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THERMAL ANALYSIS OF POLYMERIC MATERIALS LOOKED AT FROM THE ENVIRONMENTAL AND RECYCLING POINT OF VIEW

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This paper presents DSC investigations on the curing kinetics of an epoxy-polyester (EP/PE) powder coating system with two different accelerators and on the crystallization behaviour of a semicrystalline thermoplastic containing regranulate. In addititon thermal degradation and entropy relaxation effects of an amorphous thermoplastic due to different injection moulding parameters are discussed. Thermogravimetry results are presented for quantitative analysis of rubber, and for elucidating problems which may arise during the injection moulding of thermoplastic regranulate which is obtained from painted rejects.

The measurements were carried out using NETZSCH DSC 200 (heat flux DSC) and thermobalances TG 439 and TG 209.

Keywords: environment, kinetics, paint residue, recycling, rubber, thermoplastics

Introduction

The application of polymeric materials and organic solvent-containing paints is a very controversial subject. This is because of the possibly existing, or maybe only suspected environmental incompatibility of these substances. Plastic refuse, like steel or aluminum are too valuable to be incinerated or/and deposited. From this point of view, different methods of thermal analysis are generally recognized as sensitive techniques for the qualitative and quantitative characterization of polymeric materials [1, 2].

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Experimental results

DSC investigations

Kinetic examinations of EP/PE powder coatings (paints)

Paints are used not only to attain the desired optic and haptic effects, but also for protecting against weather influences and sunlight. Powder coatings due to the absence of solvents, have in recent years, shown a far above proportional increase over conventional paints. Their disadvantage at this time is their still extremely high curing temperature when used on the surfaces of polymeric materials. Here a new multiple scan non linear regression thermokinetic analysis software module [3] proved to be a powerful technique to shorten the time to optimize such powder coating systems. These systems may be suitable for painting polymers.

EP-PE-powder coatings during the first heating cycle normally exhibit an endothermic relaxation peak superimposed on the glass transition, which the paint industry calls the 'melting area'. This effect sometimes prevents the determination of the start of reaction during DSC-measurement. For this reason the temperature schedule (Table 1) below was developed:

Table 1 Temperature schedule for the kinetic examination of EP-PE-powder coatings

Step No.	Type	Starting Temp. / °C	Ending Temp. / °C	Heating resp. cooling rate / $deg \cdot min^{-1}$	Isothermal stop / min
1	dynamic	20	85	20	–
2	isothermic	85	85	–	10
3	dynamic	85	–20	20	–
4	dynamic[1)]	–20	280		–
5	dynamic	280	–20	20	–
6	dynamic	–20	130	20	–

[1)] This step was evaluated with the assistance of the kinetic Multiscan-Software-Module. For heating rates 5, 10 and 20 $deg \cdot min^{-1}$ were chosen.

Figure 1 showed that by pre-treatment (step 1 to 3) and by considering the measurements of the cured sample (step 6), a network forming reaction (step 4) was clearly fixed. Curve fitting technique for the curves measured with the three heating rates in the conversion range from 0 to 100% with a single step first order reaction would be unsatisfactory (Fig. 2 above) with a correlation coefficiency of 0.9888369. The correlation coefficiency (0.9971326) with an acceptable curvefit would be derived if the kinetic calculation was started firstly at a conversion degree of 20% (Fig. 2 below). This indicated that in this case there had to be at least

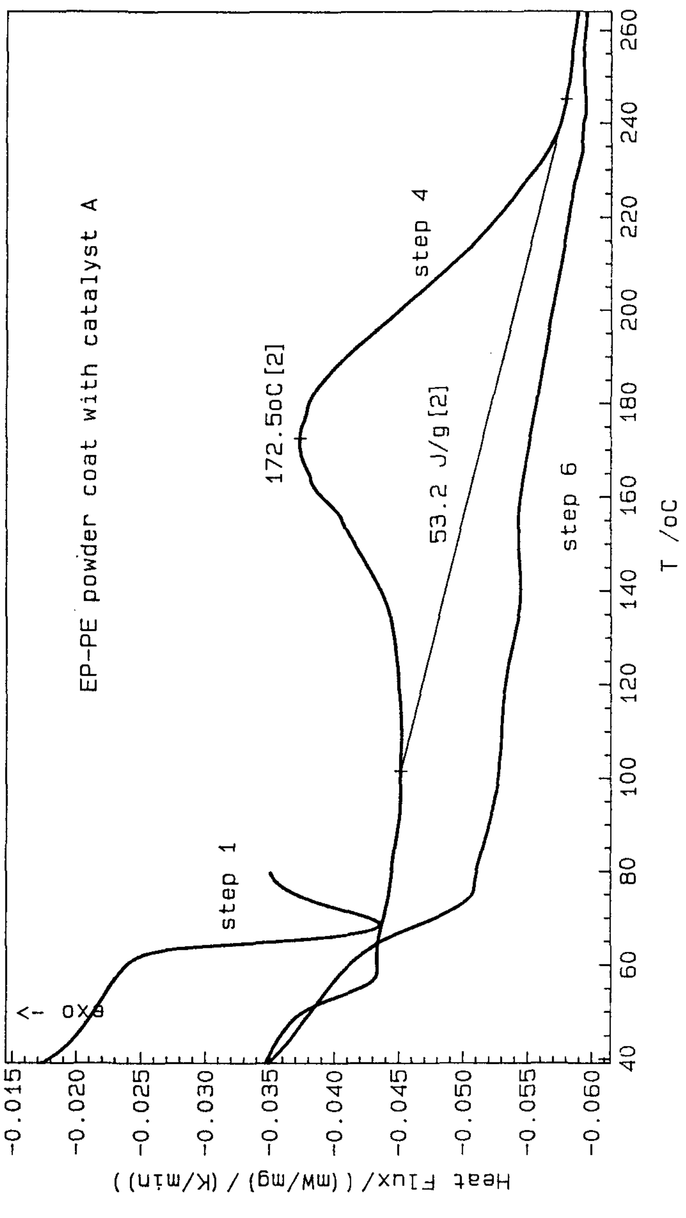

Fig. 1 DSC-curves showing the clear determination of the curing reaction

a double step networking reaction, which also shown in the representation of the activating energy in dependence on the conversion degree based on model free estimates according to Friedman [4] (Fig. 3 above) or rather Ozawa-Flynn-Wall [5, 6] (Fig. 3 below). Should one now model a double step follow on reaction of a *n*th order as first step and of a first order reaction as second step, then an excellent curvefit with a correlation coefficiency of 0.9980601 (Fig. 4) would be achieved for the entire conversion range from 0 to 100%.

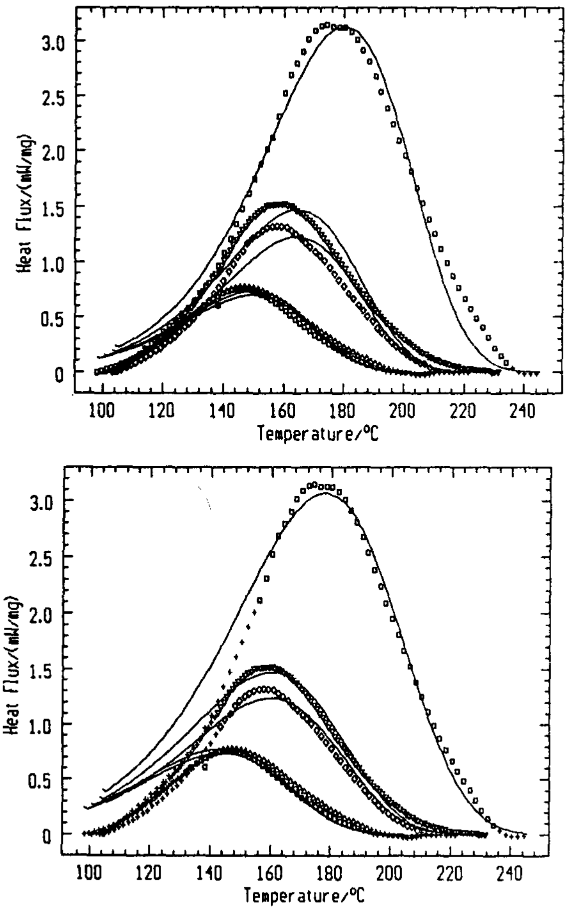

Fig. 2 Thermokinetic analysis of an EP/PE-powder coating from DSC multiple scans using of non-linear regression under the assumption of a first order reaction model above: Conversion degree 0 to 100%; below: Conversion degree 20 to 100%

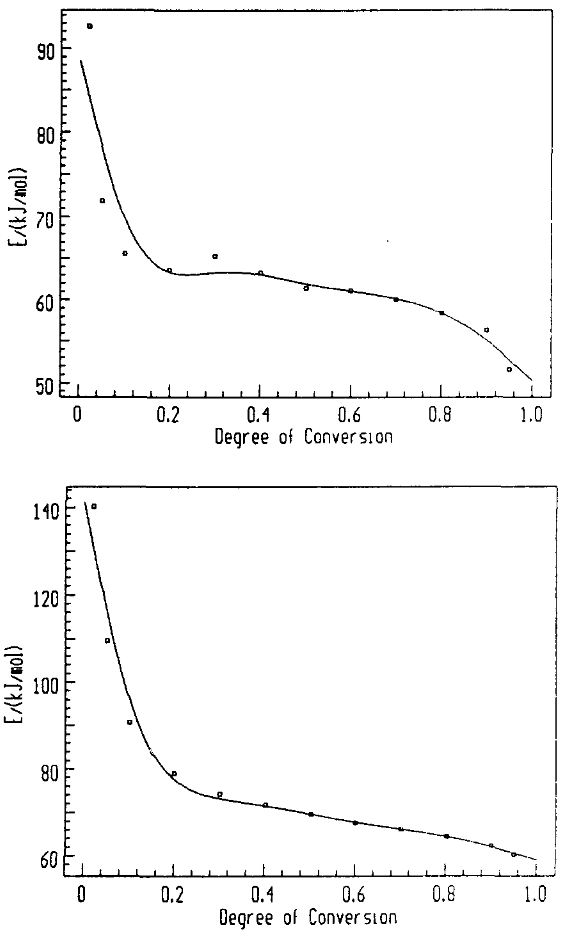

Fig. 3 Activation energy *vs.*conversion degree; above: according to Friedmann, below: according to Ozawa-Flynn-Wall

Table 2 depicts the kinetic parameters lg A (preexponential factor), activating energy E, reaction order n, share of the first step of the double step reaction for $\alpha = 0$ to 100%, which do agree very well for the second step with an only single step first order reaction starting at a conversion degree of 20%.

Thereafter, the same EP/PE-powder coating system with a different accelerator B was examined which, incomparison to the system with the original accelerator A (which has been discussed above), is presumed to have a lower curing temperature. This powder coating system could also be described to the optimum by use of a double step follow on reaction. Figure 5 depicts the Arrhenius plot of both powder coating systems.

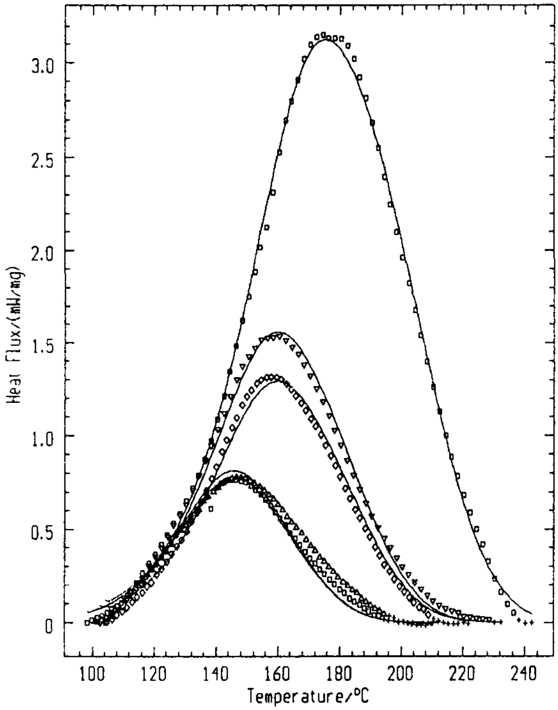

Fig. 4 Thermokinetic analysis of the EP/PE-powder coating system with aaccelerator A, as in Fig. 2, assuming a double step follow on reaction

Table 2 Kinetic parameters

Reaction model Kinetic parameter	Double step for α = 0 to 100%	Single step for α = 20 to 100%
lg A_1 (s)	7.38	–
E_1 /kJ·mol^{-1}	74.7	–
n_1	0.84	–
share of step 1 / %	18.1	–
lg A_2 (s)	4.10	4.59
E_2 /kJ·mol^{-1}	52.2	56.4
n_2	1	1

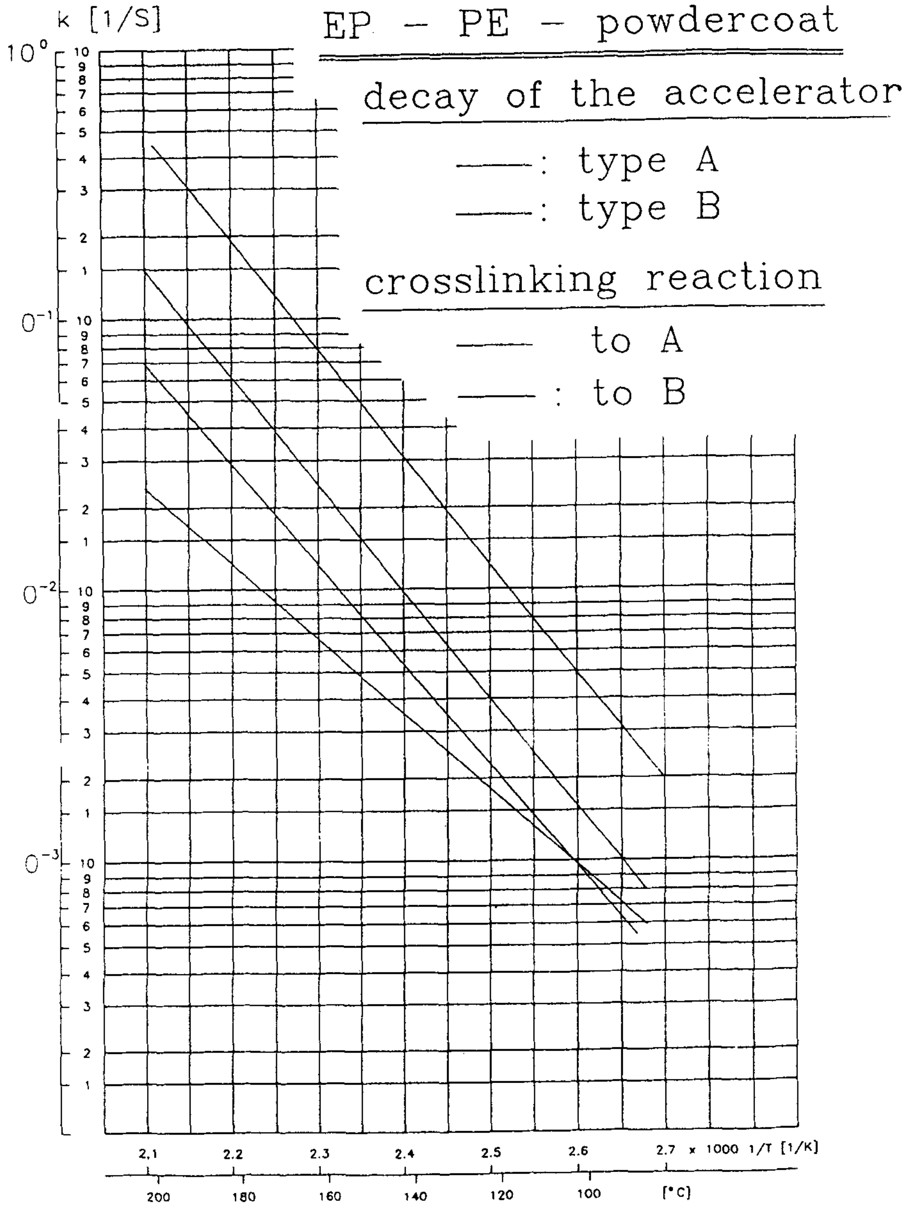

Fig. 5 Arrhenius plots of EP/PE-powder coatings using two different accelerators

System B is in fact substantially faster than system A, which makes either shorter curing times using the same temperatures or lower curing temperatures at the same curing times possible. Furthermore, the Arrhenius curves of both phases in system B are parallel to each other, compared to system A, which should lead to a uniform network of the coating and therefore to better technological attributes. This will be examined shortly. During this examination the value of the isothermal concentration-time-curve (Fig. 6) of the presumed reaction models A-B-C for the development of new powder systems and the correlation between these curves and the technological properties of the coating will be tested. In case of success the development times could be substantially shortened.

PARAMETER OF THE MODEL

lg10 (A1*s)	7.62443
E1 kJ/mol	76.46830
React.ord. 1	0.89860
lg10 (A2*s)	3.96536
E2 kJ/mol	50.97298
FollReact. 1	0.17726

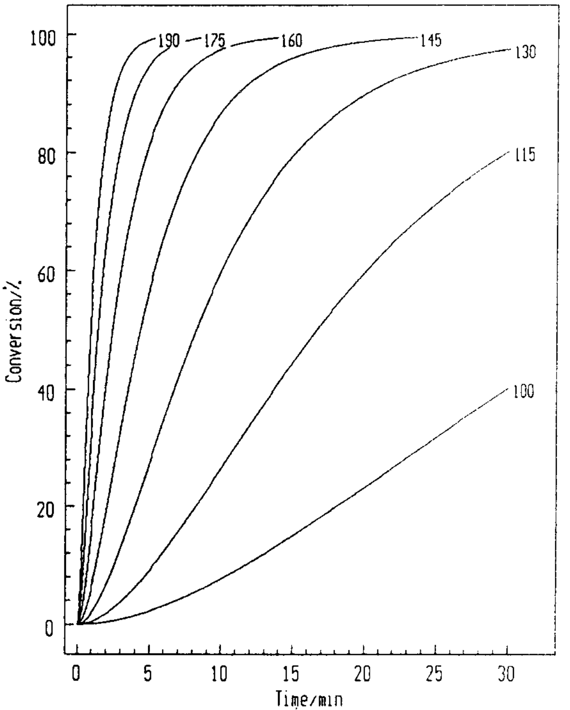

Fig. 6 Isothermal conversion *vs.* time curves based on the assumed reaction model (see Fig. 4)

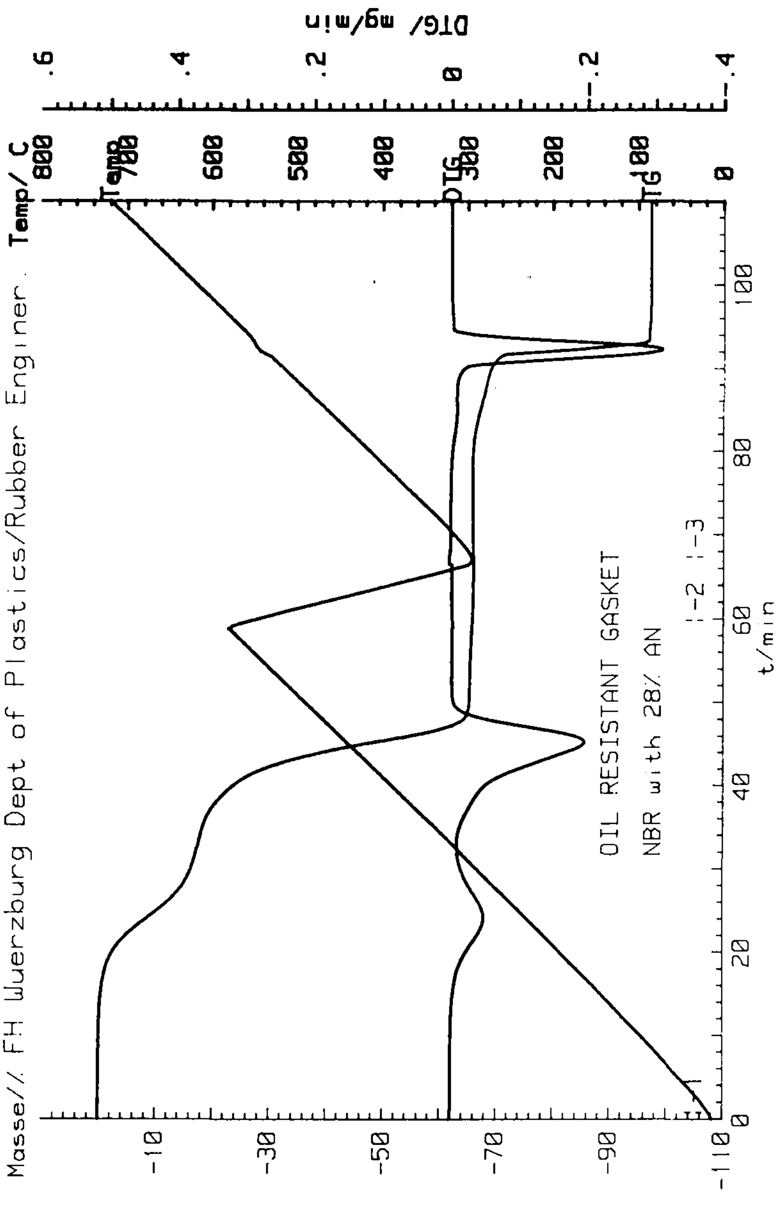

Fig. 7 LDPE cooling curves from the melt with constant cooling rates for samples with and without regranulate

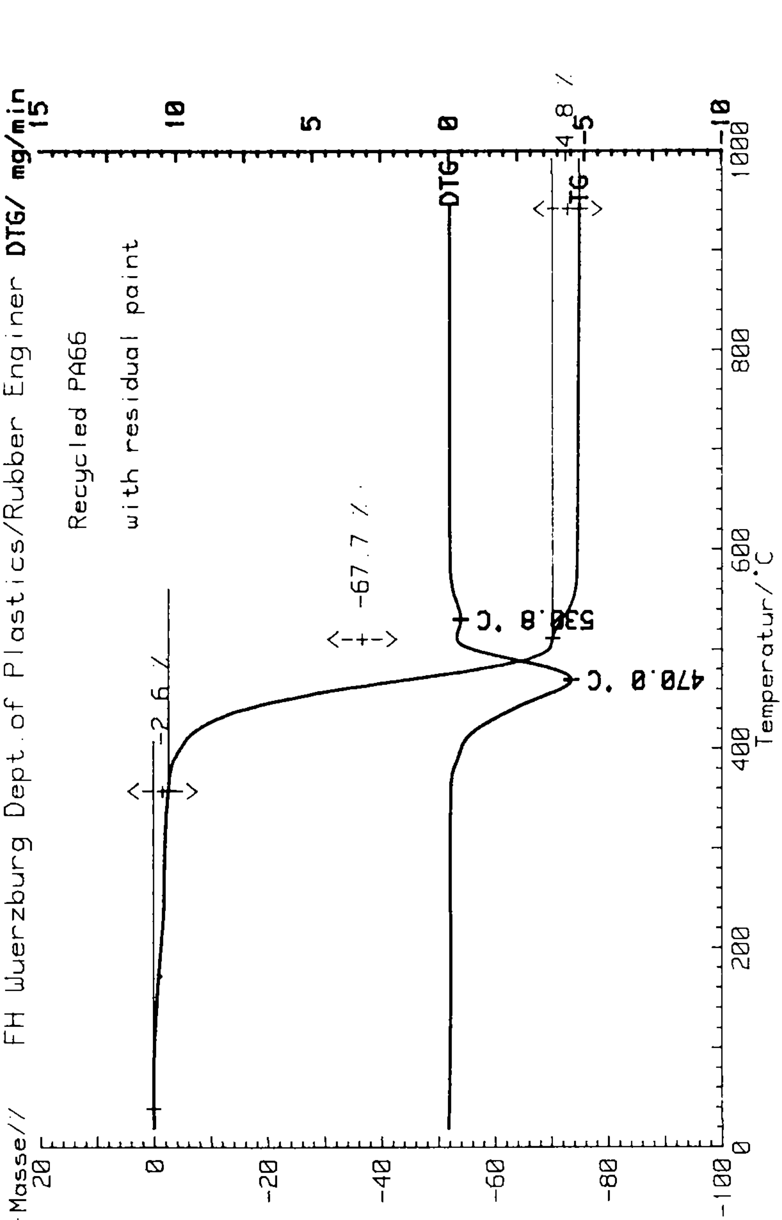

Fig. 8 DSC curves (2nd heating) of ABS as amorpphous thermoplastic in connection with processing conditions (mass and mould temperatures)

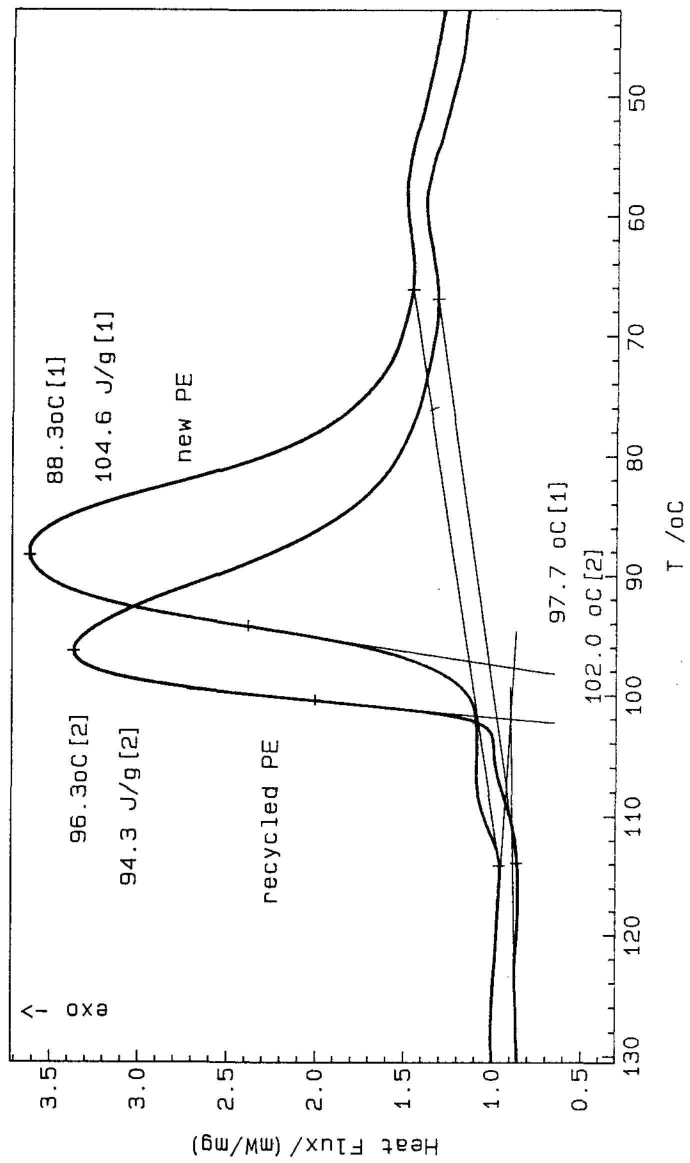

Fig. 9 Thermoanalytical curves of an oil resistant gasket made of nitrile rubber

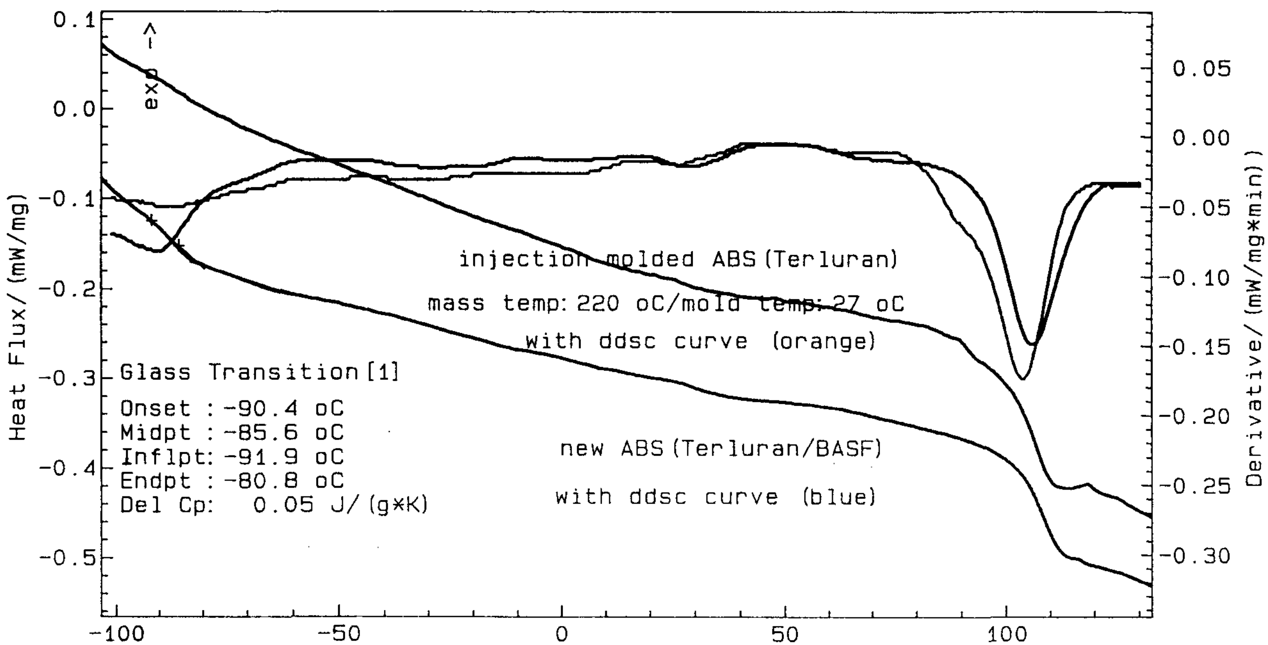

Fig. 10 Thermoanalytical curves of a P6 regranulate made of painted rejects

Crystallization of semi crystalline thermoplastics with and without regranulate

Figure 7 depicts the cooling curves of low density polyethylene (LDPE) during controlled cooling from the melt using constant cooling rates. In comparison to new material a higher onset temperature and speed (steepness of curve) of the exothermic crystallization is remarkable. Therefore the processing conditions have to be adopted to this fact. In this area also future kinetic examinations are planned.

Influence of injection moulding conditions on the morphology of amorphous thermoplastic

Amorphous thermoplastics have a most broad processing window. Nevertheless there are problems when adding pure grade recyclate to new material. The cause is depicted in Fig. 8 using the example of acrylonitril butadiene styrene copolymer (ABS). Here the butadiene block structures of ABS were clearly changed by the injection moulding process condition (see glass transition at about –85°C). Dependig on the injection moulding parameters used, exothermal entropy relaxation effects can also be seen during the first heating at temperatures just below the glass transition temperature of the styrene blocks. (These effects are not demonstrated here.)

Thermogravimetric results

Pyrolysis of rubber

Vulcanized rubber is a chemically networked material and therefore not recyclable by simple physical procedures (remelting) as thermoplastics are. Today work is being done on the pyrolytical back fission to monomers, from where polymers can be reconstructed. Figure 9 depicts the thermoanalytical curves of an oil resistant gasket made from nitrile rubber [7]. Especially interesting here is the visible small step prior to the carbon black combustion after switching from protective gas to oxygen. This represents the combustion of carbon build up during pyrolysis. It is attempted to progress in the future using the TG-coupling methods (MS, FTIR) [8].

Regranulate with paint residue obtained from painted rejets

The re-use of painted rejects still presents great difficulties today. One of the reasons is shown on the thermal curves of one such polyamid 6-regranulate (Fig. 10). A pyrolytical loss of weight is already realized in the mass temperature area of injection moulding of PA6, which could lead to bubble formation in the finished part.

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Zusammenfassung — Dieser Artikel beschreibt DSC-Untersuchungen an der Aushärtungskinetik eines Epoxid-Polyester (EP/PE) Pulverbeschichtungssystemes mit zwei verschiedenen Beschleunigern und am Kristallisationsverhalten eines semikristallinen Thermoplastes mit Regranulatanteil. Zusätzlich werden der thermische Abbau und Entropierelaxationseffekte eines amorphen Thermoplastes in Verbindung mit Parametern von verschiedenen Spritzgussverfahren diskutiert. Es werden TG-Ergebnisse für die quantitative Analyse von Gummi und für Aufhellungsprobleme dargelegt, die sich beim Spritzgiessen von thermoplastischem Regranulate aus gefärbtem Recycling-Material ergeben können.
Die Messungen wurden mittels eines NETZSCH DSC 200 (Wärmefluss DSC) und den Thermowaagen TG 439 und TG 209 durchgeführt.