILICI FUNZIONALIZZATE CON RESIDUI OLIGOMERICI ORGANOSTANNICI

L. Angiolini, D. Caretti, S. Ugolini

Organotin compounds are able to promote transesterification reactions, due to the Lewis acidity of the tin atom, but their use is limited by their well-known toxicity. This problem can be overcome by grafting the organotin derivative onto a heterogeneous support, like silica, so that the catalyst can be easily filtered off from the reaction mixture, avoiding the presence of toxic organotin residues in solution and tin release in the environment. For this reason, we have functionalized the silica with two different organotin oligomers, having respectively an aliphatic and an

ethereal chain, both bearing a triphenyltin carboxylate moiety. The resulting catalysts have been tested in a model transesterification reaction between ethyl acetate and 1-octanol: the alcohol conversion was assessed by gas-chromatography, determining the relative amount of product and starting alcohol at established time intervals.

P 4.27

COMPOSITI DI PVC-AG CON PROPRIETA' ANTIMICROBICHE

D. Zampino, T. Ferreri, C. Puglisi, D. Carbone, M. Mancuso, R. Zaccone, R. Scaffaro, A. Fiaccabrino

This study was aimed to the development of poly(vinyl chloride) (PVC) composites containing silver nanoparticles or zeolites to prevent the bacterial colonization of polymeric surfaces. Polymer composites were prepared by mixing plasticised PVC pellets with silver nanoparticles and silver zeolite in the amount of 1-8 wt% and 2-20 wt%, respectively. The results indicate that the thermal and mechanical properties of PVC composites were not affected by the presence of both silver additives, with respect to the pure plasticised PVC. The antibacterial activity of PVC zeolites composites, examined on *Escherichia coli* and *Staphylococcus epidermidis*, in Trypticase Soy Broth and in Trypticase Soy Agar resulted promising both in culture broth and in agar plate, while PVC composites containing silver nanoparticles showed low antimicrobial activity.

P 4.28

SHAPE-MEMORY POLYMERS REINFORCED WITH INORGANIC NANOPARTICLES

E.Zini, P. Dobrzynski, M. Scandola

Composites of a terpolymer (46mol% L-lactic acid, 38mol% glycolic acid, 16mol% trimethylene carbonate) and TiO₂ nanoparticles (0-2w%) are obtained from sonicated dispersions in dichloromethane followed by solvent evaporation. All samples display a glass transition at a temperature close to body temperature; T_g of composites is slightly higher than that of the matrix polymer, indicating a degree of polymer-nanoparticle interaction. The addition of TiO₂ nanoparticles improves the mechanical properties of the polymer (tensile modulus and tensile strength increase) and enhances both the free recovery (from 92% to 100% with 1.92w% of TiO₂) and the constrained recovery in the presence of an opposing force (from 7% to 34 % with 1.92w% of TiO₂).