

Filler Impact Resistance Interactions

Abstract

A standard fine calcium carbonate filler was added to a variety of widely differing thermoplastics at 10 weight % (only ~3 volume %) in order to identify trends. It was seen that, as expected, for a fine isotropic filler, modulus increased somewhat, yield strength was largely unchanged, elongation to break decreased and melt viscosity increased. The only unpredictable property was impact resistance where the unnotched and notched Charpy results followed no discernable rules. Further analysis is underway to see whether trends can be identified when one looks beyond conventional mechanical tests. Further analysis includes looking for changes in crystallinity or crystal phase, polymer molecular weight, degree of filler dispersion and also determination of the failure mechanisms.

Introduction

Polymers play an inescapable part in our everyday lives. In fact it is very difficult to imagine a world without polymers. They help us to deliver water and to package our food so that it lasts longer. Polymers are also used in more high-tech items such as formula one cars or bullet-proof vests. It is mistakenly believed that polymers are not good for the environment, that they contribute to litter and that making polymers consumes a lot of oil. In reality it can be proven that just the reverse is the case. Life Cycle Analysis (LCA) shows that polymers are environmentally friendly compared to many other materials. When it come to oil usage, polymers account for only 4 % of the annual oil consumption whereas transportation accounts for ~40% and energy another ~40%. Startlingly, it has been shown that the use of polymers actually saves more oil that is used to make the plastics. This is primarily because plastics allow large weight savings for cars and trucks and this then results in a substantial reduction in fuel consumption. In transportation applications then it is the performance : weight ration that is paramount. In other applications such as domestic appliances performance : cost is more important. For both cases the use of composites can provide advantages compared to the polymer alone.

It has been shown previously that polymer composites can be used in two main ways. Firstly to provide comparable performance to unfilled polymer but at a lower system cost, or secondly, to provide performance well above that achievable using unfilled polymers. More than ever, the record oil prices and monomer prices are helping to drive growth in the fillers market. In this paper we will look at the use of the most common filler, calcium carbonate, in various thermoplastics. The aim is to show general trends and what to expect when adding a filler to a polymer. In addition some unexpected and less easy to understand topics will be mentioned.

Results & Discussion

Fillers can be added to polymers for a multitude of different reasons. Whatever the reason may be, cost reduction, improved performance or a combination of both, it is observed that the addition of filler changes every single property of the polymer. Some of the changes are desired and some not. Some are predictable and some not.

Here we will show what is expected and predictable and what cannot be anticipated and just has to be measured. There are different types of thermoplastic, for example amorphous and semi-crystalline, non-polar and polar, one that are inert and ones that can, at least potentially, react with the filler or degrade. All types are examined in order to draw out the common trends.

The filler concentration was chosen as 10 weight % for several reasons. Firstly, 10 weight % is enough to induce measurable changes in the polymer properties, well beyond the experimental scatter for the measurement methods. Secondly, due to the higher density of the filler (2.7 gcm^{-3}) relative to the polymers ($1-1.3 \text{ gcm}^{-3}$) 10 weight % only corresponds to about 3 volume % filler. All composite properties actually depend upon the volume percentage of each component and not the weight percentage. In effect we have only modified 3 % of our material, a relatively minor change. At such a low filler concentration we can neglect filler-filler interactions and other complications that arise at higher filler loadings.

The Polymers

Polymer	Crystallinity	Polarity	Reactivity
Polystyrene	Amorphous	Low polarity	Inert
SAN	Amorphous	Some polarity	Inert
PETG	Amorphous	Some polarity	Potentially reactive
PBT	Semi-crystalline	Some polarity	Potentially reactive
POM / Acetal	Semi-crystalline	Some polarity	Potentially reactive
Nylon 6	Semi-crystalline	High polarity	Potentially reactive

Chosen Filler

The filler chosen was calcium carbonate. A high quality, white, pure grade of marble with surface treatment using stearic acid was selected, namely Carbital 110S from Imerys. The particle size was selected to be that for a typical polymer grade filler, i.e. D_{50} 1.8 microns and D_{98} of 10 microns. This is an excellent grade to choose as a standard when looking at filled polymers. Similar grades are available from various suppliers, for example Omyacarb 2TAV from Omya. The surface treatment with stearic acid helps to ensure good dispersion in the polymers but does not promote adhesion.

Melt Viscosity / Processability

The viscosity of the polymer melt is important because it affects the throughput of extrusions and that equates directly to processing costs. Furthermore, high flowability of the polymer helps in filling complicated moulds and in speed to fill, again reflected in processing costs. Addition of any particulate matter to a liquid at low

concentrations is expected to decrease flow (increase viscosity) as described by the Einstein Equation for dilute systems. For this study we worked at 10 weight % filler which corresponds to ~ 3 volume %, this is in the dilute region where particle-particle interactions are negligible and so the Einstein Equation can be applied.

Normally melt flow index (MFI) is used as a crude measure of polymer viscosity. For filled systems it is misleading to use MFI because MFI is expressed in mass per unit time (grams per 10 minutes) and the addition of filler increases the density of the material. This complicates matters and can lead one to believe that an increase in flow rate has occurred when in reality, the density of the material has simply increased and the viscosity has not improved afterall.

In order to avoid the abovementioned confusions from MFI it is better to use the melt volume flow rate (MVR), which expresses the results from the measurement as ml per 10 minutes. This is a valid way to compare flow rates of unfilled polymers and their filled counterparts.

An increase in MVR corresponds to a decrease in viscosity. Furthermore, the MVR is made at one shear rate only and so care must be used when extrapolating MVR data to predict flow behaviour under the higher shear rates encountered for example in an extruder or during injection molding. Having said that, Shenoy has presented convincing evidence that, using the correct equations, one may extrapolate MVR data of filled polymer to higher shear rates.

Polymer	Crystallinity	Polarity	Reactivity	MVR (ml/10min)	
Polystyrene	Amorphous	Low	Inert	6.4/5.4	-15%
SAN	Amorphous	Some	Inert	29/17	-40%
PETG	Amorphous	Some	Potentially	37/27	-27%
PBT	Semi-crystalline	Some	Potentially	---	
POM / Acetal	Semi-crystalline	Some	Potentially	8/7	-12%
Nylon 6	Semi-crystalline	High	Potentially	---	

Table 1 Effect of filler on polymer melt viscosity (MVR)

Mechanical Properties

The mechanical properties of polymers are also affected by filler. The idea composite, if such a thing is possible would probably have infinite modulus, strength, heat

distortion temperature and impact resistance. In reality such a material cannot exist and instead we are forced to make compromises. For a given application some properties are more important and others less important or not important at all. For example the base of a washing machine needs mainly impact resistance and only limited modulus and strength. The washing machine tub (the part around the metal drum holding in the hot water) needs primarily modulus and heat distortion temperature plus some strength but no impact resistance. The ideal composite then depends on the application in question and is the material that meets the requirements at the lowest cost.

Modulus

Modulus may be measure in tension, compression or in flex. The values and trends seen are similar and usually the tensile modulus is taken for convenience. As mineral filler all have moduli considerably higher than those of polymers, the addition of filler always raises the modulus of the polymer. The modulus is unaffected by the size of the filler or the amount of adhesion between the filler and the polymer. The reason that the modulus is independent of adhesion is that modulus is measured at such a low stress and strain that the strength of the filler / polymer interface is not tested. Even weak van der Waals forces are enough to ensure adhesion during testing of modulus.

Polymer	Crystallinity	Polarity	Reactivity	Modulus (MPa)	
Polystyrene	Amorphous	Low	Inert	3156/3527	+12%
SAN	Amorphous	Some	Inert	3793/4200	+11%
PETG	Amorphous	Some	Potentially	1949/2235	+15%
PBT	Semi-crystalline	Some	Potentially	2458/2807	+14%
POM / Acetal	Semi-crystalline	Some	Potentially	2664/3063	+15%
Nylon 6	Semi-crystalline	High	Potentially	2719/3578	+32%

Table 2 Effect of filler on modulus

As pointed out in the introduction, the low amount of filler used (~3 volume %) means that the modulus should increase measurably but not excessively. The linear rule of mixtures can be used to approximate the expected increase in modulus due to filler addition, assuming that the polymer is not itself changed in some way by filler addition. The results are as expected for all polymers except nylon 6. The modulus increase for nylon 6 is too high to be explained using the linear rule of mixtures and this is a hint that something unexpected has occurred. To obtain such a high modulus,

the filler must have altered the nylon phase in some way. For example, an increase in crystallinity or a change in crystal phase could be the cause of the large increase. This is being investigated and we will report the molecular weight and crystallinity effects later. For now we note that the nylon is behaving in an atypical way and so all of the other nylon results need to be considered accordingly.

Tensile Strength

The yield strength is the peak of the stress-strain curve of a polymer. It represents the point at which the material has failed. Brittle materials do not yield and so in that case the stress at break or ultimate tensile strength is reported. In reality parts are designed so that in use they will never experience a force anywhere near the yield or break strength. Unlike modulus, the yield strength is measured at stresses and strains that are high enough to test the adhesion between the filler and the polymer matrix. This means that filler particles with higher surface area (more polymer-filler contact area) lead to better yield strength. Another way to promote yield strength is to add a coupling agent that bonds to the filler and entangles with the polymer. Yet another factor is that polar interactions between the filler surface and the polymer may lead to enhanced adhesion and therefore yield strength. Clearly, such polar-polar interactions are only possible when both polymer and filler are polar. In our case some of the polymers are relatively polar but the filler is surface treated with stearic acid rendering it non-polar because the aliphatic carbon chains are facing outward from the filler and into the polymer.

Polymer	Crystallinity	Polarity	Reactivity	Strength (MPa)	
Polystyrene	Amorphous	Low	Inert	54.9/51.1	-7%
SAN	Amorphous	Some	Inert	86.8/77.6	-11%
PETG	Amorphous	Some	Potentially	47.9/49.0	+2%
PBT	Semi-crystalline	Some	Potentially	56.5/56.9	±0%
POM / Acetal	Semi-crystalline	Some	Potentially	64.6/56.5	-13%
Nylon 6	Semi-crystalline	High	Potentially	74.8/84.6	+13%

Table 3 Effect of filler on tensile strength

Elongation to Break

Elongation to break is not one of the most important properties and is only reported for the sake of completeness. In some specific cases it is a requirement, one example being cable jacket formulations where the cable needs to be bent around sharp corners during installation and must not break.

Polymer	Crystallinity	Polarity	Reactivity	Elongation (%)	
Polystyrene	Amorphous	Low	Inert	3.1/2.4	-23%
SAN	Amorphous	Some	Inert	0/0	±0%
PETG	Amorphous	Some	Potentially	33.8/20.9	-38%
PBT	Semi-crystalline	Some	Potentially	70.6/13.3	-80%
POM / Acetal	Semi-crystalline	Some	Potentially	26.7/18.2	-32%
Nylon 6	Semi-crystalline	High	Potentially	76.6/8.5	-89%

Table 4 Effect of filler on elongation to break

So far the mechanical properties have behaved as expected from experience and from theory, regardless of whether the polymer is amorphous, semi-crystalline, polar or non-polar. There are relatively successful equations for predicting and modeling the changes in modulus and yield strength. Elongation is very hard to model well because once that material is so highly stretched, it bears little resemblance to the starting material and so models break down. Some attempts at modeling elongation have had limited success.

Impact resistance

The impact resistance is one of the key properties. There are many ways to measure it and the method chosen should be the one that most closely relates to the actual use of the part. Furthermore, each method gives different information so that must also be considered. Impact resistance is composed of two distinct parts, first the energy needed to initiate (form) the crack and then secondly the energy needed to propagate (grow) the crack through the sample. The most common test methods are probably Izod and Charpy tests whereby a pendulum hits the sample at a specific point. Very commonly people measure the notched impact resistance because it gives results with less scatter i.e. sample to same variation. However, while it is useful the notched impact is not always the appropriate method to use.

It should be mentioned that the notched and unnotched impact resistance was measured at 23°C, 0°C and -30°C for all samples. However, the trends were the same for all temperatures and so the results at 23°C alone are presented.

The notched Charpy is probably the most commonly quoted value and the one that is often scrutinized the most closely by designers and molders. It represents only the energy needed to grow the crack because a large well-defined crack (the notch) is

already introduced to the specimen to force it to break at a predetermined place. Notched impact is particularly relevant for products and parts that may become scratched during use because these scratches act like the notch, helping to induce failure.

It is seen that most of the polymers are rather insensitive to filler addition. The exceptions are POM and nylon which are very sensitive. Often one finds that notched impact resistance is completely insensitive to filler or only somewhat sensitive.

Polymer	Crystallinity	Polarity	Reactivity	Notched Charpy (kJ/m ²)	
Polystyrene	Amorphous	Low	Inert	1.45/1.48	±0%
SAN	Amorphous	Some	Inert	1.6/1.5	±0%
PETG	Amorphous	Some	Potentially	6.1/5.5	-10%
PBT	Semi-crystalline	Some	Potentially	3.7/3.6	±0%
POM / Acetal	Semi-crystalline	Some	Potentially	6.40/3.95	-38%
Nylon 6	Semi-crystalline	High	Potentially	6.28/3.15	-50%

Table 5 Effect of filler on notched Charpy impact resistance

The unnotched impact resistance of polymers is usually far higher than the notched impact resistance. In the case of the unnotched test the energy measured is the sum of two components. Namely the energy needed to create a crack, often relatively high, plus the energy needed to grow the crack, usually much lower. Unnotched impact resistance is most appropriate for products and parts that are not exposed to scratching or direct impact. As an example, the base of a washing machine is enclosed within a metal housing. The plastic base cannot be scratched as it is protected by the metal case, but it still needs to survive impact, for example a short fall during shipping, handling and installation.

Filler particles that are too large (or smaller particles that are agglomerated to form larger effective particles) act as flaws where a crack can be initiated upon impact. For this reason it is important to make sure that the filler used is fine enough and perfectly dispersed. The mean particle size is not as important as the top cut (D_{98}) because it is the biggest particles and agglomerates that dominate. Using the correct surface treatment can help to deagglomerate and disperse the filler particles and correct extruder set-up is crucial as well. Twin screw extruders are more effective than single screw machines.

The PBT, POM and nylon show the expected behaviour, that is, reduced impact resistance, presumably due to the filler particles acting as flaws. One might be tempted based on the results to conclude that semi-crystalline polymers suffer from reduced unnotched impact resistance when filler is added. However it is widely known that PP homopolymer has a far better unnotched impact resistance when this type of filler is added so the hypothesis breaks down. Interestingly, PS and SAN, very brittle polymers with poor impact resistance, actually improve significantly due to filler addition. This is almost certainly because on impact the filler-polymer interface debonds and crazes are initiated. Such crazing helps to delocalize the energy of impact and leads to a better impact resistance. The mode of failure with and without filler is under investigation.

Polymer	Crystallinity	Polarity	Reactivity	Unnotched Charpy (kJ/m ²)	
Polystyrene	Amorphous	Low	Inert	16.8/28.8	+42%
SAN	Amorphous	Some	Inert	21.4/27.1	+19%
PETG	Amorphous	Some	Potentially	261/276	±0%
PBT	Semi-crystalline	Some	Potentially	281/132	-53%
POM / Acetal	Semi-crystalline	Some	Potentially	195/102	-48%
Nylon 6	Semi-crystalline	High	Potentially	396/91.3	-77%

Table 6 Effect of filler on unnotched Charpy impact resistance

When studying filled polymers it is more useful to look at the unnotched impact resistance as it is very sensitive to large particles or agglomerates. So, for example, the unnotched impact resistance can be used as an indicator of extruder performance and as a tool to optimize extruder set-up. The absolute value of the unnotched impact resistance is one indicator, but also the amount of scatter in the results (the value for the standard deviation) can be used to tell how uniform the material is. Lower standard deviation indicating good extruder set-up.

Polymer	Crystallinity	Polarity	Reactivity	Penetration Test (J)	
Polystyrene	Amorphous	Low	Inert	0.5/0.9	+44%
SAN	Amorphous	Some	Inert	0.5/0.2	±0%
PETG	Amorphous	Some	Potentially	43.4/43.4	±0%
PBT	Semi-crystalline	Some	Potentially	41.1/31.3	-24%
POM / Acetal	Semi-crystalline	Some	Potentially	0.4/0.6	±0%
Nylon 6	Semi-crystalline	High	Potentially	49.8/12.2	-76%

Table 7 Effect of filler on penetration test

Conclusions

Polymers and filled polymers are essential in our everyday lives. Filled polymers are used in two ways, either to match the properties of an unfilled polymer but at reduced cost, or the addition of filler can provide acceptable cost but with performance far superior to that attainable with neat polymer. In recent times, the dramatic increase in oil price has given an extra incentive to look closely at the opportunities for using fillers.

Fillers can help processability and improve mechanical properties at the same time. Several of the most important properties respond in predictable, well-understood ways to addition of fillers. The one exception is the impact resistance because that is affected by so many parameters that no satisfactory theory exists. The results presented show that modulus always increases, strength is relatively unaffected by isotropic fillers like calcium carbonate and impact resistance is may increase sharply, decrease sharply, or remain the same.

From the conventional mechanical results shown it is not possible to put forward any sensible theory to explain the impact resistance results. To gain further understanding we are looking in more detail at the materials presented. For example, we will look for changes in molecular weight and crystallinity of the polymers coupled with analysis of the failure mechanism upon impact, i.e. crazing versus shear yielding. It is hoped that this supplementary information will shed some light on the behaviour of filled polymers.

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