IN-SITU SAXS INVESTIGATION OF THE TRANSIENT NANOSTRUCTURE OF METALLOCENE POLYPROPYLENE/MONTMORILLONITE COMPOSITES UNDER UNIAXIAL LOADING

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1 Introduction

Introduction of nanoparticles into polymer matrices is known as a promising route to make light weight composites with improved mechanical, physical and thermal properties. The significant improvements caused by the inclusion of nanoparticles are not solely due to the inherent properties of the nanoparticles (high modulus and stiffness), but also due to the alteration of the microstructure of the surrounding polymer matrix [1]. In the case of semicrystalline polymers, nanoparticles may affect the crystallization kinetics and consequently the type and microstructure of the crystallites. In addition, nanoparticles can act as stress transmitters and thus they influence the fracture mechanisms and the behavior of polymers under mechanical deformation.

Understanding structure-property relationship is a prerequisite for designing composite materials with desired properties. Therefore, it is necessary to apply structure characterization methods which are able to investigate the variations of structure during loading the material without disturbing the on-going mechanical test.

Time-resolved x-ray scattering experiments are effective direct methods to follow microstructural variations of polymers and polymer based composites under thermal and mechanical loads [2-6]. One challenge of this kind of experiments is, however, the huge number of grabbed patterns. In addition, several pre-evaluations such as background correction, centering and rotation should be done on each single pattern before extracting nanostructural parameters form the SAXS data [6]. Hence, fast automated computer programs are required to accelerate data evaluation and to reduce the ultimate analysis time.

2 Results and Discussion

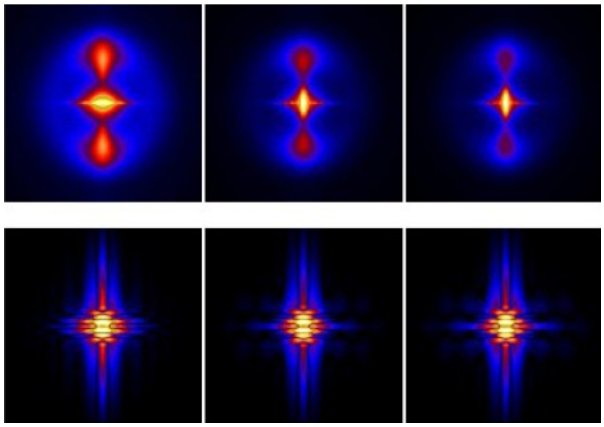
We apply time-resolved small angle x-ray scattering (SAXS) to investigate microstructural variations of metallocene polypropylene (PP) and its composites with montmorillonite (PP/MMT) during uniaxial stretching and load cycling.

Table 1. Composition of the nanocomposite samples

sample	composition
PP	pure polypropylene
PP+MMT	PP + 3 wt.-% freeze-dried MMT
PP+lcMMT	PP + (3 wt.-% MMT + 4.65% ABC)
PP+hcMMT	PP + (3 wt.-% MMT + 8.0% ABC)

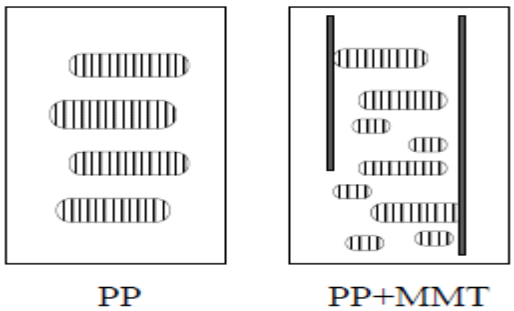
We present briefly the data evaluation methods and discuss fatigue mechanisms with regard to the nanostructural parameters extracted from the SAXS patterns and their corresponding chord distribution functions (CDFs). For example, the nanoscopic strain is determined and compared to the macroscopic strain. Ultimately, the variation of nano-structure parameters is discussed in relation to the changing macroscopic load.

Figure 1 presents the variations of SAXS pattern and the corresponding CDFs during load-cycling of pure polypropylene. This patterns are typical for injection molded polypropylene. The 2-point pattern shows that the material is highly oriented. Based on the features revealed by the CDF a simple model for the microstructure of pure polypropylene and polypropylene/montmorillonite composites is proposed, Fig. 2.



(a) (b) (c)

Figure 1 SAXS pattern and corresponding CDFs of the nanocomposite sample at different stages of load-cycling: (a) initial state, (b) first strain maximum, (c) first strain minimum



Simplified structural model for the semicrystalline structure of the pure polypropylene (left) and of the polypropylene phase in the nanocomposites (right).

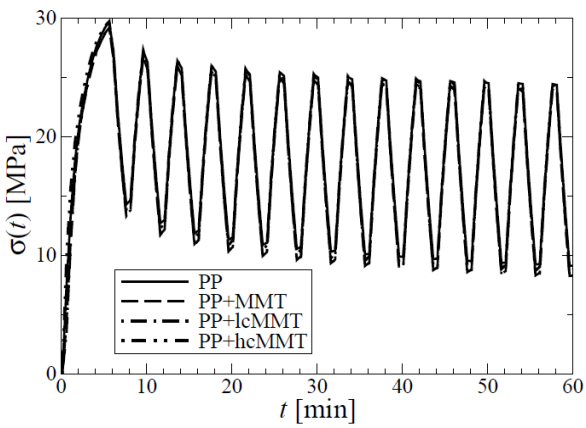


Figure 3 Variations of stress during load-cycling

The fatigue behavior of the samples have been assessed by following variations of stress during load cycling, Fig. 3. Figure 4 shows the variations of the running average of the stress during load-cycling. As revealed in Fig. 4 the PP/MMT and PP/lcMMT samples have lower resistance to fatigue compared to the neat polypropylene. Only the sample containing higher amount of compatibilizer shows slightly better fatigue properties in comparison with polypropylene.

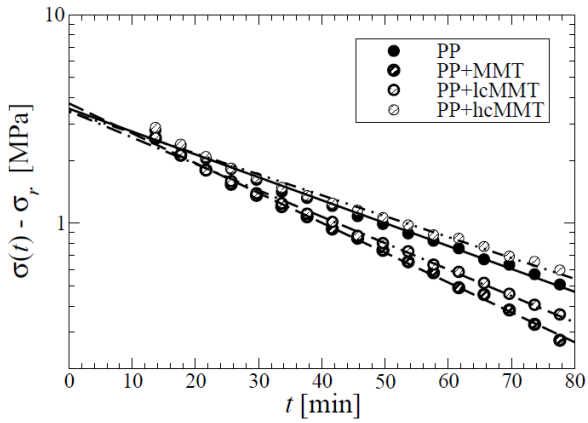


Figure 4. Assessment of fatigue by exponential regression of the linearized running average of the stress.

The position of the first negative peak of CDF gives the long period and the variation of long period with time is regarded as the deformation of the crystalline regions. Variations of long period during load cycling are presented in figure 5. All nanocomposite samples have lower long periods (thiner crystallites) compared to neat polypropylene. This can be due to the nucleating effect of montmorillonite. The variation of long period is in phase with the macroscopic load. This means that the amorphous phase between the lamellae is deformed during loading. The nanostructure fatigue is assessed by the variations of running average of long period during load cycling, Fig. 6. Interstingly the nanostructure of the neat polypropylene is the most stable one. The nanostructure fatigue is enhanced by increasing the compatibilizer content and improvement of exfoliations of MMT layers.

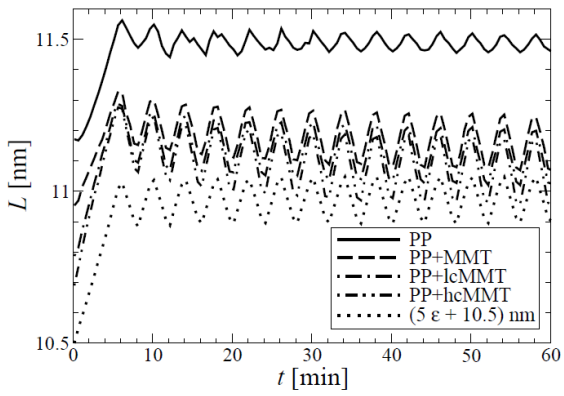


Figure 5 variations of long period during load cycling

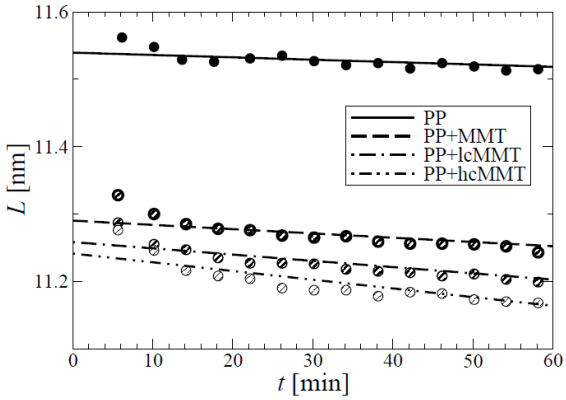


Figure 6 Assessment of nanostructure fatigue

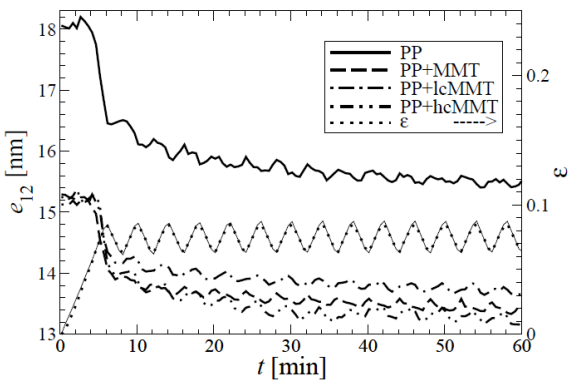


Figure 7 variations of lateral extensions of the crystallites during load-cycling.

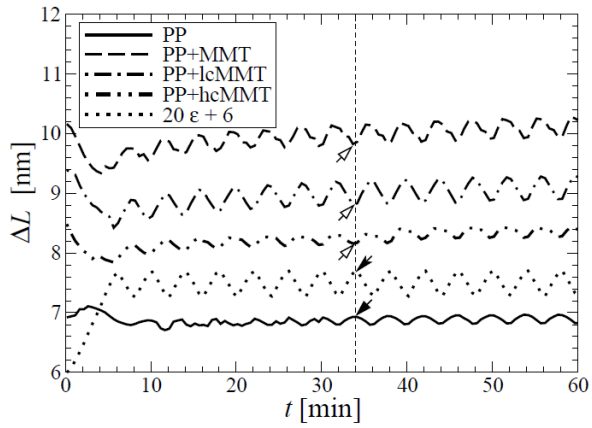


Figure 8 variations of the breadth of the long period peak.

Figure 7 presents variations of the lateral extensions of the lamellae during load-cycling. The crystallites of the pure polypropylene have the largest lateral extension. Addition of the montmorillonite restricts the lateral growth of the polypropylene lamellae.

During pre-loading the lateral extension of the crystallites decreases. This is due to lateral deterioration of the lamellae. During load-cycling e_{12} oscillates with a small phase shift with respect to the macroscopic strain.

Variations of the breadth of the long period peak are shown in figure 8. As observed in figure 8 the neat polypropylene has the narrowest distribution of the crystalline thickness. Indeed addition of montmorillonite has destabilized the nanostructure of the neat polypropylene. Thus, the PP/MMT nanocomposites have lower fatigue resistance compared to the neat polypropylene. The destabilization of the nanostructure can be due to the nucleating effect of montmorillonite.

Conclusions

Small-angle X-ray scattering has been used to moit- or slow mechanical tests of a set of nanoco posites from polypropylene (PP) and a layered silicate (montmorillonite, MMT). By comparing the extracted evolution information on nanostructure to

the mechanical data it has been found that missing improvement of mechanical properties appears to result predominantly from the inhibition of a load-bearing semi-crystalline morphology inside the PP by the MMT.

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