THERMAL ANALYSIS OF FIBRE FORMING POLYMERS
Multiphase systems

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Abstract

Different levels of fibre technologies and application, from synthesis to degradation has been studied using the methods of thermal analysis. Recent results of these studies on synthetic and natural fibres are summarized. The effect of chemical and physical modification of polyolefin fibres as well as the synthesis of polymer emulsion used as additive in fibre technologies could be followed by DSC, DMA, TG methods.

Keywords: composite fibres, DMA, fibre structure, flame retarded polypropylene DSC, grafted polyolefin fibres

Introduction

The knowledge of the thermal properties of fibrous materials played always an important role in the human history. It was the case at the beginning with wood which is in fact a fibre reinforced natural composite. Rubbing of wood for initiating fire was based upon the first knowledge of thermomechanical behaviour. Later examples are the Turin shroud, with its unsolved questions and nowadays the high performance fibres in space vehicles that must bear extreme thermal circumstances [1, 2]. It is the quick development of advanced fibre technology that initiates the application of more and more liable analytical methods, so the stress in this paper is put also on the technology of fibres.

The appropriate control of the properties of the fibres require the consideration of the structure-property relationship at each level of processes, as it is shown in the Fig. 1. Several elements of structure can be studied by the methods of thermal analysis, such as DSC, MDSC, TMA, DTMA, TSP, TSD, TG-MS and temperature controlled microscopy, but in some cases these must be combined with other methods.

Comparing to other fields, a lot of special technical problems may occur during the analysis of fibres. These problems and their solutions are summarised in Table 1.
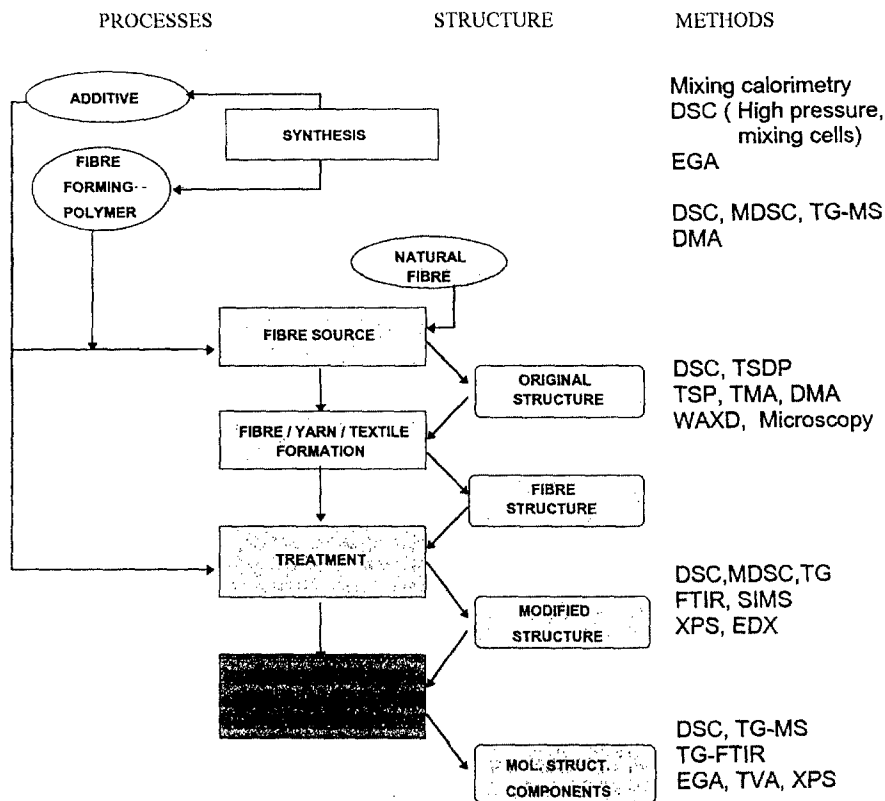
Fig. 1 Processing steps and relating structure control by the most effective TA and additional methods to ensure optimal fibre properties

Experimental

Materials

The polymer grades used in this study were:

Linear polyethylene (LPE): Tipelin PS 380 09 product of Tisza Chemical Works (Hungary) density: 0.938 g cm^{-3}, melt index: 1 g min^{-1} (50 N, 190°C)

Polyproylene (PP): Tipplen H534 and Tipplen K793 polypropylenene homopolymer and ethylene-propylene copolymer products of Tisza Chemical Works (Hungary) density: 0.9 g cm^{-3} melt index: 4 and 0.8 g min^{-1} (21.6 N, 230°C) respectively.

Elastomer: Ethylene vinyl acetate copolymer (EVA): EVA 3325 (ICI), Vac content: 33%, density: 0.98 g cm^{-3}, melt index: 28.8 g min^{-1} (21.6 N, 230°C), Ethylene-propylene-dien terpolymer (TPEPDM): Vestopren FB 10000 (Hüls) (mixture of amorph EPDM and HDPE).

Table 1 Methodical problems of thermal analysis of fibres

Problems	Solution
Difficult to ensure the reproducible pre-treatment of long fibres	cutting, winding
Difficult to achieve thermal equilibrium in the sample	using of tightly closed crucibles
The thermal history effects the results	repeated heating up after controlled cooling from temperature ~15°C higher than the melting temperature of the fibre
Relaxation of the fibre due to heating modifies the original structure	constraining the sample
The ratio of heating rate and relaxation speed effects the results	rate dependent studies
Degradation may occur at melting temperature	fast heating method
Sensitivity of TG results to specific surface of fibres	careful grinding

Filler: $CaCO_3$, Millicarb, mean particle size: 2.5 μm (Omya).

Flame retarding additives: Commercial samples of ammonium polyphosphate(APP) (Hostaflam 422, Hoechst), pentaerythritol D/S (PER) (Degussa), and melamine (ME) (Reanal) were used as supplied. Their ratio in the intumescent system was APP:PER:ME = 1:0.2:0.2.

Measurement

DSC measurements were performed using Setaram DSC 92, sample weight: 10 mg, heating rate: $10°C \ min^{-1}$, atmosphere: static air or flowing nitrogen (if not stated in Figures otherwise).

DuPont Dynamic Mechanical Analyser 981 was used for thermomechanical (DMA) measurements with sample dimensions of 1×5×10 mm, and at heating rate of $5°C \ min^{-1}$. Depending on the modulus of the sample the frequency changed between 38 and 3 Hz.

Derivatograph MOM 3427 simultaneous thermal analyser was used for TG, sample weight: 100 mg, heating rate: $10°C \ min^{-1}$, atmosphere: air.

Results and discussion

Considering the different processes listed in Fig. 1, we chose some characteristic examples from our practice and from the literature in order to extend an excellent earlier review of this field with some recent results [3].

Synthesis

PA 6, which is one of the most important synthetic fibre, can be produced by hydrolytic, or more generally, by cationic polymerization. The later complicated mechanism can be studied through the amine salt initiated polymerization of caprolactam, which includes subsequent steps of hydrolytic polymerization due to water formed in a simultaneous reaction [4]. High pressure chamber has been applied to carry out the polymerization at 14 bar [5]. DSC curves clearly demonstrated, that the presence of the two kinetic stage of the polymerisation depend on the initiator concentration [5].

Polymer emulsions are commonly used as additives in the fibre technologies. DSC investigation of emulsion polymerization, however has been hindered by the lack of intensive mixing and other special requirements. The Table 2 summarizes the methods we found to be effective to overcome these difficulties.

The emulsion polymerization of styrene has been carried out as model tests in Setaram DSC 92. The curves of anisotherm and isotherm polymerization in Fig. 2 and 3 respectively show the characteristic three stages of emulsion polymerization: the increasing speed up to $65^{\circ}C$, than stationary stage between $65-79^{\circ}C$ and decreasing speed between $79-81^{\circ}C$ in Fig. 2 and similar ranges of time in Fig. 3.

The small peaks at $77^{\circ}C$ and at 4750 s respectively are characteristic for gel effect. This results prove that the preparation of stable miniemulsion (particle size 100–500 nm, compared to 1–10 µm in the conventional emulsions) by using special surfactant-cosurfactant combination is successful process for DSC investigation of emulsion polymerization. In Fig. 3 the importance of avoiding the transient instabilities can be seen as well. Without applying a heating program

Table 2 Methodical problems of thermal analysis of emulsion polymerization

| Problems	Solution
Instability of the monomer emulsion, without stirring	preparation of miniemulsion by appropriate surfactant-cosurfactant combination
Initiation of the reaction may occur before starting the measurement	sample preparation at low temperature using liquid nitrogen
Base line instabilities at transients of heating program of isothermal tests	multi stage heating program at the end of fast heating
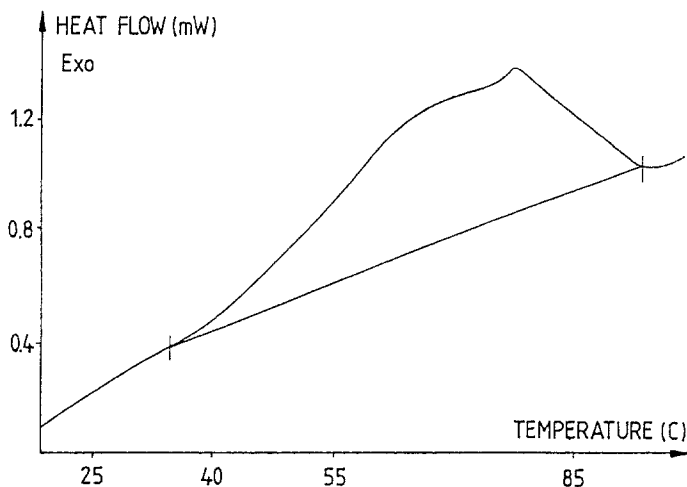
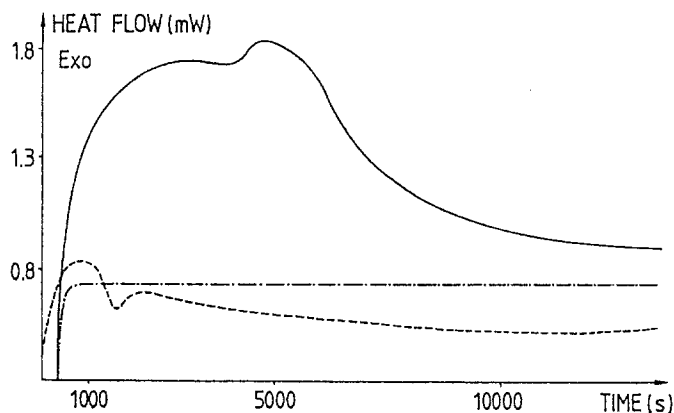**Fig. 2** Anisothermal DSC curve of polymerization of styrene emulsion Heating rate: 0.2°C min^{-1}

Fig. 3 Isothermal DSC curve of polymerization of styrene (——) at 60°C Control curves (with empty crucibles): - · - · - heating up with 100°C min^{-1};---- heating up with three stage program

of three stages: 100°C min^{-1} up to 55°C, 10°C min^{-1} up to 59°C and 2°C up to 60°C, the unstable region covers the 10% of the reaction time.

Fibre formation

The final properties of the fibres may differ substantially from each other even if their chemical composition and origin are the same. These properties can not be governed without understanding the relationship between the processing conditions and the structure. Several authors have pointed out the
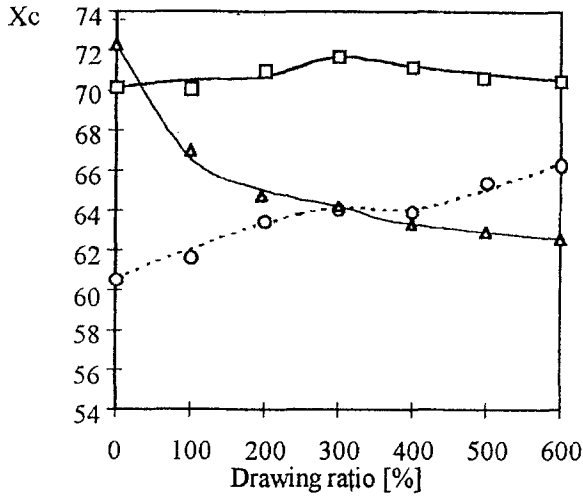
Fig. 4 Degree of crystallization (x_c) of the phases in PP and PP + LPE fibres: ---o--- $X_{c\ PP}$ [%] of PP fibres; —□— $X_{c\ PP}$ [%] and —△— $X_{c\ LPE}$ in 20% LPE containig PP fibres
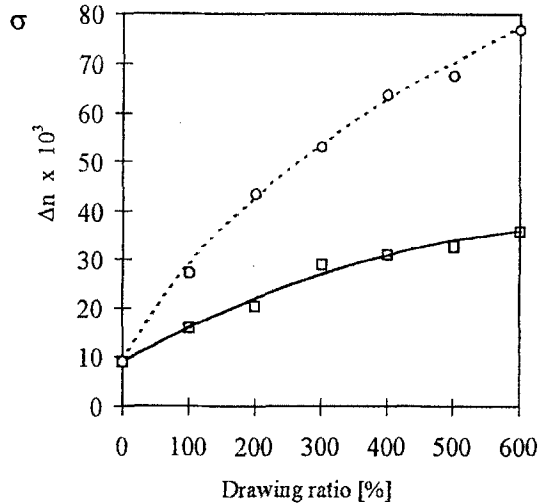

Fig. 5 The tensile strenght (σ) [mN/dtex] and birefringence ($\Delta n \times 10^3$)(degree of orientation) of PP + 20% LPE fibres against drawing ratio: —□— Birefringence; ---o---Tensile Strenght

differences of thermoanalitical behaviour due to the modification of processing conditions [6–10]. The more complicated case of multiphase fibrous systems (such as bi- or multicomponent fibres etc.) however, which is effected by the composition and the original structure as well, is much less studied.

In case of polypropylene (PP), the effect of drawing ratio on the degree of crystallinity (calculated on the base of apparent heat of fusion) is shown in the Fig. 4.

The increase of enthalpy of fusion (as well as melting temperature) is a result of recrystallization and crystal-perfecting process of drawing [8, 9]. The presence of linear polyethylene (LPE) in PP fibre however modifies this relationship between drawing and melting characteristics: The relatively high crystallinity in PP phase does not change while in the LPE phase decreases (Fig. 4). The tensile strength and birefringence of blend fibres increase with drawing ratio due to the orientation of amorph and crystalline phases (Fig. 5), suggesting that the interaction of the components promotes the formation of highly ordered crystallyne phase, but the drawing temperature is high for LPE phase so the forced alignment of structure elements in this phase occurs mainly in the amorph region. Further details concerning the processing of fibre forming polyolefin blends has been reported earlier [11].

The thermomechanical spectrums (TMA, DMA or DTMA) serve more detailed information about fine structure of fibres and physical transitions than DSC or DTA experiments.

Recent TMA shrinkage results of polyester fibres proved this structure sensitivity: Not only the transitions of the phases could be determined, but the results reflected the presence of rigid-amorph material at the phase border as well. The amount of shrinkage of different polyester fibres is in correlation with the concentration of the tie molecules, rather than the orientation of the amorph phase [10].

The composite fibres represent a new type of engineering fibres. Flexible control of their properties can be achieved not only by changing the processing conditions, but also through the design of the ratio of components and the original structure. Such a PP fibre containing filler and elastomer additive is shown in the Fig. 6. In this case the DMA thermograms served the most detailed information about the structure. The loss modulus (E'') peaks belong to physical transitions of the polymer components. The interaction between the phases and the structure of the interphase can be evaluated on the base of the place and magnitude of these loss peaks: The shift towards higher temperature and increased intensity of the loss peak at the glass transition temperature of PP under the influence of filler is a consequence of the interaction between the phases [12]. Just the opposite change can be seen on the curve of PP composites when elastomer and surfactant as interfacial additives are present suggesting interaction between the filler particles and the surrounding elastomer phase instead of filler and PP phase. These results are in accordance with the earlier results of Electron Microscopy, Dielectric Spectroscopy and Secondary Ion Mass Spectroscopy [13–15].
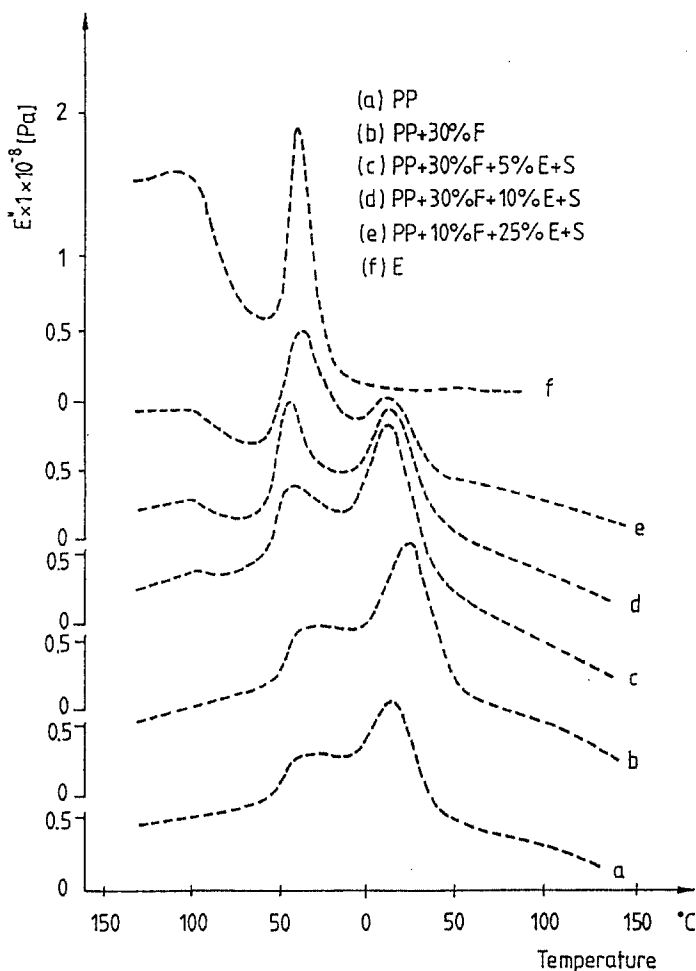
Fig. 6 The loss modulus curves of PP composites. F: CaCO$_3$; E: TPEPDM; S: Glycerol monostearate

Treatment

The grafting of PP fibres by monomers containing acidic groups modify the physical- chemical characteristics of the hydrophobic fibres. Thus, the incorporation of such groups renders the fabric more hydrophilic. These modifications cause significant changes in the thermal behaviour of the fibres as well. Grafting of PP fibres with acrylic acid is reported to reduce the crystallinity and increase the decomposition temperature [16]. In presence of filler in such system the acidic groups may react with the OH groups on the filler surface giving rise to better interaction at the interface. The Fig. 7 shows the DMA traces of
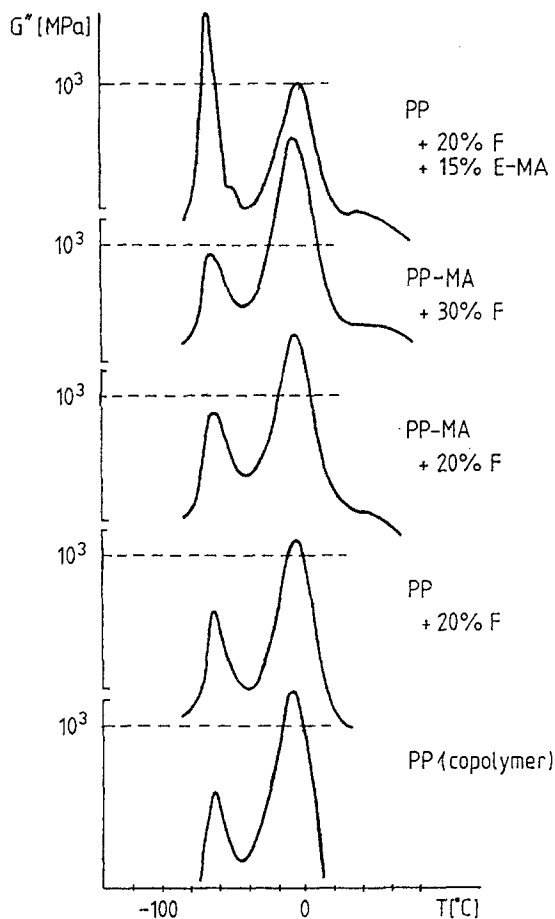
Fig. 7 The loss modulus curves of grafted PP composites. F: glass fiber; E: TPEPDM; PP-MA: PP grafted with 1% Maleic anhydride; E-MA: TPEPDM with 1% Maleic anhydride

this later interaction in presence of modifier acidic groups. The increased intensity of the loss peak at glass temperature of PP is a sign of improved interaction. If an elastomer as additive is grafted with acidic group the peak characteristic to elastomer-filler interaction is increased.

The methods of thermal analysis proved to be successful to follow the effects of treatments in case of the natural fibres as well. In the complicated composite structure of wool fibre fibrous elements of different thickness are embedded into each other: macrofibrils, microfibrils, protofibrils. The most important properties of the fibres are determined by the α-helix content of protofibril, which can be modified by physical, or chemical treatment. Comparative WAXD and thermoanalytical studies in Wollforschungsinstitut Aachen proved that the

enthalpies of the endotherm DSC peaks at 230–240°C are in good correlation with the helix content [17]. It serves a quick and reliable way for checking the effects of modifications.

Degradation

Degradation is one of the most thoroughly studied processes of fibre technology. The combination of TG measurements with other methods further extended the possibilities in this field. Simultaneous TG-FTIR investigations clarified for example that the simple TG curve of wood covers complex reactions over the temperature range of degradation [18]. The TG-MS method contributed to the understanding of the formation of C fibres through controlled degradation of polyacrylonitrile fibres and the mechanism of degradation of film or fibre forming polyethylenes through the identification of the molecules in the evolved gas [3, 19].
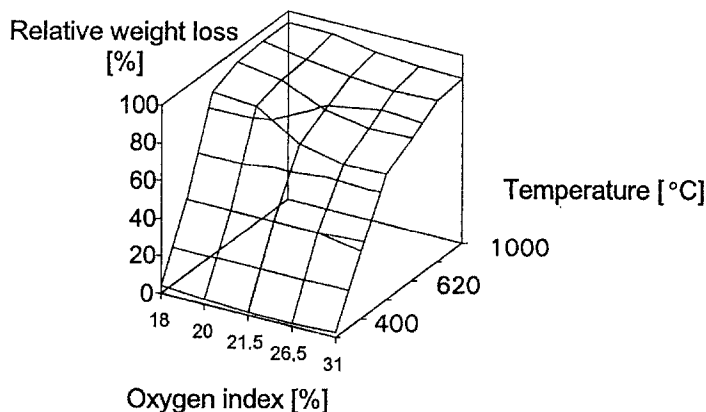

Fig. 8 TG results of PP vs. flame retardant efficiency

The degradation of flame retarded fibres is a subject of TA for a long time. Several halogen and phosphor containing additives have been applied for finishing of cellulose fibres [20]. In recent works the stress is put on the application of halogen free, intumescent flame retarding additives especially for synthetic fibres. The TG results are in good correlation with the efficiency of flame retardants, like in the case of PP on the Fig. 8.

The efficiency of flame retardants is expressed here by the maximum oxygen ratio, at which they still prevent the ignition. Increasing the oxygen index the loss curve is more and more moderate. The high volatility components of the evolved gas of such materials has been determined by SA-TVA method [21]. Recently published DSC studies of these flame retarded fibres clarified the main steps of chemical reactions in course of the process that may contribute to find the optimal technology [22].

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