

Recent advances in thermal analysis of polymers, copolymers and related polymer composites (A review)

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ABSTRACT

Thermo analytical methods play a significant role in the characterization of polymers and related composite materials. Methods include characterization of polymers through simultaneous TG-DTA, DTG and DSC and thermal data are used to evaluate the non isothermal kinetics and thermo dynamics of the solid state decomposition of polymers and related composite materials used non isothermal kinetics. The present review highlights recent developments in the thermal characterization of common thermoplastics, thermosetting polymers, resins, copolymers and polymer composites.

Key words: Thermal analysis, polymers, copolymers and composites.

INTRODUCTION

In recent decades thermoplastic materials, because of their inherent physical properties and low processing temperature have gained significant technological incentives and rapidly replaced more traditional materials such as steel and nonferrous metals, as well as natural polymers such as wood, cotton, and natural rubber. However, apart from a series of weak aspects including resistance against biodegradation, difficulties associated with recycling, melt processing, blending with other polymers, thermoplastic materials have well recognized over steel and other metals. Thermal, mechanical stability and enhanced electrical insulation of these materials impose their wide range of high temperature applications for defence, biomedical engineering, automobile, transportation, textiles and as commodity articles¹⁻⁴.

Among a wide range of thermoplastic materials, the most widely used are polyethylene,

polypropylene, polyvinyl chloride and polystyrene due to their relative ease of molding into articles. Understanding about stability of these thermoplastic materials against thermal and thermo oxidative degradation, constitute an integral part of plastic moulding technology that require prior knowledge of single particle kinetics of their thermal degradations under non isothermal conditions and their thermodynamic parameters. In this connection, a wide range of polymers including thermoplastic materials has been investigated for their non-isothermal kinetics and thermodynamics of decomposition since long time. The kinetics, thermodynamics and mechanism of thermal degradation of thermoplastic materials is governed by a series of factors particularly their molecular mass, structure, nature of substituents, crystallinity, crosslinked density⁵⁻⁹.

Thermoplastics

Thermoplastic is a material that is plastic or deformable, melts to a liquid when heated and

freezes to a brittle, glassy state when cooled sufficiently. Most thermoplastics are high molecular weight polymers whose chains associate through weak van der Waals forces (polyethylene); stronger dipole-dipole interactions and hydrogen bonding (nylon); or even stacking of aromatic rings (polystyrene). Thermoplastic polymers differ from thermosetting polymers (Bakelite; vulcanized rubber) as they can, unlike thermosetting polymers, be remelted and remoulded. Many thermoplastic materials are addition polymers; e.g., vinyl chain-growth polymers such as polyethylene and polypropylene¹⁰.

Polyethylene

Reported¹¹ that a forensic sample consisting of melt-recrystallized polymers that was recovered from the scene of a fire in a factory was identified by DSC. The forensic sample and reference samples of materials were subjected to infrared spectroscopy and pyrolysis GCMS measurements, which revealed their polyethylene nature. The thermal behaviour of the samples was examined by DSC and they were found to be blends of two kinds of polyethylene, LDPE and LLDPE. The samples could be identified and distinguished from each other via DSC measurements.

Thermal properties of polyethylene prepared by γ -ray-induced polymerization in various solvents were examined by differential scanning calorimetry. The solvents used were ethyl and *n*-butyl alcohols, tert-butyl alcohol containing 25 vol.% of water, 2,2,4-trimethylpentane, 2,2,5-trimethylhexane, and cyclohexane. In all solvent systems, the melting point and heat of fusion of the polymers decrease continuously with polymerization temperature. This decrease is caused by an increase in branches with reaction temperature. The melting point and heat of fusion are 100-124°C and 30-44 cal/g, respectively, and no superheating is observed. These facts suggest that folded chain crystals are commonly formed in these systems¹².

LDPE

Studied¹³ that the thermal degradation mechanism of LDPE harnessing a high-pressure autoclave surrounded by a furnace was investigated. In this work the rates of formation of gas, liquid,

and solid during degradation of PE plastic wastes in cyclohexane as solvent at 400 and 425°C have been experimentally determined. Four reaction mechanisms have been proposed and tested to estimates of gas, liquid, and solid. Proposed mechanisms are based on the assumption that the reactions are pseudo-first-order with respect to the reacting species. Pseudo-first-order rate constants for each of the indicated mechanistic steps have been calculated by nonlinear regression analysis. The best fit was obtained by pure parallel reaction mechanism, and its activation energy was determined.

HDPE

Kinetic study of the thermal degradation of HDPE was studied. The thermal degradation of HDPE has been modeled by the random breakage of polymer bonds, using a set of population balance equations. The model fits to the data suggested a second order mechanism in addition to random breakage at slow reaction rates¹⁴.

Polypropylene

Electrophilic substitution of cyclopropenium ions on aromatic polymers offers a unique opportunity to introduce polar functionality in a controlled manner to conventional, nonpolar polymers was studied. Phenylcyclopropenone substituted polystyrene with predictable chemical composition and narrow molecular weight distribution were prepared. Scanning electron microscopy demonstrated the absence of branching or cross-linking in these functionalized polystyrenes during electrophilic substitution of the parent homopolymer. ¹³C-NMR confirmed that the degree of phenylcyclopropenone substitution was both highly efficient and predictable over a broad compositional range. The T_g of the polymers was found to vary linearly with mole % phenylcyclopropenone substitution of the polystyrene. TGA indicated that thermal decarbonylation of the appended cyclopropenones occurred at approximately 180°C. Weight loss vs. temperature profiles correlated reasonably well with levels of substitution based on ¹³C-NMR analysis, confirming that decarbonylation of the calculated cyclopropenone substituents was the predominant thermal decomposition pathway¹⁵.

Polyvinyl Chloride

Some aspects of the non-isothermal kinetics of the thermoxidative decomposition of polymethyl metacrylate, PVC, polyvinyl acrylate and polyvinyl alcohol has been presented. Both the apparent activation energies and the pre-exponential factor depend on conversion and exhibit a pseudo-compensation effect¹⁶.

The kinetics of the thermal decomposition of PVC by a conventional TGA technique under various heating rates in flowing nitrogen was studied¹⁷. The kinetic model that accounts for the effects of scission of the polymeric chain at any time was proposed to describe the thermal decomposition of PVC. The thermal decomposition was found to be a complex process composed of at least two steps for which kinetic values can be calculated. The kinetic analysis of PVC gave apparent activation energy for the first step of 159.7 kJ/mol, with a value of 189.6 kJ/mol for the second step.

The thermal stability of commercial poly vinyl chloride and its four fractions having different intrinsic viscosities (1.152-0.397 dl/g) has been investigated through TGA in the presence of atmospheric oxygen, up to a temperature of 400°C, by using the non-isothermal technique. The results indicate that the thermal stability of the polymer is inversely proportional to its intrinsic viscosity. The kinetic parameters have been evaluated for the early stages of decomposition (2% to 20%). The results have been explained on the basis of different structures of the polymer chain in fractions of high and low intrinsic viscosity¹⁸.

Polystyrene

The thermal behavior of PS composites reinforced with short sisal fibers was studied by means of TGA and DMTA. The thermal stability of the composites was found to be higher than that of sisal fiber and the PS matrix. The effects of fiber loading, fiber length, fiber orientation and fiber modification on the dynamic mechanical properties of the composites were evaluated. Fiber modifications were carried out by benzylation, PS/Maleic anhydride coating and acetylation of the fiber that has improved the fiber-matrix adhesion. PS/sisal composites are thermally more stable than unreinforced PS and sisal fiber. The addition of 10%

fiber considerably increases the modulus but the increase is found to level off at higher fiber loadings. The T_g values of the composites are lower than that of unreinforced PS and may be attributed to the presence of some residual solvents in the composites entrapped during the composite preparation. The treated-fiber composites show better properties than those of untreated-fiber composites¹⁹.

When the DTA of polystyrene is carried out in air in a platinum sample holder, an anomalously high endothermic effect is observed²⁰. This effect was found to be related to gas-phase catalytic styrene oxidation occurring on the surface of both operating and reference platinum sample holders. Methodological recommendations are given concerning the DTA procedure for organic substances, making it possible to avoid this type of anomaly. T_g , cold crystallization, premelt crystallization, and melting in polyethylene terephthalate and co polyesters have been studied by DTA. The transitions are affected by changing the chemical composition of the polyesters through replacing one monomer partially or completely with a different monomer. Quenching, annealing, and/or drawing, which render different degrees of crystallinity to a polyester, can also be detected directly from the thermo grams²¹.

Thermal analysis of polystyrene particles synthesized in the presence of Cetyltrimethyl ammonium bromide and CMC, with the degree of substitution 0.7 and weight average molecular mass of 9.0×10^4 and 2.5×10^5 g/mol was carried out. PS chains grown in the presence of CMC having weight average molecular mass of 9.0×10^4 g/mol presented T_g at 375 K, which is in agreement with the literature value. However, the PS chains grown in the presence of longer CMC chains (weight average molecular mass = 2.5×10^5 g/mol) presented T_g at 352 K. This 23 K decrease in the T_g value was caused by the increased polydispersity, which was confirmed by Gel permeation chromatography. Five mass loss steps between 298 and 873 K were shown by TGA. When the DTA of PS was carried out in air in a platinum sample holder, an anomalously high endothermic effect was observed. This effect was found to be related to gas-phase catalytic styrene oxidation occurring on the surface

of both operating and reference platinum sample holders. Methodological recommendations are given concerning the DTA procedure for organic substances, making it possible to avoid this type of anomaly²².

Polyacrylonitrile

The melting point of PAN was determined directly by DTA at fast heating rate²³. The experimental value of 326°C agrees well with predicted values of the melting point. The disparity between oxidative and thermal decomposition of the polymer is noted.

The effects of some kinds of metal ions used as chemical modifications on the thermal properties of the modified PAN fibers by DTA, TG, GC and cone calorimetry. The apparent activation energies for the decomposition of the unmodified and modified PAN fibers were determined using Kissinger equation and Broido equation²⁴.

Modification of the physico-chemical properties of hydrous TiO₂ was conducted by using binding PAN for the preparation of larger size particles having higher granular strength. The thermal behavior of the obtained composite has been studied by thermogravimetric and differential thermal analysis (TG/DTA). Sorption behavior of the TiO₂-PAN composite for removal of some hazardous radio nuclides has been studied at different conditions such as, pH, contact time, ion concentrations and reaction temperature as well as the drying temperature. The effects of interfering ions as well as some complexing agents on the distribution ratio of the sorption process have been determined. As a result of the obtained data, the optimum conditions for the removal of the studied radionuclides were recommended²⁵.

Polytetrafluoroethylene

Thermal conductivities of bulk technical samples of PTFE and PCTFE were measured in the temperature range 4.2–20 K by application of the steady-state method. An interpretation of the thermal conductivity data in terms of the available theoretical and empirical models is presented²⁶. The reversibility of crystallization and melting of PTFE has been investigated as function of crystallization conditions and temperature by

temperature-modulated DSC. The total and average specific reversibility of the melt-crystallized PTFE is considerably larger than in case of as-polymerized powder. This experimental observation must be attributed to different coupling between crystallized sequences of the molecules within the globally semi-crystalline superstructure. The crystallinity of as-polymerized PTFE is close to 100%, and the crystals melt in a narrow temperature interval close to the equilibrium melting temperature. Melt-crystallized PTFE, in turn, shows a crystallinity of about only 40% and melts at lower temperatures. The morphology of the melt-crystallized PTFE allows molecule segments to melt and crystallize reversibly as a function of temperature. The extended-chain conformation, evident in as-polymerized powder, inhibits reversible melting due to required molecular nucleation after complete melting of a molecule. The experimental findings were discussed within the framework of a similar investigation on polyethylene of different crystal morphology and support both the concepts of lateral-surface activity and molecular nucleation²⁷.

Thermosetting Polymers

The dielectric measurements covering a wide frequency range has provided one of the few practical methods for monitoring the cure of thermo sets (epoxy, etc.) using relatively non-intrusive sensors. The measurements from the basis of a manufacturing control cycle, in the autoclave, provided the rheological state of the thermo set can be related to the Di electric constant and loss factor²⁸.

Thermosetting plastics (thermosets) are polymer materials that cure through the addition of energy, to a mechanically stronger form. The energy may be in the form of heat (generally above 200 °C) through a chemical reaction (two-part epoxy, for example) or irradiation. Thermoset materials are usually liquid, powder, or malleable prior to curing and designed to be molded into their final form, or used as adhesives²⁹.

Polyethers

Polyether having well-defined comb-shaped architectures were prepared by using poly (4-hydroxystyrene) as a multifunctional initiator for graft polymerization of either Ethylene Oxide (EO)

or a mixture of EO and propylene oxide (PO). The grafting process was performed in 1, 4-dioxane using Sodium Hydrate as ionizer for the poly (4-hydroxystyrene) hydroxyl groups. The precursor poly (4-hydroxystyrene) was prepared by first polymerizing 4-tert-butoxystyrene, using butyl lithium as initiator in Tetra hydro furan at -60° C, and then deprotecting the butoxy groups. Finally, the terminal hydroxyl groups of the polyether grafts were end-capped with hexadecanoyl units through esterification. The monomer addition sequence in the graft copolymerization with the same EO/PO feed ratio proved to have a great influence on the crystallization temperature and the crystallinity of the grafts. Also, the end-capping was found to reduce the degree of crystallinity as compared to the corresponding uncapped polymers. Solid polymer electrolytes containing lithium triflate (LiSO_3CF_3) salt had ambient temperature ion conductivities of $\sim 10^{-5}$ S/cm at $[\text{Li}]/[\text{O}] = 0.025$. Thermal analysis of the electrolytes showed that the polymers aggregated through phase separation of the hexadecanoyl chain ends³⁰.

Polycarbonates

Dynamic mechanical behavior of polycarbonate has been compared with that of polyester carbonate. The nature of mechanical relaxations in these materials was discussed. The results indicate that the energy requirements for the motion of ester groups are not significantly different from those of the carbonate units³¹. Thermal degradation of bisphenol. A polycarbonates with aromatic side groups was studied³². It was indicated that there may be little difference in the manner in which these materials degrade compared to the degradation pathways for unsubstituted bisphenol-A polycarbonate. In studying the thermo-oxidative stability of polyimides, cross-linking during the degradation process was reported which was believed to be due to side chain rupture and recombination. In studying the degradation of acid doped polyanilines, it was reported that the initial process was the loss of the dopant leaving behind a polyanilines system, which upon further heating degraded at lower temperatures than polyaniline, which had never been doped.

Polyaniline

Dynamic mechanical and dielectric thermal

analyses together with infrared spectroscopy was used to identify molecular motions in polyaniline films cast from emeraldine base powder dissolved in the solvent N-Methyl 2-Pyrrolidinone. These relaxations include a librational ring motion at around -80°C and a T_g centered at 100°C. A permanent film hardening process at around 180° C was observed which is ascribed to polymer chain cross-linking both physical (associated with chain entanglements) and more importantly chemical (chain-chain chemical bonding). Chemical cross-linking can be further identified with chain defects and residual impurities in the polymeric material. The importance of precise control of polyaniline synthesis and processing is therefore strongly emphasized. These results have clear implications for the thermal orientation process in polyaniline³³.

Polyimides

The method of comparative thermal analysis has been used to determine the thermal stability of polyimides and their model compounds. The extent of defects in the investigated polyimides was determined by gas chromatography. The dependence of the extent of the defects on the chemical structure of the initial components and the super molecular structure of the polyimides was established³⁴.

A series of new polyimides were prepared from the reaction of 2, 3, 3', 4'-biphenyltetracarboxylic dianhydride (a-BPDA) with various aromatic diamines. The properties of the a-BPDA polyimides were compared with those of polyimides prepared from the reaction of 3, 3', 4, 4'-biphenyltetracarboxylic dianhydride (s-BPDA) with the same aromatic diamines. Films of the a-BPDA polyimides had higher T_g and less color than the corresponding s-BPDA polyimide films. Light transmission at 500 nm, solar absorptivity, and thermal emissivity were determined on certain films. Films of similar polyimides based upon a-BPDA and s-BPDA containing *meta* linkages and others containing *para* linkages were each cured at 250, 300, and 350 °C. The films were characterized primarily by T_g , color, optical transparency, tensile properties, dynamic mechanical thermal analysis and coefficient of thermal expansion. The a-BPDA *meta* linked polyimide films had tensile strengths and moduli higher than films of the a-BPDA *para*

linked polyimide. The same phenomenon was not observed for the *s*-BPDA *meta* and *para* linked polyimides. The chemistry, mechanical, and physical properties of the polymers and films are discussed³⁵.

Polyhydrazides

Polyhydrazides containing pyridine rings in the backbone by interfacial or solution polycondensation from 2, 5-pyridine dicarboxylic acid and three dihydrazides or hydrazine was synthesized³⁶. Heating conditions suitable for the formation of polyoxadiazoles by dehydration of the polyhydrazides were studied by infrared analysis. The polyoxadiazoles formed were thermally stable but poorly soluble. The polyhydrazides were soluble and could take up cobalt (II) ions. The potential applicability of the polyhydrazides to a reverse osmosis membrane was demonstrated.

New interesting class of novel polyhydrazides containing 1, 3, 4-thiadiazole moieties in the main chain was synthesized through solution polycondensation technique. The new monomer namely: 2, 5-bis (mercaptoacetichydrazide)-1, 3, 4-thiadiazole was synthesized from the nucleophilic replacement of 2, 5-dimercapto-1,3,5-thiadiazole with ethylchloroacetate, followed by hydrazinolysis. The model compound was synthesized from the monomer 2,5-bis(mercaptoacetichydrazide)-1,3,4-thiadiazole with benzoyl chloride and characterized by ¹H- NMR, IR, and elemental analyses. The polyhydrazides were synthesized from the polymerization of monomer 2,5-bis(mercaptoacetichydrazide)-1,3,4-thiadiazole with 4,4'-biphenic, 3,3'-azodibenzoyl, 4,4'-azodibenzoyl dichlorides. These polymers were characterized by elemental and spectral analyses, viscometry and solubility. The thermal properties of these polymers were determined by TGA, and DSC, and correlated with their structure. The crystallinity of some polymers was tested by XRD³⁷.

Polyurethanes

DSC was applied to investigate the thermal behaviour of a series of segmented polyurethanes based on diphenylmethane-4,4'-diisocyanate (MDI), polyoxypropylenediol (POPD) and 3-chloro-1,2-propanediol (CPD)/1,2-propanediol (PD). It has been found that the heat of thermal transition in the range of 250–300°C increases with the amount

of CPD, which also causes a decrease of polyurethanes' flammability, characterized by its Limited Oxygen Index (LOI) value. On the basis of obtained results it can be concluded that DSC may be applied for flammability evaluation of segmented polyurethanes³⁸.

Polyamides

Heat resistant polyamides containing the 4,4'-disubstituted-2,2-bipyridyl moiety by phosphorylation polycondensation from 2,2-bipyridyl-4,4-dicarboxylic acid and a series of primary aromatic diamines with triphenylphosphite and pyridine as the agents was synthesized³⁹. Polyamides exhibiting improved solubility in organic solvents and strong acids, melting transitions at low temperatures and good thermal properties were prepared by introducing bulking methyl and fluoro groups and flexible ether and propyl linkages and by using monomers with reduced symmetry. Solutions of the polyamides with rigid main chains showed birefringence at concentrations of 5, 10, and 15% (w/v) polymer/solvent. The chelation of ruthenium(II) ions resulted in the preparation of directional metallopolyamide systems based on the geometrically favorable tris(2,2-bipyridyl) ruthenium (II) complex. The three-dimensional polyamides, which absorbed at a max of 476 nm and emitted at a max of 620 nm, exhibited a high thermal stability and improved solubility, making them suitable candidates for compressive strength studies and cyclic voltametry studies as part of an effort to address the corrosion of graphite fiber-reinforced composites.

Poly-p- xylene

The insertion of meta units in the chain of poly-p-xylene decreases both the onset temperature of oxidative degradation and the rate of decomposition. Fictionalization of the polymer with chlorine and sulphonic groups makes the chain more resistant to high temperature treatments, notwithstanding the low stability of the substituent groups⁴⁰.

Copolymers and polymer mixtures

A heteropolymer or copolymer is a polymer derived from two (or more) monomer species, as opposed to a homopolymer where only one monomer is used. Copolymerization refers to

methods used to chemically synthesize a copolymer.

Polyamic acid (PAA) fural alcohol (FA) and their mixtures in different ratios were investigated by DTA. The effects of the solvent and the component ratio on the thermal characteristics of the final products were established. It was shown that when the PAA-FA composition is heated, PAA is the initiator of the polymerization of FA, and the interaction in the system is profoundly affected by the component ratio and the temperature. The existence of an interaction between the components of the system was confirmed by TGA, IR and NMR spectroscopy⁴¹.

Thermal characteristics of polyaniline (PANI), poly(*o*-amino benzoic acid) (POABAC) and poly(*o*-amino benzyl alcohol) (POABOL) was studied through TGA and DSC. The higher thermal stability of POABOL is attributed to heat-induced condensation between the polymer chains. The DSC results suggest both intra- and inter-molecular interaction in the form of hydrogen bonding due to the substituent group in POABAC and POABOL. These interactions, however, occur mainly in the doped form and is greatly reduced when the dopant is expelled from the system at higher temperatures⁴².

Thermal stability of a polypropylene copolymer at several stages during the processing of the material into its final product in order to obtain information on the influence of processing steps such as grinding and thermal heating on the expected lifetime of the material. Mass loss kinetics in an inert atmosphere were able to detect differences in thermal stability, but oxidative DSC studies proved to be a more sensitive technique. A comparative study of a specially prepared series of samples revealed the importance of additives on measured thermal stability and indicated that both mechanical and thermal processing can cause reduction in measured thermal stability⁴³.

Thermal degradation and combustion process of liquid crystalline polyesters was studied by directly coupled thermal analysis-mass spectrometry. The specific interactions and degradation features in this blend system was

investigated by using Raman and Fourier transform infra-red (FTIR) emission spectroscopy. No appreciable hydrogen bonding between the amide groups in PVP and the α -hydrogen in PVC is observed, but the presence of dipole-dipole interaction between C-Cl and O=C leads to decreased association of PVP chains and good dispersion in PVC⁴⁴.

Some new thermally stable co-polyhydrazides were synthesized using a low-temperature solution polycondensation technique. Polycondensation of hydroquinone-1,4-diacetic acid dihydrazide and 2-bromo-, 2-chloro- and 2-nitrohydroquinone-1,4-diacetic acid dihydrazide with terephthaloyl or isophthaloyl chloride in dimethylformamide gave the corresponding co-polyhydrazides respectively. Their thermal analysis, solubility in different solvents and the effects of variable reaction conditions on the yield percents and viscosity values are studied. The structures of the prepared co-polyhydrazides were confirmed by elemental analysis, infrared and ¹H-NMR spectroscopy⁴⁵.

Formation of polyaramides as intermediates in the decomposition process was detected. These amide bonds subsequently degrade by homolytic breaking, yielding nitriles. The final carbonaceous residue is rich in nitrogen and retains a certain degree of anisotropy, a fact that was explained by the conservation of crystallinity at an intermediate decomposition stage⁴⁶.

Thermal decomposition of the polypropylene and liquid paraffin mixtures was studied with inorganic additives were studied in dynamic conditions. Typical thermal analyses were carried out and thermal decomposition of samples in a specially designed apparatus was also processed. For the samples of sufficiently low mass, thermal analysis allowed clear distinction of samples that contain and do not contain liquid paraffin, respectively. Moreover, it was possible to separate two stages of the decomposition process. The relationship between the logarithm of conversion degree and temperature (so called three-parameter model) was used for the description of these processes. Relations between coefficients in three-parameter equation in micro-scale, and charact-

eristic temperatures of thermal decomposition in laboratory scale were observed in spite of meaningful differences in the course of the processes⁴⁷.

The oxidation of Poly (acrylonitrile-co-methyl methacrylate) films in an air oven and in an oxidation chamber was studied at temperatures of 80 to 200°C. DTA of these oxidized films showed that the exothermic peaks increased with increasing oxidation temperature. The change of viscosity, the insolubility in dimethyl-formamide and IR analyses indicate both intermolecular and intermolecular reactions⁴⁸.

The effect of low temperature cold-crystallization on quenched poly (p-phenylene sulfide) (PPS) amorphous phase behaviour was systematically investigated by DSC and DMTA over the entire range of the process, from its early stage to the end. For the first time a well resolved double T_g of partially cold-crystallized samples was evidenced. A T_g steady increase was observed during the primary crystallization process, due to the reduction of amorphous chain segmental mobility imposed by the growing rigid phase. A shift of the relaxation temperature of about 10 °C was recorded at the end of the primary crystallization process. As the secondary crystallization takes place, a new glass transition appears at higher temperature. For longer annealing time the lower T_g disappears while the intensity of the upper one increases. The upper temperature glass transition of semi-crystalline PPS is explained as a consequence of the PPS secondary cold-crystallization process⁴⁹.

Molecular motions and thermal transitions in polyaniline fibers, cast from emeraldine base powder dissolved in N,N'-dimethylpropylene urea, have been investigated by DMTA. For this purpose, a special picopendulum has been used and a double sweep DMTA study has been performed. From these preliminary experiments, different relaxations observed have been discussed and compared to what is found in the literature⁵⁰.

Resins

Phenol formaldehyde resins

DTA and TGA combined with an infrared

absorption study have been used to examine the mechanisms involved in cross-linking or curing of phenol formaldehyde novolac resins with hexamine. It has been shown that the curing reaction is a three-stage process. The first stage is the physical change of melting and subsequent formation of hexamine solutions. The second and third stages were found to be two, distinct, cross-linking reactions occurring in two, successive, temperature regions. The presence of absorbed moisture modifies the melting and curing processes⁵¹.

2,4-Dihydroxybenzaldehyde-formaldehyde copolymers were characterized by elemental analyses and TGA. The results of TGA reveal that each copolymer sample undergoes degradation in single step are thermally stable up to 250°. All the copolymers undergo thermal degradation at slower rate in the beginning up to 300° and the decomposition is complete at 500° where 74-97% weight loss is observed. Copolymers prepared using equimolar proportion of reactants is thermally more stable. The Broido method was applied to the TG data to determine the energy of activation⁵².

Polyester- melamine resin

The effects of diol structure and acetoacetylation on cure, viscoelastic and mechanical properties of hydroxylated polyesters (HPS)/ hexamethoxymethylmelamine (HMMM) clear coatings was studied⁵³. Acetoacetylation of HPS is a potential tool for researchers to get the equivalent or superior performance at higher application solids than their base counterpart. Differential Scanning Calorimetry (DSC), Dynamic Mechanical Thermal Analyzer (DMTA) and Thermo Gravimetric Analysis (TGA) have been utilized to study the cure and viscoelastic behavior and thermal stability of the coatings respectively. The crosslink density and elastically effective chain length between cross links of the coating films has also been determined. Furthermore, the mechanical film properties such as tensile properties, adhesion strength and hardness were measured and related to chemical composition. The results indicate that the combined analysis helps in correlating the structure property relationship with end use properties.

TGA, DSC and DMTA was used to

characterize the nature of polyester-melamine coating matrices prepared under nonisothermal, high-temperature, rapid-cure conditions. The results were interpreted in terms of the formation of two interpenetrating networks with different glass-transition temperatures (a co-condensed polyester-melamine network and a self-condensed melamine-melamine network), a phenomenon not generally seen in chemically similar, isothermally cured matrices. The self-condensed network manifested at high melamine levels, but the relative concentrations of the two networks were critically dependent on the cure conditions. The optimal cure (defined in terms of the attainment of a peak metal temperature) was achieved at different oven temperatures and different oven dwell times, and so the actual energy absorbed varied over a wide range. Careful control of the energy absorption, by the selection of appropriate cure conditions, controlled the relative concentrations of the two networks and therefore, the flexibility and hardness of the resultant coatings⁵⁴.

The melamine modified polyester amide (MPEA) by the reaction of linseed oil fatty amide were synthesized. The resin was further cured at room temperature by polystyrene co-maleic anhydride (SMA) in different phr (30–80) to obtain MPEA coatings. The probable structure of MPEA was confirmed by FT-IR, ¹H-NMR and ¹³C-NMR spectroscopic techniques. The physico-chemical characterization of these resins viz. iodine value, saponification value, refractive index, inherent viscosity were carried out by standard methods. MPEA (40 wt%) solution in ethylene glycol monomethyl ether (EGME) was applied on a mild steel strip of standard sizes to study their physico-mechanical and chemical resistance properties. It was found that coatings of MPEA with 60 parts per hundred of the resin (phr) of SMA showed the best performance in physico-mechanical and alkali resistance properties. Thermal stability and curing behavior were studied by TGA and DSC, respectively⁵⁵.

Urea formaldehyde resin

The activation energy and viscoelastic properties of urea-formaldehyde resin, melamine-formaldehyde resin and urea-formaldehyde-melamine-formaldehyde resin mixtures was

investigated through by DSC and DMTA⁵⁶. The purpose of adding melamine-formaldehyde resin to the urea-formaldehyde resin was to reduce the formaldehyde emission. As the melamine-formaldehyde resin content was increased in the urea-formaldehyde-melamine-formaldehyde resin mixture, the formaldehyde emission decreased. The storage modulus, loss modulus and loss factor of each resin were measured by DMTA. With increasing temperature, as the resin cured, the storage modulus increased in all resin systems. The storage modulus increased both as a function of increasing temperature and with increasing melamine-formaldehyde resin content. The activation energies of the curing reactions of the urea-formaldehyde and melamine-formaldehyde resins alone, as well as the mixed resins, on different substrates, were calculated on the basis of the variation of the temperature of the maximum of each DSC scan exotherm using the Kissinger equation. The activation energy value of the urea-formaldehyde resin decreased as the melamine-formaldehyde resin content ratio increased, and because of this lower activation energy the urea-formaldehyde-melamine-formaldehyde resins cured faster than the urea-formaldehyde resin. Formaldehyde is incorporated more easily and completely into melamine than into urea. The results showed that melamine-formaldehyde resin reacts with formaldehyde faster than UF resin because of its high "NH content.

Furan resin

The effect of Ti, Nb and Ta on the anti-oxidation of furan-resin-derived carbons was investigated by TGA combined with GCMS. Hall coefficient and magneto resistance measurements, transmission electron microscopy, and X-ray diffraction analysis. Hall coefficient and magneto resistance measurements revealed that the electronic properties of carbons with the above metal elements, and thus their crystallinity, are similar to that of neat carbon. The oxidation rates of the carbons with a small amount of Ti or Ta are decreased up to 1000°C compared to that of neat carbon. The number of working active sites in carbons with Ta or Ti is smaller than that in carbons with Nb or neat carbon. Ta or Ti terminates some active sites in the carbons, or somehow modifies the structures of the active sites and retards the

formation of oxygen–carbon intermediate products (surface complexes) on the materials. Thus, the oxidation rate of the carbons is decreased⁵⁷.

The oxidation behavior and structural changes of furan-resin-derived carbon heat treated at 3000°C were investigated at 500 and 700 °C under dry air. TGA, Raman spectroscopy and X-ray photoelectron spectroscopy were employed to detect and understand this behavior and the changes. Effect of tantalum on anti-oxidation property of Ta-alloyed carbon was also analyzed. The neat and Ta-alloyed carbons had insignificant weight losses even after being kept at 500 °C for 12 h, while the Ta-alloyed carbon had weight loss lower than that of the neat carbon after being kept at 700 °C for 6 h. It has been found by XPS that oxidation involves oxygen in internal area as well as on external surface of the carbons. It was also inferred that the carbon stored with oxygen in deeper internal area was easily oxidized. Ta alloying leads to change of the state of the Fermi energy on the specimens, which may cause the anti-oxidation property⁵⁸.

Polystyryl pyridene resins

The cross-linking or curing reaction of polystyrylpyridine has been studied by means of thermal reactions of its model compounds. Compounds 2, 6-distyrylpyridine, 4-stilbazole(4-styrylpyridine), and deuterated 4-stilbazole were pyrolyzed at 200-325°C both in air and under vacuum in a sealed tube. The major pyrolysis products were diary ethane and stilbene, and were characterized by GCMS. Major dimeric products were naphthalene or quinoline derivatives. Mechanisms for the pyrolysis are suggested, and a crosslinked structure for cured PSP is proposed based on the thermal reaction products of model compounds⁵⁹.

Polydimethyl siloxane resin

TGA, DTA and IR spectroscopy was used to investigate the process of thermal destruction of adsorbed polydimethyl siloxane (PDMS) in air. The disperse adsorbents were pristine fumed silica and modified fumed silica whose surface contained oxygen compounds of phosphorus. It was shown that under the given experimental conditions the thermal destruction of PDMS on the fumed silica

surface was accompanied by the complete transformation of the adsorbed PDMS to SiO₂. In the case of phosphorus-containing silica, the thermal destruction proceeded in a different way. It was found that at 140–300°C depolymerizations of the siloxane chains of a certain part of the adsorbed polymer took place with the concurrent removal of volatile products of the reaction. However, the remaining part of the adsorbed PDMS interacted with the modified silica surface to form chemisorbed dimethylsilyl structures. The thermal destruction of the chemisorbed fragments of PDMS in air was initiated at 400°C or above for both types of silica investigated⁶⁰.

A combination of traditional kinetic formal treatments and computer simulation has been made to analyze polydimethyl siloxane (PDMS) thermal degradation. It was shown that PDMS thermally decomposes to cyclic oligomers through Si–O bond scission in a chain-folded cyclic conformation energetically favored by overlapping of empty silicon d-orbitals with orbitals of oxygen and carbon atoms. Kinetic treatment shows that PDMS thermal volatilization, as rate of heating increases, becomes dominated by rate of diffusion and evaporation of oligomers produced on its decomposition. At high heating rate (e.g. 100°C min⁻¹.) thermal decomposition in nitrogen and in air tend to overlap because the rate of reaction between the material and oxygen is strongly reduced by low-oxygen solubility and high-thermal degradation rate. In nitrogen a small black residue is formed (silicon oxycarbide) which is produced by an alternative decomposition path leading to cyclic oligomers, made possible at high heating rate⁶¹.

Composites

A composite is the combination of polymers of different properties blended physically or chemically to result a hybrid material comprising combined properties of each of the components. 56 Alkyd-allyl moulding compounds containing diallyl orthophthalate were investigated as networking monomer and five other unsaturated polyester resins by DTA. The analysis of DTA curves allowed choice of the alkyds forming well-cured moulding compounds within the investigated monomer. The thermal resistance and acetone absorption of the cured sample confirmed the choice of the alkyd.

The influence of 6 different powder fillers on the exothermic effect of curing of alkydallyl moulding compounds was evaluated by DTA⁶².

Blends of polycarbonate and LDPE of different compositions, in the form of slabs obtained by melt extrusion, have been examined by DSC and DMTA. DSC measurements show that the melting, crystallization and glass transition temperatures of the two polymeric components in the blends are slightly affected by the composition. On the contrary, large differences are observed in the melting behaviour of layers cut at various depths, parallel to the slab surfaces of samples. This supports the occurrence of different crystal morphologies and distribution of the two components within the samples. The study of the crystallization kinetics from the melt blends shows that the crystallization processes of LLDPE are affected by the presence of polycarbonate. The dynamic mechanical analysis indicates that modulus, transitions and relaxational behaviour of the polymer components are scarcely affected by the composition. Some variations of the damping factor have been interpreted as due to the phase heterogeneity of the system, arising from the processing conditions and rheological behaviour of the blends⁶³.

The effects of phosphorous and chlorine-containing reactive antipyrenes with different compositions and structures on the mechanism and kinetics of the total thermal decomposition of rigid polyurethane foams, together with the possibility of evaluating their effectiveness as combustion inhibitors, were studied by means of a combined thermal analysis technique. It is shown that dynamic thermal analysis can register the changes resulting in the mechanisms and kinetics of the thermal decompositions of the investigated polyurethanes from comparatively low concentrations and differences in the concentrations and from differences in the chemical compositions and structures of the antipyrenes. The most sensitive characteristics associated with the influence of antipyrenes in this case were the coke residue determined at 850 in an inert medium and the areas of exothermic peaks I and II in the DTA curve in air medium reported that Silicone elastomers are often used as a base for controlled-release systems material for drugs. The modulation of drug diffusion

by varying the mesh size of a silicone elastomer network has already been studied. The influence of vulcanization conditions and chemical modifications on the network mesh size by thermal analysis and measurement of the swelling ratio was investigated. In parallel, the influence of these same parameters on the diffusion of model drugs has been studied⁶⁴⁻⁶⁵.

Blends obtained from polyamide 6 and polyester or polyether polyurethanes were investigated by means of DMTA. The blends were prepared by compounding in a twin-screw Brabender-Plasticorder. Changes in composition did not influence the glass temperature of the amorphous fraction of the polyamide, but also no distinct transition for separated polyurethane soft segment was visible. Therefore the blends seem to be multiphase systems, where the elastometric polyurethane phase is dispersed in a continuous polyamide phase. From changes in the α relaxation region of the polyamide better miscibility of polyester polyurethanes comparing to polyether polyurethanes was explained by hydrogen bonding in the common amorphous phase⁶⁶.

New rocket insulator compositions have been studied by adding various types and amounts of fillers, such as graphite and asbestos fibers, Al_2O_3 , MgZrO_2 , Cr_2O_3 , SiC, carbon powders and phenolic resin to the base EPDM gum and graphite, Kevlar, E type glass fibers to the base phenolic resin in order to improve thermal and ablative efficiency. The degradation of the insulators has been investigated by TGA to 900°C and DSC analysis to 500°C. Conversion curves of the insulators at different heating rates were performed and maximum degradation temperatures were found as 646 and 661°C for EPDM P and phenolic resin, respectively. The kinetic parameters for degradation have been evaluated and the lifetime of the rocket insulators has been estimated. Thermal analysis has been conducted on the insulators and the in depth temperature distribution was evaluated in order to find optimum insulation thickness⁶⁷.

Eight amorphous Polyethers and poly(ether ketones) were synthesized and characterized by gel permeation chromatography, thermogravimetric analysis, differential scanning

calorimetry, and dynamic mechanical thermal analysis. Polymers containing bulky, cyclic 2,2'-biphenyl side groups were found to have the highest glass transition temperatures, were more thermally stable and exhibited the highest intramolecular barriers to rotation. Incorporation of perfluorophenylene groups resulted in internal plasticization and a relative lowering of T_g . The steepness of cooperatively plots determined from Williams-Landel-Ferry shift factors correlated with the rigid nature of the polymer chains, but not with the broadness of the relaxation (characterized by the Kohlrausch-Williams-Watts stretch exponent as predicted by the coupling model. A β -process observed in the polymers containing cyclic biphenyl side groups was similar in appearance to a typical "structural" relaxation. The position, intensity, and breadth of the process were sensitive to chemical structure and absorbed moisture⁶⁸.

Facile dehydrochlorination of PVC in the blends is promoted by PVP in that increasing the amount of PVP in the blends decreases the dehydrochlorination temperature. At elevated temperatures there are longer sequences of polyene in the blend which are formed at lower temperatures than in PVC homopolymer. However, in the early stage of degradation, the polyene structures are developed in a more regular trans configuration, yielding significant amounts of poly(acetylene)-like structures before further degradation reactions occur. This seems to suggest that dehydrochlorination of PVC in blend systems might be controlled to give conjugated polyene structures with fewer defects⁶⁹.

A series of blends of PVC and polyaniline PANI was prepared by solution casting and investigated by methods of thermal analysis, namely TG, coupled with TG-FT/IR and DSC. It was found that the thermal stability of this polymer system depends on the composition of blend; the main product of prevailing PVC decomposition process - hydrogen chloride - seems to play specific role during degradation since it can react with PANI structures, characterized by different protonation degree⁷⁰.

Benzofuro[2,3-*b*]benzofuran - 2, 9 - dicarboxylic acid, 4, 4 - [sulfonylbis (*p*-phenyleneoxy)]

dibenzoic acid, and 2,7-biphenylene dicarboxylic acid were reacted with a number of diaryl ethers in phosphorous pentoxide/methane sulfonic acid (PPMA) media. Diacid also was reacted with an equimolar mixture of two diaryl ethers. FT-IR spectroscopy and elemental analysis data confirmed the molecular structure of the polymers. They show good thermal stability⁷¹.

Phenolphthalein poly(ether ether ketones) (PEK-C) was found to be miscible with uncured tetraglycidyl 4,4-diaminodiphenylmethane (TGDDM), which is a type of tetrafunctional epoxy resin (ER), as shown by the existence of a single T_g within the whole composition range. The miscibility between PEK-C and TGDDM is considered to be due mainly to entropy contribution. Furthermore, blends of PEK-C and TGDDM cured with 4,4-diaminodiphenylmethane (DDM) were studied using DMA, FTIR spectroscopy, and SEM. DMA studies show that the DDM-cured TGDDM/PEK-C blends have only one T_g . SEM observation also confirmed that the blends were homogeneous. FTIR studies showed that the curing reaction is incomplete due to the high viscosity of PEK-C. As the PEK-C content increased, the tensile properties of the blends decreased slightly and the fracture toughness factor also showed a slight decreasing tendency, presumably due to the reduced crosslink density of the epoxy network. SEM observation of the fracture surfaces of fracture toughness test specimens showed the brittle nature of the fracture for the pure ER and its blends with PEK-C⁷².

DSC, TGA and DMTA of the blends of epoxy cresol novolac resin toughened with liquid carboxy terminated butadiene-co-acrylonitrile rubber have been carried out. Exothermal heat of reaction (ΔH) due to crosslinking of the resin in presence of diaminodiphenyl methane (DDM, as amine hardener) showed a decreasing trend with increasing rubber concentration. Enhancements of thermal stability as well as lower percentage mass loss of the epoxy-rubber blends with increasing rubber concentration have been observed in TGA⁷³.⁷⁴ reported study of the thermal stability of some aromatic copolyethers containing a hexamethylenic spacer. The polymers were synthesized by phase transfer catalysis (in a liquid/liquid system) starting from 1,6-dichlorohexane and different bisphenols:

4,4'-dihydroxyazobenzene, 4,4'-dihydroxydiphenyl, bisphenol A and 2,7-dihydroxynaphthalene. Thermal stability was investigated by TGA, in a static air atmosphere the heating rate being 10°C/min. Molecular modeling was used as a complementary analysis method for the best understanding of the relationship between the chain conformation and polarity and the thermal behavior. CERIU² and HYPERCHEM programs were used to perform the molecular modeling. All the synthesized polymers present similar values of the starting point of the weight loss. This behavior can be explained by supra-molecular ordering, which is probably more important than the chemical structure. The presence of the hexamethylene spacer leads to a micro-phase separation, with a favorable influence on the ordering in the solid state. All polymers showed low values of the polar surface, with interchain interactions playing a secondary role in the thermal stability.

TGA combined with mass spectrometry of some aromatic Polyethers and copolyethers was studied in order to obtain information on the degradation mechanism. The investigated polymers were synthesized starting from 3,3-bis(chloromethyl) oxetane and various bisphenols: 4,4'-dihydroxyazobenzene, 4,4'-dihydroxydiphenyl, bisphenol A and 4,4'-dihydroxydiphenylether. The presence of an oxetanic spacer in the structure, permitting the opening of the cycle, induces more complications in the characterization procedure. But, due to the possibilities relative to the modification of polymers or cross-linking reactions, the presence of the oxetanic moiety may offer some advantages. Out of all the investigated polymers, those containing azobenzenic moieties have the lower thermal stability. If the chain flexibility is augmented, the degradation mechanism is based on chain transfer reactions. All polymers present higher thermal stability in an argon atmosphere. Based on mass spectra, a degradation mechanism sustained with the assumption that the oxetanic unit is the most labile was proposed. The opening of the oxetanic cycle begins with the most tensioned bond ($-C-CH_2-$) and generates across-linking process, which is more evident if the polymer melts below 200°C⁷⁵.

Kinetic parameters of thermal degradation

of polyethylene glycol-toughened novolac-type phenolic resin were investigated. Through measurement of the miscibility and thermal degradation DSC results confirmed that the phenolic resin/PEG blend was blended completely. Infrared spectra show that hydrogen bonding existed in the blends. Thermal degradation of PEG blended with novolac-type phenolic resin was studied utilizing a dynamic thermogravimetric technique in a flowing nitrogen atmosphere at several heating rates (i.e., 5, 10, 20, 40°C/min). Thermal degradation of phenolic resin/PEG blends takes place in multiple steps. The thermal behavior and the thermal stability affected the thermal degradation, which coincided with the data from the thermal degradation of novolac-type phenolic resin/PEG blends by TGA⁷⁶. The thermal properties of HDPE and LDPE filled with different biodegradable additives (Mater-Bi AF05H, Corn last, and Bioeffect 72000) were investigated with TGA and DSC. The DSC traces of the additives indicated that they did not undergo any significant phase change or transition in the temperature region typically encountered by a commercial composting system. The TGA results showed that the presence of the additive led to a thermally less stable matrix and higher residue percentages. The products obtained during the thermo degradation of these degradable polyolefin were similar to those from pure polyethylenes. The LDPE blends were thermally less stable than the HDPE blends⁷⁷.

Thermal stability of polymer blends was investigated by means of gas GCMS and thermal analysis. Evaluated changes in thermal stability can be attributed to blending. A new scheme of thermal degradation for polystyrene-polydimethyl siloxane (PDMS) blend was suggested. In the case of PS as a part of the blend, the products of degradation of PS diffuse through the phase boundary, which cause interaction with PDMS polymers. Apparently, PDMS acts as an inert component, slowing down the termination reaction by dilution of macro radicals formed in random scission degradation process of the PS component. On the other hand, it stabilizes the PS by means of interpolymer recombination, which leads to cross products of thermal degradation. Two of the degradation products: 2-phenyl-4(1',3',3',5',5'-pentamethylcyclotrisiloxane)-butane and 2-phenyl-4(1',3',3',5',5',7',7'-heptamet-

hlycyclotrisiloxane)-butane were assigned to the products of cross-interpolymer recombination which can accelerate the process of PDMS depolymerization by means of radical initiation of PS fragments. The connection between a polymer thermal oxidative degradation and its combustion under diffusion flames condition was shown by using composition of polypropylene-polypropylene-copolyethylene (PP/PP-co-PE). In general, the solid-phase polymer reaction can play a very important role in the reduction of polymer combustibility. It was shown that the composition of PP/PP-co-PE(62:38) has the highest induction period of auto-oxidation, which correlates with its combustibility⁷⁸.

A critical analysis of the isoconversional methods was conducted for evaluating kinetic parameters of decomposition of solids from isothermal TG data is presented. This method allowed removing the errors due the correction of the degradation time by subtracting the induction period to onset of the main reaction (also including the time required to heat the sample to the temperature at which the isotherm is recorded). This procedure was used to study the degradation of two series of polymeric materials, PVC/ABS blends and PVC/CPE blends⁷⁹.

Melt blends of polycarbonate and poly(ethylene terephthalate) by continuous extrusion and injection-molded into bars were prepared for mechanical testing⁸⁰. Thermal analysis was used to ascertain transitional behavior and the level of PET crystallinity at various points in the fabrication and testing process. The mechanical properties showed little departure from additives except for the percent elongation at break which was substantially larger for certain blends than expected. T_g behavior suggests two amorphous phases for PC rich mixtures and only one mixed phase in the polyethylene terephthalate rich region. Crystallizability of the polyethylene terephthalate after the blend was held for prolonged times in the melt state suggests that interchange reactions do not occur to any great extent.

Synthesis and characterization of 8-quinolinyl methacrylate with methyl acrylate and vinyl acetate copolymers were extensively investigated. These materials are applicable in

modern science due to their antimicrobial and ion exchange properties. TGA of copolymers was performed in static air atmosphere whereas differential scanning calorimetry of the copolymers was also discussed. TGA of copolymers were carried out at a 10°C/min heating rate in nitrogen atmosphere. The thermal data in various kinetic parameters of thermal degradation for both copolymer are observed that p (8-QMA), PMA and PVAc starts degrading at 300°C, 275°C and 200°C respectively⁸¹⁻⁸².

Conductive elastometric blends based on ethylene-propylene-5-ethylidene-2-norbornene terpolymer (EPDM) and polyaniline doped with 4-dodecylbenzenesulfonic acid [PAni (DBSA)] were cast from organic solvents. Functionalization of the elastomer was promoted by grafting with maleic anhydride. Vulcanization conditions were optimized with an oscillating disk rheometer. The conductivity, morphology, thermal stability, compatibility, and mechanical behavior of the obtained mixtures were analyzed by *in situ* direct current conductivity measurements, atomic force microscopy, transmission electron microscopy, wide-angle X-ray scattering, thermogravimetric analysis, differential scanning calorimetry, dynamic mechanical thermal analysis, stress-strain and hysteresis tests. The vulcanization process was affected by temperature, the PAni content and maleic anhydride. A reinforcement effect was promoted by the vulcanizing agent. The formation of links between the high-molar-mass phases and oligomers of PAni (DBSA) in the elastomeric matrix enhanced the thermal stability and ultimate properties of the blends. By the appropriate control of the polymer blends' composition, it was possible to produce elastomeric materials with conductivities in the range of 10^{-5} - 10^{-4} S · cm⁻¹ and excellent mechanical properties⁸³.

The kinetic analysis of thermal degradation of polymers was investigated using a dynamic method⁸⁴⁻⁸⁵. The integral thermal effects in heating of some polymeric materials within the 293-1173 K range were determined by adiabatic calorimetry. The measured dissociation values represent enthalpy changes for the overall reactions polymer-degradation products under standard conditions (pressure 10.5 Pa, temperature 298 K). A

comparative analysis of the thermodynamic characteristics of thermal degradation of filled polymeric compositions based on ethylene-propylene and butadiene-nitriles rubbers was made⁸⁶.

Wood polyacrylonitrile composite from poplar wood was synthesized. Modification of the properties of wood polymer composites over untreated wood was evaluated in terms of compression, impact strength and simultaneous DTG-TG-DTA in air. Compression, impact strength and resistance of wood against thermo-oxidation were improved with impregnation of polyacrylonitrile. Impregnation of polyacrylonitrile into poplar wood was ascertained through UV-vis spectroscopy and SEM⁸⁷.

A series of composite materials was prepared incorporating polyhedral oligomeric silsesquioxane (POSS) derivatives into polycarbonate, by melt blending. Significant differences in compatibility were observed depending on the nano-scale filler's specific structure: trisilanol POSS molecules generally provided better compatibility with PC than fully-saturated cage structures, and phenyl-substituted POSS grades were shown to be more compatible with PC than fillers with other functional groups. Trisilanolphenyl-POSS/PC composites possess the best overall performance among the POSS materials tested. The high compatibility between the trisilanolphenyl-POSS and polycarbonate matrix results in generation of transparent samples up to 5 wt% POSS content. Slightly enhanced mechanical properties including tensile and dynamic mechanical modulus are observed with the increase of trisilanolphenyl-POSS loading at the cost of decreasing ductility of the nanocomposites. Importantly, upon orientation of the PC/POSS nanocomposites, crystallization of POSS within the oriented material results-this observation is consistent with a growing number of observations which suggest that 'bottom-up' formation of structures incorporating multiple POSS cages result from orientation of these nanocomposites, and that the hybrid organic-inorganic inclusions may be at the heart of observed nano-scale reinforcement⁸⁸. The degradation of poly (ethylene oxide) and polyacrylamides in aqueous solution were studied

with ascorbic acid. Gel permeation chromatograph was used to monitor molecular weight dynamics with time. A model based on continuous distribution kinetics showed that the experimental data matched well with theory. The results showed that the degradation of polymers is significantly enhanced in the presence of ascorbic acid. The degradation rate initially increased with ascorbic acid concentration but was independent of it at higher concentrations⁸⁹.

Poly (vinyl chloride)/calcium carbonate (PVC/CaCO₃) composites with micrometer or nanometer CaCO₃ as fillers were prepared by the solution blending method. The TGA of the composite films conducted in N₂ atmosphere showed that the addition of the CaCO₃ fillers could improve their thermal stabilities. It was also found that the nanometer CaCO₃ filler provided better thermal stabilities than the micrometer fillers even with a smaller amount. The mechanism of the improvements was investigated by a facile chemical analysis developed to examine the thermal stabilizing effect of calcium carbonate particles with different sizes in PVC/CaCO₃ composites after the pyrolysis of the samples in an air atmosphere in an oven⁹⁰.

Four types of fabrics woven from various polyaramid fibers of Nomex and Kevlar blends were characterized by morphology, XRD, elemental analysis, thermal analysis, and moisture adsorption isotherms. The blends consisted of Polybenzimidazole/Kevlar blend (40% PBI and 60% Kevlar→, Nomex Delta A (blend of 60% Kevlar and 40% Nomex→, Nomex Delta T (blend of 75% Nomex, 23% Kevlar, and 2% P140 antistatic fiber), and Nomex III (fabric with a 95/5 blend of Nomex and Kevlar) containing 1% steel fiber. TGA and DTG curves have been compared to evaluate thermal behavior of the PBI, Kevlar, and Nomex blends and the results were correlated with the moisture sorption data. The data were also compared with fiber morphologies provided by SEM and crystallinities derived from XRD diffractograms. Moisture adsorption isotherms were correlated with a number of empirical models. The linear regression models were statistically analyzed to obtain the best fitting model that explains the sorption profiles of the samples and theoretical monolayer moisture

capacities of Nomex and Kevlar blends were calculated by using Hüttig isotherms⁹¹.

The miscibility behavior of melamine-formaldehyde (MF) resin and PVAc blends for their use as adhesives for bonding fancy veneer and plywood in engineered flooring was studied, by differential scanning calorimetry DSC, TGA and FT-IR. Blends of various compositions of MF resin/PVAc were prepared. To determine and compare the effect of PVAc content, blends with PVAc to MF resin weight ratios of 0, 30, 50, 70 and 100% were prepared. These blends displayed a single cure temperature over the entire range of compositions indicating that this blend system was miscible in the amorphous phase due to the formation of hydrogen bonding between the amine groups of the MF resin and the carbonyl groups of PVAc⁵⁶.

Rubber modified polysulphone synthesized using an extrusion process without addition of compertabilizer. The main properties required are flexibility and thermal resistance of material. We choose a polysulfone for its properties of thermal behaviour, and interpenetrating network as minority flexible phase. The blends carried out contain 5, 10, 15, 20, 25, 40, 50, 60% of rubber flexible phase. We follow the evolution of the mechanical properties

by the study of the storage modulus of blends. The thermal properties come from the change of T_g of each component in the blend. The stability of the properties of the blends can be connected to their internal morphologies. All these properties have been studied with the traditional techniques of characterization: DMTA, TGA, and SEM. Results tend to showed the immiscibility of phases in these blends. However, in spite of the presence of two different phases, the blends presented interesting mechanical and thermal properties thus a uniform morphology⁹².

Conclusions

Thermal characterization of materials and evaluation of thermograms to ascertain the kinetics, mechanism and thermodynamics of solid state decomposition under isothermal conditions has recently gained great analytical potentials for polymers and related composite materials. Since past few years, a variety of polymers and related materials were investigated for their thermal properties and the thermal data were further extended to explore the kinetics and thermodynamics of solid state decompositions. The thermal data reveled that thermal properties of polymers are greatly influenced by their structure and applied modifications.

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