Final Report

on the work done in the project OTKA K 129270 on the

"Hybrid composites: structure, properties, functionality"

1. Introduction

Composites were developed in the last few decades for wide range of applications. In the 21th century smart materials and sustainability became the key factor both in the development and application of new materials. Former the motive to develop polymer based composite materials was to utilize them as structural materials. Nowadays the requirements of both industry and consumers changed the direction of development for a new class of materials, which possess beside good stiffness and strength also some functional properties. Shape memory, responsive and desiccant properties are investigated more frequently in the literature. Hybrid composites could be a realistic answer for the challenges of advanced materials. On one hand, different reinforcement or additives incorporated into the polymer matrix collectively could have a synergistic effect on the composite properties. On the other hand, the incorporation of various fillers with functional properties enable the development of advanced composite materials. The aim of the research project was to establish fundamental structure and property correlations of hybrid composite materials with different reinforcement and matrices.

Polymers can be modified in many ways. Copolymerization, grafting, or most polymer analogous reactions are usually complicated and economically not feasible for industrial applications. Another possibility of modification is offered by the addition of a second component to the matrix polymer. Depending on the type of the modifier, heterogeneous polymers can be classified in several ways. Arbitrarily, we generally divide them into three categories: polymer blends, particulate filled polymers and fiber reinforced composites. Some decades ago, the aim of developing polymer composites was to utilize them as structural materials. Hybrid materials or hybrid composite materials can provide a feasible answer to the challenges that advanced materials face today. Hybrid composites are systems in which one type of reinforcing material (filler or fiber) is incorporated in a matrix consisting of a mixture of different polymers (blends), or two or more reinforcing and filling materials are present in a single polymer matrix. The incorporation of two or more different types of fibers into a polymer matrix has led to the development of hybrid composites. The properties of traditional composites can be calculated usually with the rule of mixture, while in the case of a hybrid composite that contains at least two types of fibers, the advantages of one type of fiber might compensate for the shortcomings of the other. As a consequence, a balance in cost and performance can be achieved through proper material design.

2. Reinforcements

The use of plastic composites as structural materials, especially in the automotive industry, requires excellent mechanical properties, particularly large impact resistance and stiffness. Carbon and glass fiber reinforced composites have been used for decades, but increasing environmental awareness and some economical aspects created much interest for natural fibers (wood, hemp, flax, etc.). Several attempts have been made to achieve the goal of increasing stiffness and impact resistance by the combination of various fillers and fibers with elastomers in hybrid composites, but these attempts proved unsuccessful especially in the case of natural reinforcements. Our approach is completely new, besides the natural and synthetic reinforcing fibers we use polymeric fibers in order to achieve the best combination of properties in heterogeneous polymer composites.

2.1. Traditional reinforcements

The first phase of our research was a comparative study to determine the advantages of three different fibers - wood, glass and carbon - in reinforced PP composites. The results proved that all three have advantages and drawbacks. The stiffness of the composites depends on the modulus of the fiber, their aspect ratio and on composition, but coupling does not influence it practically at all. Properties measured at larger deformations, on the other hand, are influenced quite strongly by interfacial adhesion and local deformation processes related to the fibers. The effect of adhesion depends on the type of the fiber. Large wood particles debond from the matrix very easily without coupling, while their fracture is the dominating process at good adhesion, which leads to immediate failure in PP/wood composites. Increased interfacial adhesion improves reinforcement, but decreases impact resistance in carbon fiber reinforced composites. The glass fiber used in the study offers good adhesion even without coupling. The initiation of some local deformation processes does not result in the immediate failure of the composites, but that of others leads to catastrophic failure. Characteristic stresses related to the initiation of local processes correlate well with macroscopic properties. Due to its natural and renewable character as well as low price, wood is a good reinforcement when the increase of stiffness is the main goal of modification, but it cannot be used in applications in which impact resistance is important. Carbon fibers are rather expensive and their composites are very stiff, but otherwise they possess intermediate properties. If adhesion is good, glass fibers offer a good balance of properties including stiffness, strength and impact resistance (Várdai 2020).

2.2. Organic fiber reinforcements

The study of the effect of four organic fibers (wood, flax, PET, PVA) on the properties of PP showed that these fibers increase stiffness only moderately; because of the flexibility of the fibers, they do not orientate in the direction of the load. Consequently, the aspect ratio of the fibers is less important than in the case of stiff fibers like glass and carbon. Composite strength changes in a wider range and it depends on coupling. PP composites containing PVA and flax fibers have the largest strength when adhesion is good. The deformability of the composites also varies considerably, more plastic deformation occurs in composites prepared with the PET and PVA fibers. Compared to traditional, stiff fibers, impact resistance can be improved significantly with PET and PVA fibers; an impact strength as large as 30 kJ/m2 can be achieved with PVA fibers. Fiber type and coupling influence the local deformation processes occurring around the fibers considerably, but does not change fracture energy much. The combination of deboning and subsequent plastic deformation is the most efficient in the improvement of impact strength. Fiber fracture dominates in wood and flax composites at good adhesion, but it does not consume sufficient energy to increase impact resistance. (Várdai 2020b)

The comparison of the effect of polymeric fibers (PET, PVA) in two PP matrices (hPP, ePP) showed that different inherent matrix characteristics result in dissimilar combination of properties. The PVA fiber proved to be more efficient as reinforcement in both matrices than the PET fiber; the former increases both stiffness and strength more than the latter. The strength of the composites depends very much on interfacial adhesion, the application of the MAPP coupling agent resulted in stronger composites in all cases. The effect of the factors studied (fiber and matrix type, interfacial adhesion) is stronger and more complicated in the case of impact resistance. Both fibers improve impact strength in the hPP matrix, but the effect depends on fiber type and interfacial adhesion. The changes in impact resistance cover a wide range in the ePP matrix; impact strength may increase or decrease depending on fiber type and adhesion, however, it remains always smaller than the fracture resistance of the matrix. Interfacial adhesion influences local deformation processes very strongly and these processes determine the macroscopic properties of the composites. Shear yielding and cavitation occur in the matrix, while debonding, fiber pullout and fracture are the main deformation mechanisms in the composites. Shear yielding induced by the debonding of the fibers consumes much energy, the fracture of the fibers is less efficient in the increase of impact resistance, while cavitation in the ePP polymer results in inferior impact strength. A combination of stiffness and impact resistance in excess of 3 GPa and 40 kJ/m^2, respectively, can be obtained in PP homopolymers modified with PVA fibers, while this type of modification is less advantageous for elastomer modified PP grades. (Várdai 2020c)

The next part of the research showed that sugarcane bagasse fibers reinforce polypropylene similarly to other natural fibers such as wood flour. They increase stiffness, and in the presence of a maleated polypropylene coupling agent also yield stress and tensile strength. Although the very large bagasse fibers debond more easily from polypropylene than the smaller wood fibers used as a reference, most properties are very similar in the two types of composites. The impact resistance of the composites increased in the presence of both wood and sugarcane bagasse fibers compared to the neat matrix. The analysis of local deformation processes indicated that debonding is the dominating process in the absence of the coupling agent, while mainly fracture occurs in its presence. Increased plastic deformation after debonding results in slightly improved impact resistance (Anggono 2019). We also tried to improve the properties of bagasse fiber reinforced PP composites by alkali treatment of the fibers. The results showed that alkali treatment leads to an increase in composite stiffness and strength. The increase in properties was assigned to the improvement in inherent fiber characteristics due to change in fiber composition. Increased inherent strength of the fibers results in an increase of the initiation stress and fracture energy of the composites. Interfacial adhesion has a slight effect on stiffness, but much more significant on strength and impact resistance. Using the sugarcane bagasse fibers results in a simultaneous increase of stiffness and impact strength in PP composites. (Bartos 2020a, Bartos 2020b)

In the next part of our research work we wanted to identify the reinforcing capacity of various fiber which can be good candidate to prepare composite systems. Milled sunflower husk was added to three types of polyolefins (polypropylene, low-density and high-density polyethylene) in a wide composition range. Composite series were prepared with or without maleic anhydride-grafted polyolefin coupling agents to investigate the effect of coupling on the mechanical properties and micromechanical deformation processes. Several independent approaches were followed to estimate interfacial adhesion qualitatively and quantitatively, respectively. The results show that interfacial adhesion is significantly improved in the presence of a coupling agent (Kun 2021). As a result, coupling changes the dominant deformation process from matrix/filler debonding to the fracture of sunflower husk particles. Milled sunflower husk can enhance significantly the modulus of polyolefins; however, elongation-at-break values are very small, especially at larger filler content, which represents the largest obstacle of practical application. (Kárpáti, 2021)

2.3. Hybrid reinforcements

Besides the studies on single traditional and natural reinforcements, we started the investigation of hybrid reinforcing materials. The results obtained on hybrid PP composites containing traditional reinforcements (wood, GF or CF) and a polymeric fiber proved that impact modification with polymer fibers (PET) works for all reinforcements and, not only for wood as shown earlier. Approximately the same impact resistance can be achieved with PET fibers, which depends on the amount of PET fiber used; impact strength as large as 15 kJ/m^2 can be obtained with the approach. The large impact resistance is the result of local deformation processes initiated by the polymeric fiber. Irrespective of the strength of interfacial adhesion, the main local process is the debonding and/or pullout of the PET fibers, which facilitates also the plastic deformation of the matrix polymer. The combination of these local processes results in large energy consumption and increased impact resistance. Other properties depend on the type of the reinforcement and on interfacial adhesion. The application of carbon fibers results in composites with large stiffness, while the strength of glass fiber reinforced composites is the largest at good adhesion. The proper selection of components, composition and interfacial adhesion allows the adjustment of overall composite properties in a relatively wide range. (Várdai 2019)

Impact strength was successfully improved in wood and in traditional, glass and carbon fiber reinforced composites by the incorporation of PET fibers. We proved that the concept works with other natural fibers as well; the impact strength of flax and sugar palm fiber reinforced composites could be also improved considerably. The mechanism of impact modification is always the same, the debonding or pullout of the PET fibers initiates the local yielding of the matrix, which consumes considerable energy. The fracture of PET fibers might also contribute to energy absorption. The type of natural fiber used as reinforcement does not influence the effect, the amount of PET fibers determines the fracture resistance of the composites. Improving interfacial adhesion by coupling in-creases strength and slightly improves impact resistance. The overall properties of the hybrid composites prepared are acceptable, sufficiently large stiffness and impact resistance can be achieved for a large number of structural applications. (Várdai 2021)

The results obtained on hybrid PP composites containing a traditional reinforcement (carbon, glass or wood) and a polymeric (PVA) fiber proved that the novel concept of using synthetic polymeric fibers for impact modification works for all reinforcements. The impact resistance of the composites increases with increasing PVA fiber content. The extent of improvement in impact strength depends on fiber type and content, but also on interfacial adhesion which strongly influences the local deformation processes occurring around the fibers during fracture. Both the reinforcing and the synthetic fiber take part in these processes and contribute to energy consumption. Debonding and the subsequent plastic deformation of the matrix consumes energy the most efficiently, but the fracture of the PVA fibers also requires energy, thus PVA fibers improve impact resistance both at poor and good adhesion. The approach allows the design of materials for structural applications, the combination of a stiffness of 4-6 GPa and an impact resistance of 20-25 kJ/m^2 exceeds the properties of most PP composites available on the market. (Várdai 2022)

Lignin is a natural polymer available in the second largest quantity in nature, and it usually forms as waste in the cellulose and the biofuel industry. Because of its large number of functional groups and polar structure, the interactions among lignin molecules are strong thus it is not miscible with most polymers available on the market, but proper homogenization and the use of coupling agents result in structural materials with acceptable properties from it. Blends with considerable stiffness and strength were prepared from polypropylene and lignosulfonates, but the deformability of the materials was rather small thus hindering application in several areas. Using lignin as a blend component has the advantage of improving stiffness, carbon footprint and price. Accordingly, hybrid composites were prepared from a polypropylene reactor blend (rPP), lignin and flax fibers. Interfacial adhesion was improved using a functionalized PP (maleated PP, MAPP) coupling agent. The combination of lignin and flax fibers yields materials with an advantageous property profile, considerably decreased carbon footprint and acceptable price. The application of flax compensates for the deteriorating effect of lignin on deformability and especially on impact resistance. Significant improvement was achieved in stiffness and strength. In order to obtain this property combination, the application of a coupling agent is necessary because of the poor interaction between PP and natural reinforcements. The compounds developed may successfully compete with materials offered on the market. (Pregi 2022a, Pregi 2022b)

2.4. Modification of biopolymers by hybridization

The concept of adding synthetic polymer fibers for the impact modification of poly(lactic acid) (PLA) was investigated in a further study. Poly(ethylene terephthalate) (PET) and poly(vinyl alcohol) (PVA) fibers were used as impact modifiers, while wood flour as reference. Polymer fibers increase stiffness moderately but fracture resistance considerably. Impact modification remains effective even at −20 °C that cannot be achieved by traditional approaches. Local processes and fiber content are the main factors in determining the improvement in impact resistance. The mechanism of the dominating local process depends on fiber characteristics and interfacial adhesion. Different local processes influence dissimilarly the two steps of fracture, crack initiation and propagation. The absolute value of impact resistance is determined by the total energy consumption of local processes. PVA fibers are the best impact modifiers among the reinforcements studied. Plastic deformation initiated by debonding and fiber fracture consumes considerable energy. The 5 GPa stiffness and 15 kJ/m^2 impact resistance of PLA/PVA fiber composites is useful for structural applications and have not been achieved before. (Ferdinánd 2023a, Ferdinánd 2023b)

2.5. Hybrid nanocomposite systems

Polypropylene composites were prepared with a new, commercially available hybrid nanofiller and talc as a reference. The detailed analysis of the nanofiller proved that its two components are sepiolite and possibly laponite and that it was surface coated with an ammonium ion having long aliphatic chains. The results showed that the concept of hybridization does not necessarily work in all cases. Although an even, homogeneous spatial distribution of the nanofiller was achieved, the nanosized filler particles aggregated above the filler content of 3 wt%. Model calculations yielded a slightly larger reinforcing effect for the nanofiller compared to talc. On the other hand, the absolute values of the most important mechanical properties achieved by the addition of the nanofiller were somewhat worse than those obtained for the talc filled composites. The presence of aggregates and weak interfacial interactions resulting from surface treatment led to only a moderate performance of the nanocomposites. (Ferdinánd 2023c).

3. Possible applications

Our research group has been taking part in an international project together with Borealis AG, which is one of the largest manufacturers of polyolefins in the world producing also short fiber reinforced raw materials. The purpose of the cooperation was to develop materials that satisfy the requirements mentioned earlier for composite materials. The participation of industry offers the possibility to introduce the results into practice. Composites developed by us are already potential raw materials for bumpers in the automotive industry.

4. Summary

The financial support obtained in the framework of the OTKA K 129270 contract offered us the possibility to continue our work in the field of heterogeneous polymer systems that we have been doing for many years. Ongoing research in some areas has earned our group international recognition. We have made significant progress in the analysis of micromechanical deformation processes in hybrid polymer systems, but we also consider our work on the application of synthetic polymer fibers to be pioneering and very important. Our work involves a number of young researchers and we dedicate considerable efforts to find practical application for the materials and/or technologies developed.