Chapter 13
Quasistatic to Dynamic Behavior of Particulate Composites for Different Temperatures

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Abstract In automotive industry, polypropylene based composites are generally used in the manufacturing of car bumpers. In such a case, a detailed study of high strain rate and temperature sensitivities of polypropylene based composites is essential since the bumpers undergo compressive impact loading in a wide range of temperatures. The considered fillers consisted of ethylene octane copolymer and talc. The investigated filler content was 0, 10. and 20 wt. The dynamic behavior was investigated by using split Hopkinson pressure bars, at different strain rates and temperatures. We found that neat polypropylene and polypropylene talc composites were brittle at low temperatures. The addition of ethylene octane copolymer inclusions improved the impact resistance of materials. The dynamic properties are correlated with the morphological investigations of the studied composites by means of the optical microscopy. Finally, we also identify the effect of soft and rigid fillers in the quasi static to dynamic transition.

Keywords Polypropylene • Talc • Nodules • Dynamic • Temperature

13.1 Introduction

Polypropylene (PP) is one of the most widely used plastics in the automotive industry. In a continuously increasing part of this market, the material needs to be recycled. Actually, the growing plastics waste forces governments to legislate for the limitation of such waste by introducing the concept of isofunctional recycling [1]. The recycling effects on polypropylene based materials were studied [2–8]. Degradations induced by the ageing and the recycling of composite based polypropylene were quantified under quasi-static loading by Bahlouli et al., Pessey et al., and Luda et al [2–4]. After multiple extrusion/crushing processes, the main result is that polymer chain scission induces the degradation of the mechanical properties. The recyclability of other PP composites has also been investigated by Bahlouli et al. [2] and Wang et al. [5, 6, 8]. The purpose of this study has been to examine the effect of recycling on the properties of PP-based composites (rubber nodules)/PP and talc/PP) using extrusion process. Rheological, mechanical and structural properties of the composites have been determined and compared after each extrusion cycle. The results showed that the melt viscosity of the composites decreases with processing number in the same way of pure PP [9], as well as the mechanical properties of the composites decreased with processing number. All noted changes in the composites properties have been caused by the changes in the structural properties of the composites during the processing cycle. The obtained results from this work made possible the optimization of the recycling process and a better use of the recycled materials in components design. In view of these results, recycled materials suppliers must regenerated recycled materials so they can be upgraded in parts of structures. Different ways can be used to regenerate

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polypropylene [9–11]. Changing the grade of the polymer is one of these methods. Depending on the desired mechanical properties, the compounder will provide a polypropylene grade. By doing that, suppliers will be able to change the grade of recycled polypropylene by adding particles. For a low-grade polypropylene, elastomeric particles have been added. To get a higher grade of polypropylene, talc has been added. But the addition of particles not only impacts the grade of polypropylene. Indeed, the mechanical properties of a polymer strongly depend on the grade of polymers. It is important to notice that the addition of particles not only impacts the grade of polypropylene. Actually, the mechanical properties of a polymer strongly depend upon the grade of polymers. Previous rheological and morphological analyses were performed to highlight the effect of the adjunction of talc and rubber nodules on the thermal and rheological properties of polypropylene [5, 6]. This work explores the strong effects of the addition of soft particles and rigid particles in polypropylene on the thermo mechanical behavior over a wide range of strain rates. Experimental work has been conducted for a wide range of temperatures and strain rates for different filler content in PP in both quasi-static and split-Hopkinson tension bar test rigs. DMA tests were also carried out to position the temperatures tested against the different phase's transitions.

13.2 Materials and Methods

A highly isotactic polypropylene (PP) was supplied by LyondellBasell for this study (reference Moplen HP500N, Frankfurt am Main, Germany). This PP had a melt flow index (MFI) of 12 g/10 min and a density of 0.9 g/cm^3 [12]. To study the effects of soft fillers on mechanical properties of the PP, an impact modifier of PP was used. This impact modifier of PP is a metallocene ethylene octene copolymer (EOC) supplied by ExxonMobil (reference Exact TM 8230, Brussels, Belgium). This EOC had a MFI of 30 g/10 min and a density of 0.882 g/cm^3, and it contained 72 wt. % of ethylene and 28 wt. % of octene. The effect of rigid particles in PP was identified by the adjunction of talc powder which was kindly offered by Luzenac (referenced Steamic T1 CF, Toulouse, France), and had a density of 2.78 g/cm^3 and a median diameter (D50) of 1.9 μm.

PP blends containing 0 wt. %, 10 wt. % and 20 wt. % of EOC or talc (PP/EOC, 100/0, 90/10, 80/20, or PP/talc, 100/0, 90/10, 80/20, respectively) were prepared by extrusion. PP with 20 wt. % of EOC and 10 wt. % of talc (PP/EOC/Talc 70/20/10) was also processed. These compositions are similar to available commercial PP composites for car bumpers [2]. The talc powder was dried for 12 h at 80 °C before mixing. The mixing of the materials was conducted with a single screw BUSS Kneader extruder model PR46 (Pratteln, Switzerland), with a screw diameter (D) of 46.5 mm and a length/diameter ratio L/D of 11, at 200 °C and 50 rpm and under air conditions. The obtained molten filaments of PP-based composites were quenched by a cold water bath and were subsequently pelletized using a rapid granulator. The pellets were dried in an air-circulating oven for 60 min to minimize the moisture for the subsequent step [13].

The viscoelastic properties of the materials were characterized by dynamic mechanical analysis (DMA) using a NETZSCH DMA 242C instrument (Selb, Germany). Specimens of dimensions of 16 × 10 × 3 mm were carefully cut from the tensile specimens, tested with the single—cantilever bending mode at the frequency of 1 Hz and with a constant static force of 0.5 N. During this procedure, the materials were tested from −100 to 140 °C with a heating rate of 2 °C/min. For DMA, we report averaged values and representative curves resulting from three experiments per tested material.

Mechanical properties for both virgin and recycled materials were evaluated using uniaxial tension with a servohydraulic Instron testing machine model 8031 (Norfolk, Massachusetts, USA) at the room temperature (25 ± 1 °C). Based on the standard ASTM D638, the Young's modulus and yield stress were determined at a crosshead speed of 1 mm/min and the strain at break was determined at the crosshead speed of 50 mm/min. The Young's modulus and the yield stress were calculated from the initial slop of stress–strain curves and the maximum stress of stress–strain curves during the transition between viscoelastic and viscoplastic stages, respectively. Since the tensile specimens have a gauge length of 50 mm, the corresponding strain rates are 0.0033/s for 1 mm/min and 0.017/s for 50 mm/min. The engineering stress (σ_{eng}) and strain (ε_{eng}) were determined from the measured load (F) and displacement (Δl) using the original specimen cross-sectional area (S_0) and length (l_0). (σ_{eng}) and (ε_{eng}) can be used to determine the true stress (σ_{true}) -true strain (ε_{true}) curves. At least five tests were performed per strain rate, which allows determining the averaged values of each mechanical parameter.

A homemade split Hopkinson pressure bars (SHPB) was used to perform the uniaxial compressive high strain rate testing. This apparatus consisted of three parts, a striker, an input bar and an output bar made of 316L steel, with lengths of 500 mm, 2903 mm and 2890 mm, respectively, and the same diameter of 22 mm. The cylindrical samples with a diameter of 8 mm and a thickness of 3 mm were cut from the injected tensile samples and placed between the input bar and the output bar. Petroleum jelly was used as lubricant to limit the friction between the bars and the sample. A furnace with two symmetrical resistance heaters was installed for high temperature testing. For the low temperature testing, liquid nitrogen was mixed with different contents of absolute ethyl alcohol depending on the required testing temperature. Based on the classical elastic wave propagation theory, when the stress and strain fields were uniform in the specimen, the nominal stress ($\sigma_n(t)$), the

nominal strain ($\varepsilon_n(t)$) and the nominal strain rate ($\dot{\varepsilon}_n(t)$) of the tested materials were computed by the classical expressions given in [13, 15]. The recorded strain signals are post-processed with the software package DAVID to reconstruct the time histories of strain at the end of the incident and transmitter bars, following the procedures described in [16, 17]. In this study, dynamic tests were carried out at various temperatures ranging from −30 to 85 °C (−30, 0, 25, 50 and 85 °C), and various strain rates ranging from 592 s^{-1} to 3346 s^{-1} ($\dot{\varepsilon}_1 = 592p\backslash pm6.5\%\ s^{-1}$, $\dot{\varepsilon}_2 = 1276p\backslash pm7.9\%\ s^{-1}$, $\dot{\varepsilon}_3 = 2221p\backslash pm5.6\%\ s^{-1}$ and $\dot{\varepsilon}_4 = 3346p\backslash pm4.3\ s^{-1}$). Each test was repeated five times and hence, averaged strain rates and averaged curves were reported here. In the manuscript, these four strain rates were denoted as Strain-rate-1, Strain-rate-2, Strain-rate-3 and Strain-rate-4, respectively.

13.3 Results and Discussion

Attention is first focused on the impact of the EOC and the talc on the viscoelastic properties of the PP characterized by DMA, and in particular on the storage modulus (Fig. 13.1). For PP/EOC composites (Fig. 13.1 left), the storage modulus decreases with the content of EOC due to the increased amount of soft rubber phase. For the evolution of the damping factor *tan δ* with temperature (Fig. 13.1), we observed three relaxation peaks: (1) the glass transition of EOC (β_{EOC}), (2) the glass transition of PP (β_{PP}), and (3) the crystalline phase relaxation of PP (α_{PP}). It is to be noted that the crystalline phase relaxation of EOC (α_{EOC}) was not detected due to the overlapping of the α_{EOC} relaxation with the much more intense β_{EOC} relaxation [18–20]. The peak position of each relaxation process provided the corresponding relaxation temperature. For PP/talc composites (Fig. 13.1 left), the storage modulus increased with the addition of talc due to the presence of rigid talc fillers. The increase in rigidity was also explained by the formation of an interphase between the PP matrix and the rigid talc fillers, having an intermediate rigidity between that of talc and that of PP [21]. Comparing with the glass transition temperature of PP phase for neat PP and PP/talc composites, we found that the addition of talc filler slightly decreased the glass transition temperature of PP. The talc particles acted as nucleation agents of PP, and hence, the presence of talc within PP matrix resulted in a faster crystallization rate that caused an amorphous phase with a higher motion in comparison with neat PP [21]. On the contrary, the α_{PP} relaxation temperature of PP increased with the presence of talc. This is attributed to the fact that talc fillers increased the lamella thickness of PP.

Elastic properties from tensile stress–strain curves non presented here were obtained (Fig. 13.1). For PP/EOC composites (Fig. 13.2), the addition of EOC inclusions decreases the yield stress and Young's modulus of neat PP, which is consistent with the storage modulus of PP and PP/EOC blends assessed by DMA. We also measured the elongation at break of the materials (Fig. 13.2). Firstly, the elongation at break of the material increases in the following order: PP < PP/EOC 80/20 < PP/EOC 90/10. It was expected that neat PP had a lower elongation at break than the PP/EOC blends due to the toughening effect of the rubber particles, but surprisingly elongation behavior seems not to increase with the increasing

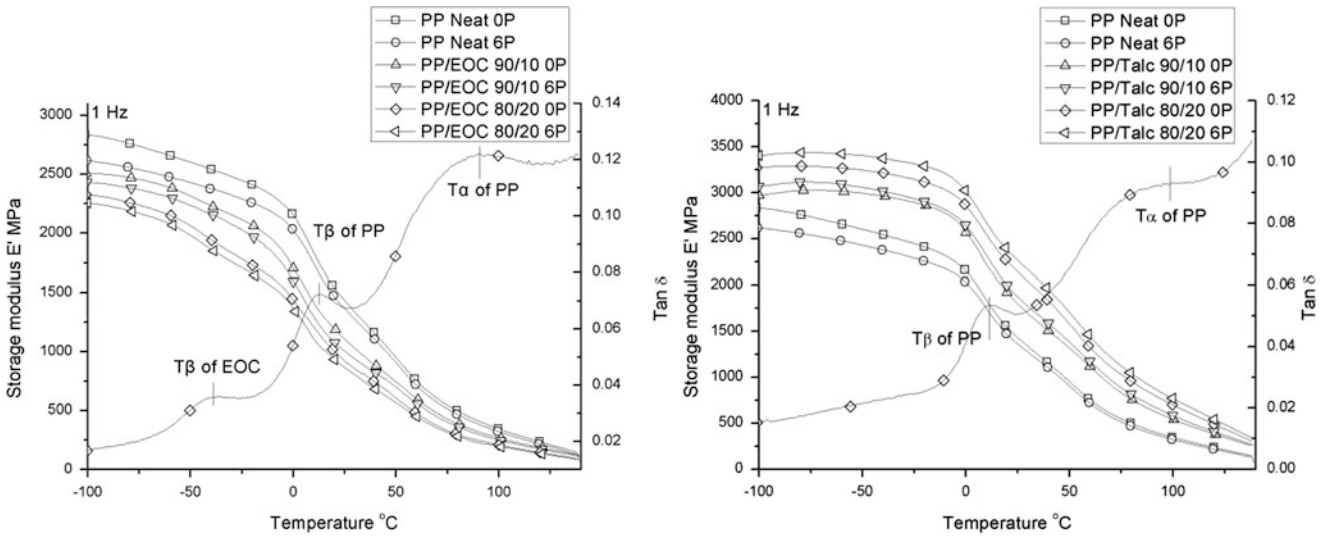

Fig. 13.1 EOC (*left*) and talc (*right*) content effect on PP storage modulus at 1 Hz

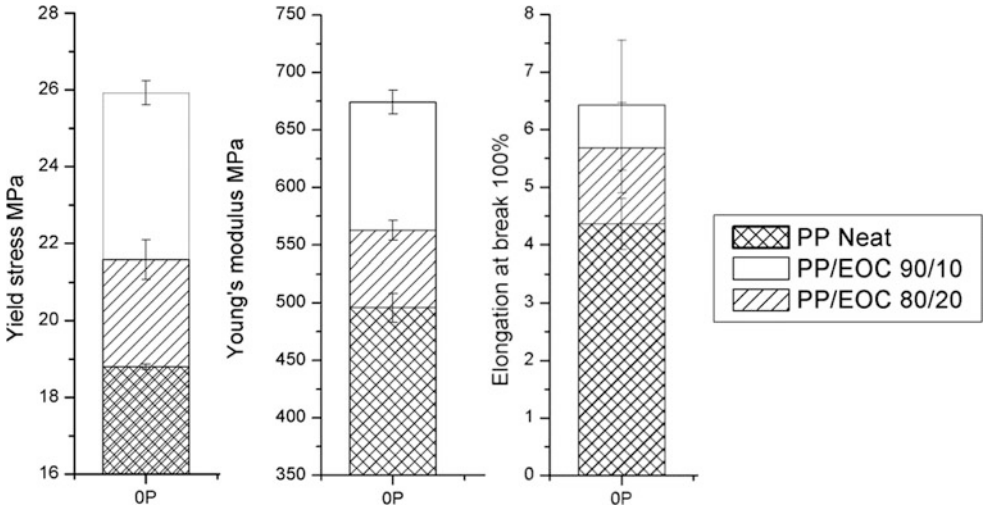

Fig. 13.2 Elastic properties for the different filler contents for quasistatic tensile tests

content of EOC. According to the currently accepted toughening theories during loading, the rubbery particles act as sites of stress concentration. Therefore, as soon as the stress around the particles overcomes the yield stress of the matrix, the deformation mechanism such as crazing and/or shear yielding become active [22, 23]. Consequently, the ductility behavior of neat PP is improved by the addition of EOC dispersed phase. It should be noted that the ductility behavior of PP/rubber blends is not persistent increasing with the increasing of the rubber concentration. This behavior is influenced by both the nature of matrix and the rubber volume fraction. At low volume fraction of rubber, the generation of crazing around the rubber particles eliminates the tendency of the matrix to strain hardening. The whitening of the specimen and the inconspicuous cross-sectional areas change between the yield stress and the failure point indicate that crazing, rather than shear yielding, is the main energy dissipation mechanism [22]. For high volume fraction of rubber, the shear bands around rubber particles interact, and microcracks develop at the areas of high mechanical constraints, leading to reduce the elongation at break [24]. On the other hand, the elongation at break appears related to the amount of β phase (Fig. 13.2): the higher the amount of β phase, the higher the ductility of PP blends. These two mechanisms can be used to explain why the elongation at break of PP/EOC 90/10 is higher than that of PP/EOC 80/20 in our case.

For PP/talc composites (Fig. 13.2), the introduction of the talc filler significantly increased the Young's modulus of neat PP For the two crosshead speeds. However, the presence of talc increased the tensile yield stress of neat PP at the lower rate (1 mm/min), but decreased the tensile yield stress at the higher rate (50 mm/min). When the talc was mixed with PP, it may accommodate one part of macroscopic stress, with limited or delayed cavitation mechanisms by debonding. In the case of a low strain rate, the accommodation of stress by the talc particles is important, resulting in an increase of yield stress and limited cavitation. For the case of high strain rates, the accommodation of stress by the talc particles is low, which results in marked cavitation mechanisms and a low yield stress [25–28]. Besides this, Zhou et al. [29] attributed the decrease of PP/talc composite yield stress compared to neat PP to the presence of thermal residual stresses in the case of the composite. In particular, the coefficients of thermal expansion of PP matrix and talc are quite different, which may induce important thermal residual stresses within the composites and hence may decrease the yield stress during the tensile test in comparison with neat PP.

Yield stress/temperature is plotted versus strain rates for the different tested materials (Fig. 13.3). A strong sensitivity to the strain rate is obtained. The neat PP and the PP/talc composites presented a brittle behavior at −30 and 0 °C. This is due to the glass transition temperature of non-recycled PP which is around 12 °C. With increasing the testing temperature, the ductility of PP and PP/talc increased gradually. This phenomenon is probably due to the increased mobility of polymer chains with increasing temperature that delays the material rupture. Concerning the yield point of these materials, it tends to increase with the content of talc particles at −30 and 0 °C. However, for higher temperatures, the yield stress of PP/talc 90/10 was higher than that of PP/talc 80/20. This result may be attributed to the damage mechanisms by matrix/filler debonding during dynamic testing. In particular, it is hypothesized that PP/talc 80/20 may exhibit more damage than PP/talc 90/10. From 0 °C, the yield point of PP and PP/talc decreased with increasing temperature.

The PP/EOC had a ductile dynamic response for all the investigated temperatures. This is due to the addition of EOC inclusions as toughening agents of PP matrix that obviously increase the impact resistance of the material. Whatever the

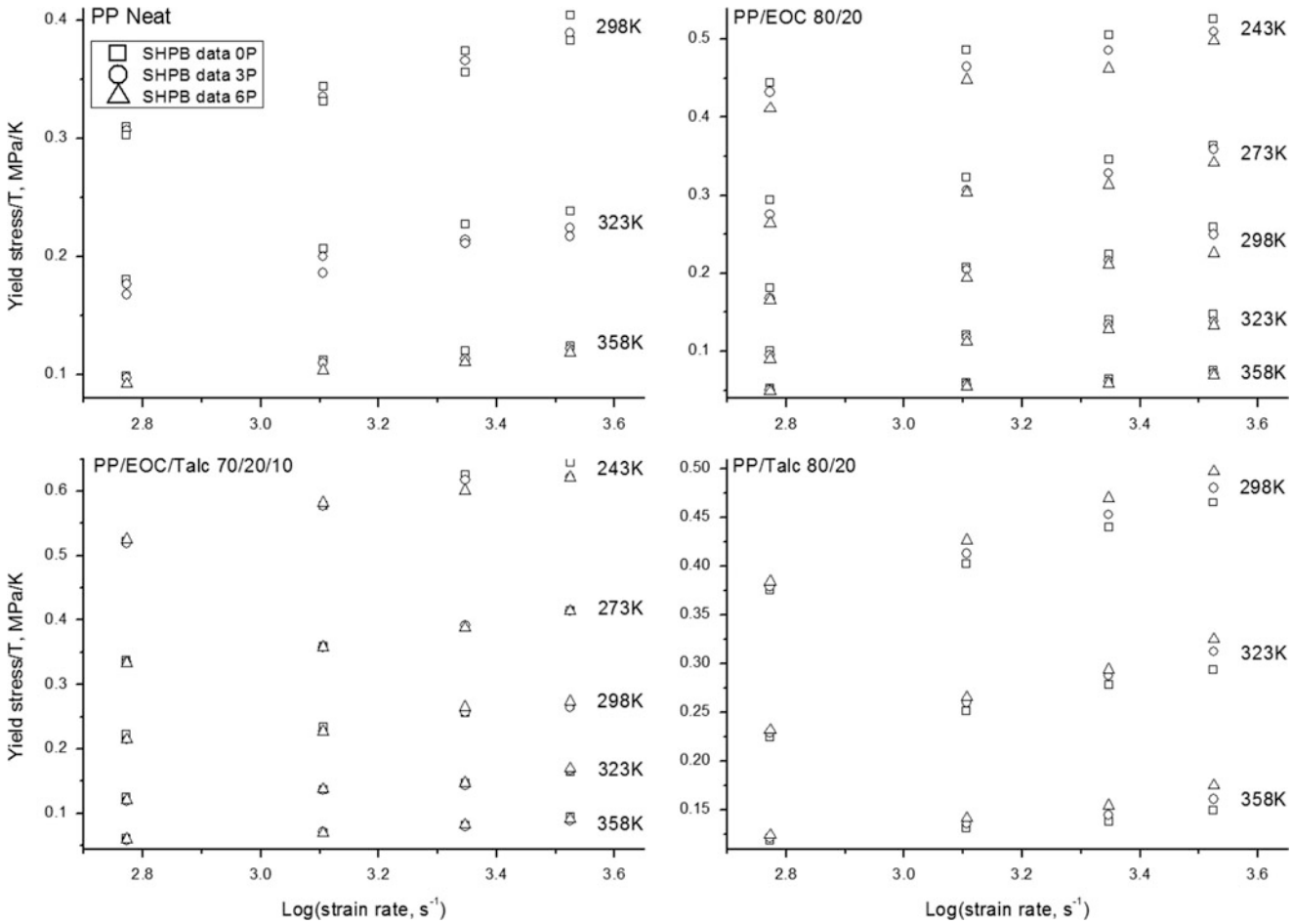

Fig. 13.3 The dependences of yield stress in dynamic compression on strain rate and recycling number at five temperatures

testing temperature, in the case of PP/EOC composites, the yield stress decreased with the amount of EOC. This can be explained by the increased amount of this soft rubber phase. With increasing temperature, the yield point of PP/EOC and PP/EOC/talc gradually decreased. In addition, we noted that the yield stress of PP/EOC/talc 70/20/10 was lower than that of PP/EOC 90/10 for the investigated testing conditions.

13.4 Conclusions

The results showed that the considered materials were strain-rate and temperature sensitive. The addition of EOC decreased the Young's modulus and yield stress of PP while the presence of talc fillers increased the Young's modulus of PP. However, the yield stress for PP/talc 80/20 was slightly lower than that of PP/talc 90/10 probably due to more important damage mechanisms by matrix/filler debonding in PP/talc 80/20 compared to PP/talc 90/10 during the dynamic testing.

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