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Report on the Workshop on Organic Materials
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A STUDY OF ORGANIC MATERIALS USING THERMAL ANALYSIS

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Thermal analysis is being used not only for evaluation of the state and composition of organic material, but also for the evaluation of the process itself. The whole process can be mimicked in the DSC cell and, in this way, a lot of material and time can be saved.

In the four following investigations which were presented in the Workshop and which are abstracted here, we clearly see how the whole industrial process is progressing in the cell; simultaneously, the properties of the materials are studied.

Four different areas were covered in the Workshop: photocuring, fiber spinning, flame proofing and surfactant mixing. These contributions cover only a small part of the application of thermal analysis in the study of organic materials.

OPTIMIZATION OF THE PHOTOCURING OF A TERNARY MIXTURE OF METHACRYLIC MONOMERS USING DSC

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The main purpose of this workshop on thermal analysis of organic materials is to discuss some technical applications of thermal analysis in the field of industrial research. In the past few years, thermoanalytical methods have started to gain a lot of attention in many fields of industrial research, especially in the areas of electronic materials and coatings. One of the best examples is the use of DSC for characterization of photochemical processes such

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as the photopolymerization of acrylic or methacrylic monomers. Almost any standard DSC cell can be used for such experiments, the only modifications needed are the replacement of the original cover of the cell by pyrex or quartz covers and the addition of a standard U.V. hand-lamp mounted at a controllable distance above the cell. Other features such as shutters or filters can be added, but are not essential for routine work. The system is easy to work with, makes use of very small samples, and can easily monitor the effects of many parameters such as the surrounding atmosphere, wavelength and light intensity, concentrations, temperature, etc. The data flow is continuous, and kinetic parameters are therefore easily retrieved. According to our experience, photocuring conditions and optimal concentrations of initiators and oxygen scavengers, as determined in small scale use of DSC, proved to give excellent results also in real-scale applications. In conclusion, DSC is recommended as one of the methods of choice for the characterization of photopolymerization reactions.

THE THERMAL RESPONSE OF HEAT RESISTANT FIBROUS INSULATIONS

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The investigation of the thermal response of heat resistant fibrous insulations exposed directly to flames and radiant heat is important to the understanding of their protective performance. Organic fibers may undergo dimensional change, endothermic and exothermic chemical transitions, surface modification and mechanical breakdown. These affect the heat flux actually transmitted through the protective insulation layer during the exposure sequence. It is therefore not surprising that initial thermophysical properties of the insulation material correlate poorly with measured protective performance.

Monitoring the spatial dimensions, thermal conductivity, heat capacity, surface properties and opacity of the insulation during thermal exposure has shown that the thermal diffusivity of the system changes as a function of exposure duration.
Non thermoplastic and endothermically charring fibers such as preoxidized acrylic, cross-linked phenolic (novoloid), FR treated cellulosics and the newly available ionically cross-linked Inidex fibers, gradually decrease bulk density while maintaining thickness and opacity to radiant heat. These materials are used as multiple thin layers in ablative systems where extended protection may be required. The sacrificial destruction of the outer layers protects the inner layers as the thermal pulse slowly advances through the insulator.

Thermal exposure and measurement of the transmitted heat is performed on a CSI thermal protection performance (TPP) tester.

The instrument allows control of the thermal flux level, the balance of radiant to convective heat and the exposure duration. These data coupled with the thermophysical properties of the exposed material are used in the calculation of the amount of protective material required for specified hazard conditions.

APPLICATION OF THERMAL ANALYSIS (DSC) IN THE STUDY OF POLYMORPHIC TRANSFORMATIONS

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The kinetics of polymorphic transformations in monoacid saturated triglycerides and the influence caused by the presence of certain solid surfactants were investigated.

Normal fats are polymorphic and can exist in more than one crystalline form. The main phase transitions are between hexagonal (α), orthorhombic (β') and triclinic (β) forms. In spite of the wide information available in the literature concerning the characterization of the specific polymorphs, less emphasis has been on the mechanism of transformation. Following after the polymorphic transformation during heating in the DSC, it was observed that both the mechanism and rate of transformation of the triglyceride strongly depend on its chemical structure, kinetic conditions and presence of additives. The presence of the additive did not dictate the formation of any preferred polymorph but rather controlled the extent to which the molecule could undergo configurational changes. The difference between the addition of emulsifier and addition of tripalmitin to tristearin was outlined. Their effect on the polymorphic behavior of tristearin was completely different. While the presence of the surfactant does not influence the polymorphism of tristearin, in the presence of tripalmitin the intermediate β'-form is apparently stabilized.

THE USE OF DSC IN PROCESS CONTROL IN THE PRODUCTION OF NYLON 6.6 YARNS

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DSC has been utilized in two test methods for evaluating the degree of polymer degradation and exposure to steam during the melt spinning and subsequent setting of commercial nylon 6.6 drawn yarns. Both test methods use the melting endotherms in which higher and lower temperature peaks are caused by two crystalline-type formations. Therefore, the effects of the degradation and steam treatment on the crystallization modes enables evaluation of the extent of the effect on the yarns possible.

The method for the evaluation of the degree of degradation during melt spinning is based on T.S. Long's Degradation Index*. The samples are heated to a temperature above the melting point in the DSC cell, then cooled to the crystallization onset temperature and maintained there for one hour (annealing) and then heated to a temperature above the melting point. There are two melting peaks: 255°C and 264°C. The higher to lower melting peak heights ratio determines the fiber's degradation index. We found a good correlation between the spinning temperature and the melted polymer residence time and between the fiber's Degradation Index.

The lower and higher melting endotherms may be related to two crystalline types associated with (1) the degraded lower molecular weight and (2) the unaffected higher molecular weight polymer. At the annealing stage, the higher molecular weight polymers generate longer and more perfect crystals, since they undergo a longer period of supercooling and have greater structure regularity. Those crystals melt at a higher temperature relative to those of the less perfect crystallites originating in the degraded molecules.

In the production process, the as-spun yarns undergo a steam treatment followed by a cold drawing. The drawn yarn has two melting peaks: (1) 255°C and (2) 264°C. The peak height ratio depends on the extent of steam treatment. Drawing without prior steaming eliminates the 255°C peak, while high pressure steam application generates the 255°C as a major peak. Medium and lower steam pressures yield an intermediate peak height ratio.

We relate the low melting peak to the process of crystallization of spherulites during the steaming operation, while the high melting peak is related to the more stable extended chain crystals formed during the subsequent cold drawing.

*T.S. Long, "Degradation of Nylon 6,6, using DSC", ASTM STP 516, 126,142 (1972).