FATIGUE BEHAVIOR OF POLYMER NANOCOMPOSITES

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1 General Introduction

The mechanical performance of polymers for products such as structural and load carrying parts, insulating materials or medical implants is of major importance to qualify the polymer for specific applications. Their inadequate performance or even premature failure can create damages to the product, or at its worst, by leading to the loss of human lives, if an accident due to failure of the polymer occurs. As result, the durability or long-term mechanical performance of polymeric materials has also become a prime concern in their adoption for industrial devices. Furthermore most of the loadings encountered are dynamical in nature and polymers are known to creep or relax under sustained loadings or to fail due to the formation of cracks, which afterwards start to propagate (Fatigue damage and crack growth). In view of all these, the knowledge on the long-term dynamic properties of the polymeric materials is therefore of great importance. Fatigue failure is a multi-stage process. It begins with the initiation of cracks, and with continued cyclic loading the crack propagates, finally leading to the rupture of the component or specimen. The limit between the above stages is not well-defined. The interest, to study the fatigue failure of polymers increased with the advent of industrialization. Because of the urgent need to design against fatigue failure, early investigations focused on prototype testing and proposed failure criteria similar to design formulae. Thus, a methodology developed whereby the fatigue theories were proposed based on experimental observations, albeit at times with limited scope. This type of phenomenological approach progressed rapidly during the past four decades as closed-loop testing machines became available [1].

Developments in linear and non-linear fracture mechanics provided another impetus for research on fatigue crack growth. In parallel, studies at micro-level shed light in the mechanisms of crack initiation and growth. The availability of high-magnification microscopes, such as scanning electron and transmission electron microscopes, during the same period was fundamental in identifying the governing fatigue mechanisms for various conditions. The advent of high-powered computational capabilities are now enabling a merger between the various approaches into fatigue failure process [1].

The concepts of fracture mechanics provide a detailed insight into the deformation and fracture mechanics of polymer materials. The analysis of the fatigue crack growth propagation (FCP) in particular can be regarded as an advanced technique to accurately characterize the mechanical response of a polymer material [2]. Typically, the behaviour is described by a double logarithmic plot of the fatigue crack growth rate, \( \frac{da}{dN} \), as function of the amplitude of stress intensity factor (\( \Delta K \)), acting at the crack tip. The characteristic plot emphasizes three discreet regimes (Figure 1). First the threshold regime, indication the initiation of the crack growth \( K_{th} \), then the regime of stable crack growth, and finally the fast fracture regime associated with the critical stress intensity \( K_{ic} \) [3]. The regime of stable crack growth is also referred to as Paris regime and shows a power law behaviour described by the relationship

\[
\frac{da}{dN} = C\Delta K^n
\]  

where \( a \) represents the crack length, \( C \) the crack growth rate at \( \Delta K = 1 \) MPa\(\sqrt{m} \) and \( n \) the slope of the curve on double logarithmic scale, respectively. Numerous studies demonstrate the potential of this
methodology to accurately analyze the crack resistance and inherent ductility of one-phase as well as nano-modified polymeric systems [4-6].

The exploitation of such advanced characterization technique also promises an in-depth understanding of mechanical failure of different kinds of polymeric materials, like polymer blends or reinforced polymers (including nano-additives). In order to improve polymers concerning their fatigue crack resistance there are several possibilities available. Firstly, the blending of thermoplastic polymers evolved into a well-established approach to provide materials with a set of desired properties [7,8]. In particular, multiphase blends consisting of at least two components are often favoured, as an exploitation of advantageous properties of each component appears feasible. Using the optimal blend composition therefore can lead to an improved resistance against crack growth, due to dynamic loading. Furthermore, toughening of thermosets with thermoplastic modifiers becomes very important, as the amount of such materials in the new generation of airplanes is quickly rising and some of the properties of these materials still require further enhancement. In general, epoxy resins show high strength and elastic modulus, and good heat and solvent resistance [9,10]. However, epoxies are inherently brittle [11-13]. Consequently, the increase of the crack resistance of these materials has become a major issue for the aerospace industry, and the toughness modification of epoxy resins has been taking considerable attention from the scientific community. Examples of improvement of fracture toughness of epoxy resins were attained by the modification with Polyetherimide (PEI) [14-17], Phenoxy [18] and Polysulfone (PSU) [19-21], but little is known about the fatigue crack growth of these materials.

Finally, the resistance of polymers against fatigue crack growth can further be improved by the addition of nano additives like carbon black or nanoclay [22-27]. To act as a reinforcement of the polymer matrix, the filler has to be well dispersed in the matrix, in order to absorb as much energy of the crack as possible, or by deflecting the crack and thereby preventing the crack from propagating in the polymer.

In this study, we discuss the influence of nano-clays on the fatigue crack growth of a polymer matrix, as well as correlating these results to the degree of dispersion of the nano-additives.

2 Experimental

2.1 Materials

Polyamide 6 (Ulramid B4®, BASF) was used as matrix material, which was modified by adding different amounts of organo clay (Nanofil 919®) manufactured by Südchemie AG.

2.2 Manufacturing of nanocomposites

The nanocomposites with different clay content (1, 2, 5, 10 and 15 wt.%) were produced using a Bersdorff twin-screw extruder (ZE25). Afterwards compact tension samples were injection molded (Arburg Allrounder 420 800-250 Jubilee).

2.3 Mechanical testing

Fatigue crack propagation (FCP) tests were performed at 23 °C and 50 % relative humidity, employing a computer-controlled, servo-hydraulic test machine (Schenck MHF, IST 8400), a sinusoidal waveform and a cyclic frequency of 10 Hz. The used compact tension (CT) specimens were machined out of the injection-molded rectangular plates (Figure 2). Razor-blade tapping was used to introduce a sharp crack at the notch-tip just before the start of the experiment. The specimens were loaded for crack propagation either in perpendicular or in parallel to the injection-direction (melt-flow direction).
compliance of the specimen was continuously measured by the crack opening displacement method using a transducer fixed to the front face of the CT-specimen with rubber bands. The stress intensity, \( K \), factor was calculated by the following equation:

\[
K = \frac{F}{dW} \sqrt{aY(a/W)}
\]  

(2)

where the parameters \( F \), \( d \), \( W \) and \( a \) denote the force, the thickness and the length of the specimen, and the crack length, respectively; \( Y \) denotes a geometry factor, which depends on the ratio between \( a \) and \( W \), and on the sample geometry [2]. The ratio of the minimum to the maximum stress, the so-called R-ratio, was set at 0.1, the stress intensity factors were calculated according to [2]. The FCP tests were performed at increasing stress intensity factors (\( \Delta K \)) with a constant \( \Delta K \) gradient as a function of the crack length, \( a \). It should be noted that the value for \( K_{th} \) was determined by evaluating the stress intensity at the minimum crack propagation rate observed during the test. A detailed description of this particular FCP procedure is given in [2,3].

Fig. 2. Specimens used for FCP investigations showing its geometry and dimensions.

2.3 Transmission electron microscopy (TEM)

The morphologies the Polyamide composites were observed using transmission electron microscopy. Thin layers, from 40 to 50 nm, were cut using a Microtome Ultracut E and a Zeiss 902 transmission electron microscope, operating at 80 kV, was used for the evaluation of the morphology of the Polyamide composites.

3 Results and discussion

Figure 3 shows the crack propagation rate as a function of \( K_{IC} \) for neat Polyamide and the modified nanocomposite with the different clay contents (1, 2, 5, 10 and 15 wt.%). The plot clearly shows that first at the same crack propagation rate the value for the crack intensity factor \( \Delta K \) is higher for the composite materials, until a total nanoclay content of 5 wt.%. Subsequently the slope during the linear crack propagation region is lower, showing that the addition of nanoclay up to 5 wt.% leads to an improvement of the fracture toughness.

Fig. 3. Fatigue crack growth behaviour of Ultramid B4 and the nanocomposites with a content of 1 wt. % to 15 wt.% nanoclay (Nanofil 919).

The reduction of the slope can be related to the enhanced ductility of the nanocomposites [28]. Due to the higher deformability of the material the crack tip will be blunted, which finally leads to a reduction of the effective stress intensity at the crack tip and therefore reduces the crack propagation rate through the material. From Figure 3 it is also visible, that 1 wt.% of nanoclay does not show a significant change of the curve compared to neat PA, whereas 2 and 5 wt.% show an improved toughness. A further increase of the clay content leads to a worsening and from at least 15 wt.% even to an embrittlement of
the composite, shown by the shift to lower $\Delta K$ values.

In order to clarify the effect of the nanoclay on the toughness and resistance against crack propagation of the PA nanocomposite, Figure 4 depicts the TEM images of the nanocomposites containing 1 wt.%, 5 wt.% and 15 wt.% nanoclay.

The figure above clearly shows that the differences of the toughness and therefore the differences of the resistance against crack propagation can clearly be related to the dispersion of the clay within the PA matrix. It is of major importance that the clay platelets are exfoliated in the matrix, in order to have a positive impact on the crack propagation behaviour of the nanocomposite. Up to an amount of 5 wt.% the nanoclay platelets are well exfoliated. Further increase of the nanoclay content in contrast leads to clay agglomerates and intercalated particles, which both act as stress concentrators and therefore result in an embrittlement of the materials.

Shah et al. [29] also argue that the improved toughness of the nanocomposites compared to the neat materials can be related to the possibility of the nanoparticles to follow the movements of the molecular chains and therefore are able to align according to the loading direction. This alignment of the nanoparticles is an additional energy-dissipative mechanism, which is not present in non-filled polymers and finally is responsible for the reduction of the crack propagation and the increase of the toughness of the material.

4 Conclusions

In this study, fatigue crack growth was used to characterize polymer based nanocomposites. The correlation between structure and fatigue behaviour of polymer systems in terms of their resistance against crack propagation were presented and showed the suitability of the FCP methodology to characterize the fatigue properties of Polyamide reinforced with nanoclays.

This study also demonstrated the potential of using nanoclay to reinforce Polyamide and improve the fatigue crack propagation behaviour. It is worth mentioning that not only the amount of the nanoclay content has a significant influence on the mechanical behaviour, but especially the dispersion of the nanoclay platelets within the polymer matrix is most important. An improvement in the resistance against crack propagation was achieved by adding up to 5 wt.% nanoclay for exfoliated clay dispersion in the Polyamide. A further increase of the clay content lead to an embrittlement of the material due to the formation of agglomerates and intercalated particles, which act as stress concentrators in the polymer matrix.
5 References


