VICTREX LMPAEK™ POLYMER CHEMICAL RESISTANCE, INCLUDING VICTREX AM™ 200 PRINTED PARTS

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INTRODUCTION

Understanding the chemical resistance of a polymer is critical for defining the applications where it can be used. Victrex PEEK and Victrex LMPAEK™ materials are part of the Poly Aryl Ether Ketones (PAEK) family, a group of polymers that if, allowed to crystallize during or after manufacturing of a component, will exhibit high mechanical performance, elevated thermal stability, and superior chemical resistance.

Victrex AM™ 200 filament is the latest Victrex grade developed for Additive Manufacturing (AM) processes and is based on the LMPAEK™ PEEK-based copolymer. Thanks to its slower crystallisation kinetics, this polymer can be 3D printed via for example filament fusion fabrication in amorphous and crystalline states. The chemical resistance of this material when 3D printed amorphous and crystalline are reported in this document.

This brochure is also useful for non-AM uses of LMPAEK™ polymer, as injection molded samples are also included.

SUMMARY

A cautious comparison with injection molded PEEK shows comparable results between VICTREX AM™ 200 3D printed specimens made from LMPAEK™ PEEK-based copolymer. For critical applications, end-use testing and qualification is recommended for both printed VICTREX AM™ 200 and printed PEEK. VICTREX AM™ 200 that is left amorphous and not printed or annealed to crystalline will have less resistance to certain chemicals such as toluene and chloroform.

METHODOLOGY

ISO 527-2-1BA specimens of VICTREX AM™ 200 filament have been printed via the filament extrusion process in amorphous (AM200-A) and crystalline state (AM200-C) within a Minifactory Ultra system in flat orientation. Injection molded ISO-527-2-1BA bars of the equivalent LMPAEK™ polymer to VICTREX AM™ 200 were also manufactured as representative of samples having the ideal structural integrity, i.e. voids free, smooth surfaces and ultimately mechanical isotropy (IM LMPAEK). VICTREX AM™ 200 amorphous samples had 9% crystallinity content, while AM200 printed crystalline, and injection moulded samples had more than 25%. All the sets of samples were exposed to various chemicals at different temperatures in pressure bottles. Following exposure, the specimens were removed from the solvents, washed in deionised water and dried before being tested for tensile strength, differential scanning calorimetry (DSC) and gel permeation chromatography (GPC).

Three repeats from each group (amorphous, crystalline and injection moulded) were tested with every chemical.

The list of substances and conditions of testing are reported in Table 1.

Chemical	Temperature (°C)	Duration (days)
50% Sodium Hydroxide	100	7
50% Phosphoric Acid	100	7
40% Sulphuric Acid	100	7
Chloroform	23	7
Ethyl Acetate	23	7
880 Ammonia	23	7
Calcium bromide 4.3M	100	7
Naphtha	40	14
Toluene	40	14

Table 1. List of Chemical Solutions

Some solutions were tested at temperature, while others due to higher hazard risk were tested at room temperature. To compensate for lowering testing temperature, some tests were prolonged in number of days of exposure.

TENSILE TESTING

The tensile tests were carried out on a universal Instron testing frame using wedge grips according to ISO 527-2. Stress-strain curves were generated and assessed for every chemical. The values of tensile strength at yield were considered to determine the relative change of the exposed samples from the unexposed reference samples. Any change smaller than 5% from the reference value would constitute a natural variation of the parameter and not a meaningful change in the material properties. A change between 5-10% would be considered significant but not severe. A change bigger than 10% would be considered severe. These intervals are our suggestions, what we consider severe might instead be acceptable in a given application and vice versa. Customers should verify that printed VICTREX AM™ 200 components meet their performance expectations and confirm suitability for end-use.

Figure 1. ISO527-2-1BA bars in Injection moulded LMPAEK (left), VICTREX AM™ 200 printed crystalline (centre) and printed amorphous (right)

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Crystallinity content of all specimens was checked via DSC according to ISO 11357 to detect significant changes after chemical exposure. A major variation of crystallinity can indicate that a chemical altered the structure of the polymer and therefore the ability of the polymer to crystallize is inhibited. Preliminary thermo-gravimetrical analysis was carried out on chemical exposed bars to test if any residual volatile was present and if so, those specimens were discarded from further testing. Amorphous AM200 chloroform and amorphous AM200 toluene bars exhibited the presence of residues and were discarded in the DSC analysis.

GEL PERMEATION CHROMATOGRAPHY (GPC)

DSC can detect major signs of degradation, but GPC can detect changes in the molecular weight and molecular weight distribution before they become so severe to be evident in the thermal and mechanical properties. Solutions of each sample were prepared by dissolving 40mg of material in 2 mL 4-chlorophenol at 205°C. They were then cooled and diluted before analysis in a Malvern GPC Max and Malvern TDA305.

RESULTS

DSC

The crystallinity content of reference and exposed samples are shown in Table 2.

Chemical	IM LMPAEK	AM200-A	AM200-C
Unexposed	25	9	25
50% Sodium Hydroxide	23	7	25
50% Phosphoric acid	24	8	26
40% Sulphuric Acid	24	7	25
Calcium bromide	23	7	26
Chloroform	25	NA	27
Ethyl Acetate	26	8	24
Naphtha	25	7	25
880 Ammonia	24	8	25
Toluene	24	NA	24

Table 2. Crystallinity content in Injection Moulded samples (IM), VICTREX AM™ 200 FIL printed amorphous (AM200-A) and VICTREX AM™ 200 printed crystalline (AM200-C). Deviation standard in the 0-2 points range.

Crystallinity content did not significantly change before and after chemical exposure and the values are within the expected ranges. Amorphous specimens are below the 10% crystallinity content, while molded and printed crystalline samples are well above the 20% crystallinity value. These results indicate that the chemical exposure did not alter the ability of the polymer to crystallize.

The VICTREX AM™ 200 amorphous samples exposed to chloroform and toluene could not be tested because they showed presence of the chemicals before DSC testing. This is a sign of a chemical entering the structure of the polymer and solubilizing it, and it is called plasticization. Plasticization can decrease the strength of a polymer, increase flexibility (elongation at break) and alter thermal and rheological properties.

TENSILE TESTING

The typical stress-strain curves of the Victrex AM™ 200 samples printed amorphous and crystalline are shown in Figure 2.

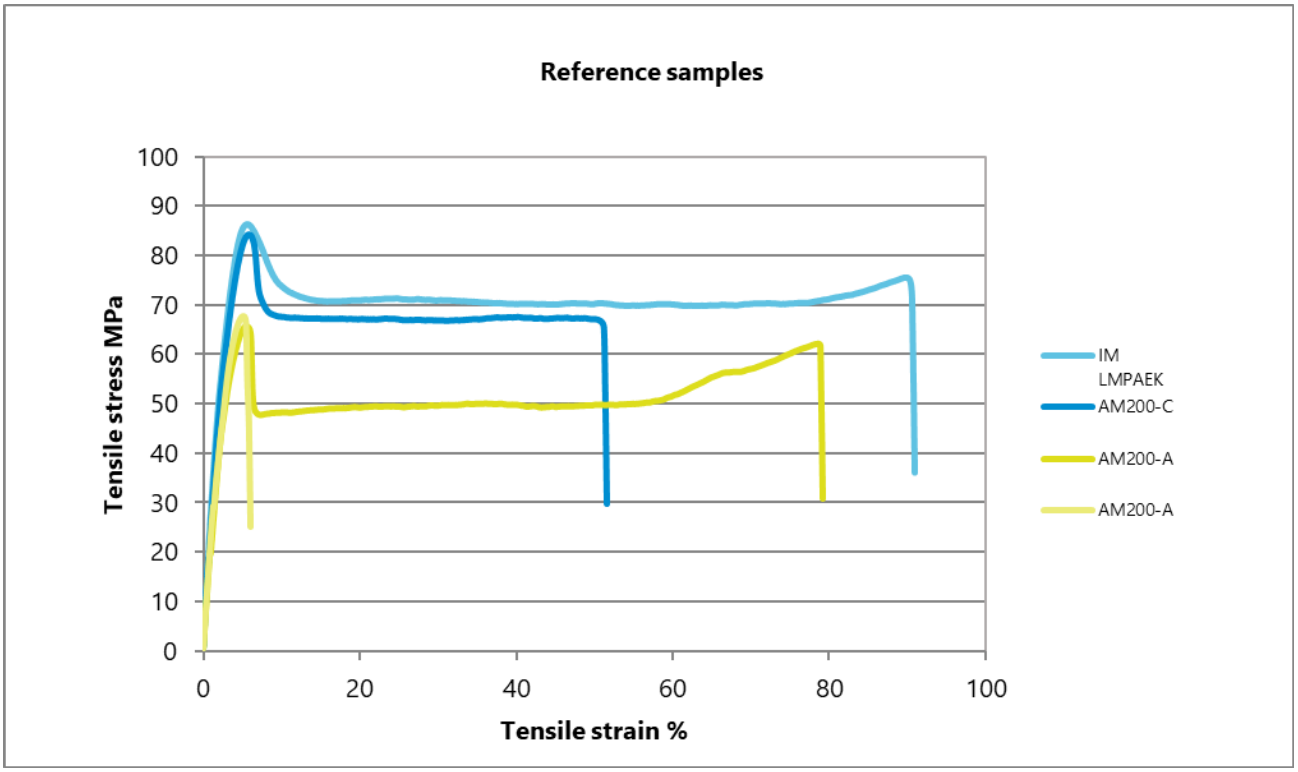

Figure 2. Tensile stress-strain curves of unexposed samples. AM200-A shows large variability in strain at break.

As expected, VICTREX AM™ 200 printed crystalline and injection molded reference show similar strength at yield, but higher elongation at break for the latter specimens. This gap is well-known in the AM industry and although materials and printers are advancing, it is still present in most filament extrusion made parts. The AM200-A samples show lower strength and much more variability in the elongation at break, hence why two curves are reported.

A summary of the results of the chemical exposure are listed in Table 3.

Chemical	IM LMPAEK	AM200-A	AM200-C
50% Sodium Hydroxide, 7 days, 100°C	-1.0% ●	1.8% ●	-0.9% ●
50% Phosphoric Acid, 7 days, 100°C	1.0% ●	2.1% ●	-1.1% ●
40% Sulphuric Acid, 7 days, 100°C	1.6% ●	1.9% ●	-1.2% ●
Chloroform, 7 days, 23°C	-3.6% ●	-75.9% ■	-3.2% ●
Ethyl Acetate, 7 days, 23°C	-0.3% ●	0.2% ●	-2.4% ●
880 Ammonia, 7 days, 23°C	-5.3% ▲	-7.0% ▲	-7.2% ▲
Calcium Bromide 4.3M, 7 days, 100°C	1.2% ●	4.6% ●	-1.6% ●
Naphtha, 14 days, 40°C	-1.5% ●	0.8% ●	-0.7% ●
Toluene, 14 days, 40°C	-1.2% ●	-29.4% ■	-1.7% ●

Table 3. Mechanical results after chemical exposure

● =No Interaction ▲ =Slight Interaction ■ =Severe Interaction

AM200-C specimens show little variation (less than 5%) after exposure for most substances. AM200-A samples are affected by chloroform and toluene. Overall, the results are not surprising because it is the crystalline regions in the polymer that act as barrier for diffusion for these two chemicals.

VICTREX AM™ 200 parts are sensitive to 880 Ammonia exposure in all conditions. Changes in mechanical performance are not very large but still significant compared to unexposed samples, thus suggesting cautious use.

A FEW EXAMPLES OF THE STRESS-STRAIN CURVES ARE REPORTED BELOW

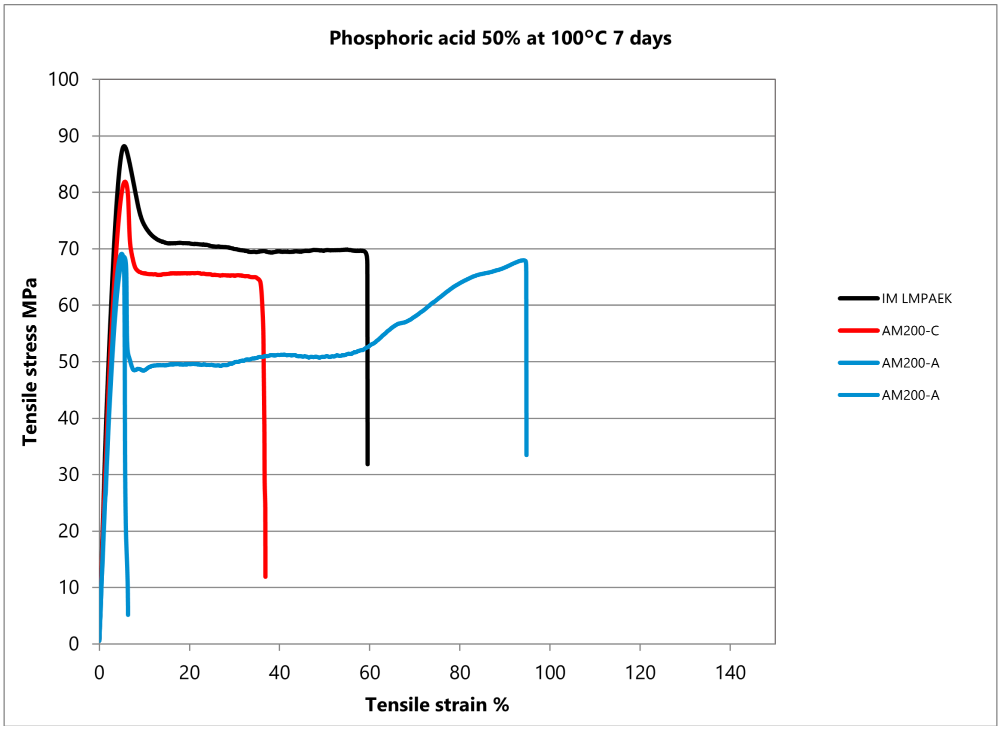

Figure 3. Phosphoric Acid exposure data

No significant changes for any group of specimens are visible within the test with Phosphoric acid. Similar stress-strain curves are found for all the other substances causing no major changes in the polymer.

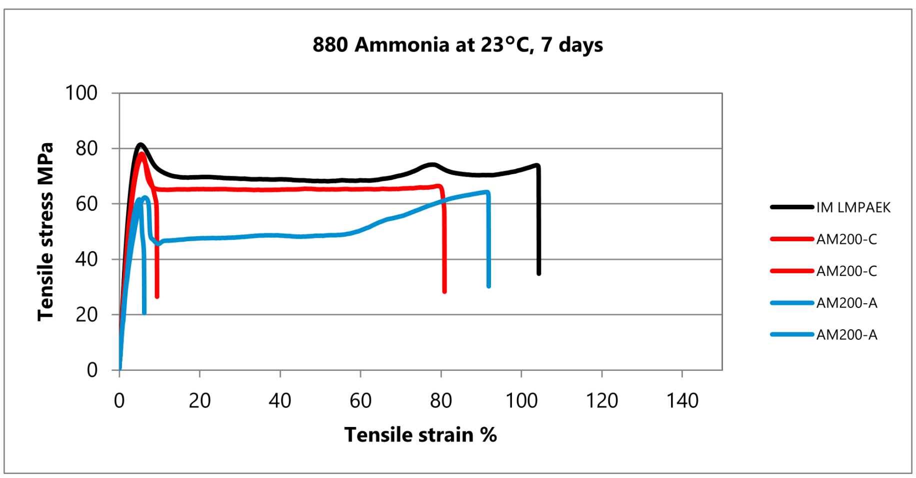

Figure 4. 880 Ammonia exposure Data

Changes in yield strength for all sets of specimens in the test with 880 Ammonia. Both AM200-A and AM200-C show a dual failure behaviour: failure straight after yield at low strain values or the more common yield-necking, plastic plateau deformation and breakage at high values of strain. The dual behaviour could be due to the combination of specimen variability because of the 3D printing process and diffusion of the chemical in the polymer, causing plasticisation of the sample.

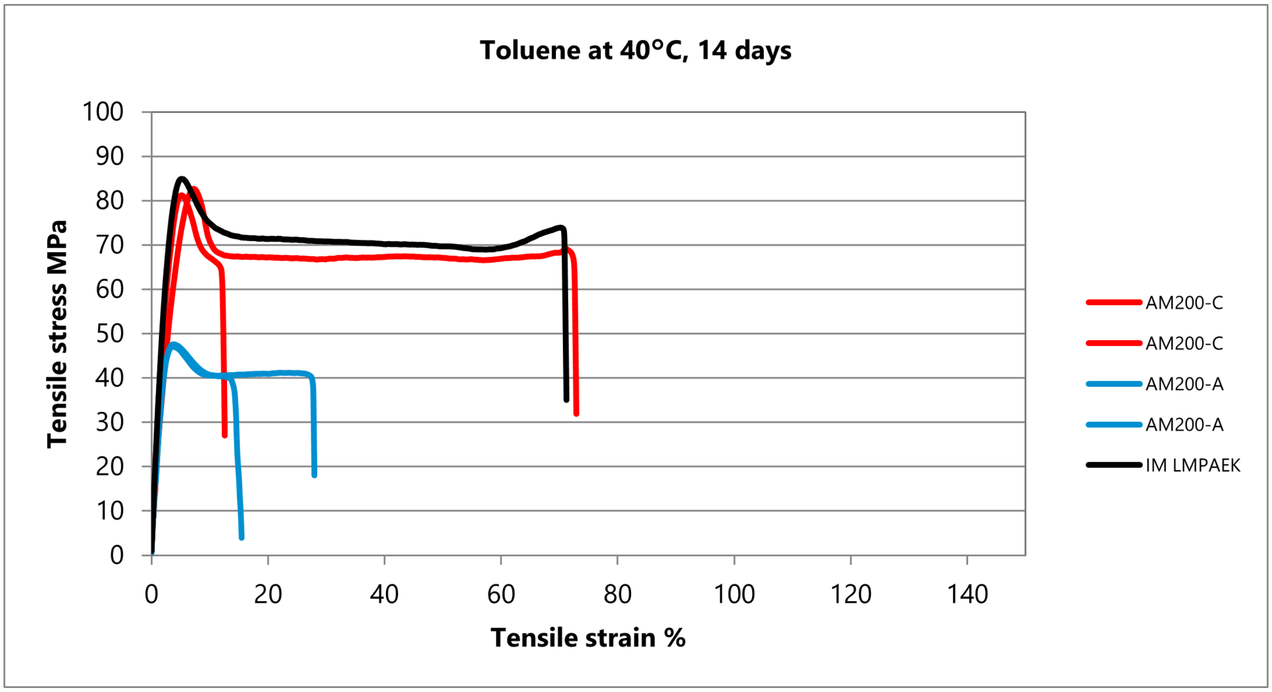

Figure 5. Toluene exposure data

Significant reduction in yield strength with Toluene for the VICTREX AM™ 200 printed amorphous samples as a diffusion of toluene into the polymer matrix and causing plasticisation.

GEL PERMEATION CHROMATOGRAPHY (GPC)

Gel permeation chromatography measures changes in molecular weight and molecular weight distribution in polymers. This technique allows to detect signs of crosslinking, chain scission or branching in polymers because of chemical exposure. Measuring via GPC allows to pick up on degradation before it manifests in the mechanical properties. The relative changes of weight average molecular weight (Mw) are reported in Table 4.

Sample	IM LMPAEK	AM200-A	AM200-C
50% Sodium Hydroxide	-1.7% ●	2.9% ●	0.5% ●
50% Phosphoric Acid	1.7% ●	2.5% ●	-1.9% ●
40% Sulphuric Acid	-0.5% ●	1.5% ●	-2.4% ●
Calcium Bromide	0.2% ●	0.0% ●	0.5% ●
Chloroform	0.0% ●	NA ●	-4.1% ●
Ethyl Acetate	-1.0% ●	-1.7% ●	-5.3% ▲
Naphtha	-0.2% ●	0.5% ●	-2.4% ●
880 Ammonia	-0.2% ●	-1.2% ●	-2.4% ●
Toluene	-1.0% ●	1.2% ●	-2.6% ●

Table 4. Mw relative changes for all sets of samples

● =No Interaction ▲ =Slight Interaction ■ =Severe Interaction

Variation in the exposed injection moulded samples from the reference samples are small and no signs of degradation can be detected. There is a minor difference between the values for any exposure route in the VICTREX AM™ 200 samples printed crystalline. This indicates lack of degradation.

Toluene, chloroform and 880 ammonia cause loss in strength in amorphous VICTREX AM™ 200 samples but no changes in GPC results. These chemicals act as solvents and are plasticising the network, leading to loss of strength/ modulus. They are not chemically changing the polymer, hence no change in Mw. When the polymer is amorphous, it is easier for a solvent to diffuse into the polymer.

COMPARISON AGAINST PEEK

The next question is natural: how does VICTREX AM™ 200 printed samples and in general LMPAEK™ polymers compare to PEEK? A comparison can be done with caution by keeping in mind that:

- No tests were performed on PEEK printed samples
- PEEK data come from injection molded specimens
- PEEK data come from different chemical resistance campaigns that have longer exposure time. The longer the exposure time the harsher it could be for the testing material to resist attack.

Data is reported in Table 5.

Chemical	IM LMPAEK	AM200-A	AM200-C	PEEK (*)
50% Sodium Hydroxide, 7 days, 100°C	-1.0% ●	1.8% ●	-0.9% ●	<5% ●
50% Phosphoric Acid, 7 days, 100°C	1.0% ●	2.1% ●	-1.1% ●	<5% ●
40% Sulphuric Acid, 7 days, 100°C	1.6% ●	1.9% ●	-1.2% ●	5-10% ▲
Chloroform, 7 days, 23°C	-3.6% ●	-75.9% ■	-3.2% ●	<5% ●
Ethyl Acetate, 7 days, 23°C	-0.3% ●	0.2% ●	-2.4% ●	<5% ●
880 Ammonia, 7 days, 23°C	-5.3% ▲	-7.0% ▲	-7.2% ▲	<5% ●
Naphtha, 14 days, 40°C	-1.5% ●	0.8% ●	-0.7% ●	<5% ●
Toluene, 14 days, 40°C	-1.2% ●	-29.4% ■	-1.7% ●	<5% ●

Table 5. Chemical exposure results. Comparison against PEEK

● =No Interaction ▲ =Slight Interaction ■ =Severe Interaction

**Exposure time: 28days. Injection moulded samples*

Victrex AM™ 200 samples printed crystalline show similar level of chemical resistance to injection molded PEEK. Similar but not same because the exposure time of the PEEK samples was longer. As expected, VICTREX AM™ 200 samples printed amorphous plasticize when exposed to chloroform and toluene, this does not occur in both PEEK and VICTREX AM™ 200 crystalline thanks to the crystallinity regions.

All samples exposed to 880 Ammonia show some changes in the mechanical properties, however no major changes were detected via GPC. 880 Ammonia refers to the maximum concentration of ammonia in water and at this concentration it might start to act like a solvent for the polymer causing plasticisation, i.e. decrease in mechanical performance but no change in molecular weight. More dilute aqueous ammonia solutions are much more common and this effect may not occur. We suggest further testing before use in the application.

CONCLUSIONS

The chemical resistance of LMPAEK™ printed specimens is reported here for the first time. The importance of crystallisation for those applications requiring exposure to certain chemical agents is evident and end users should be aware of it.
The effects of chemical exposure were investigated with multiple analytical techniques to provide more confidence in the interpretation of the results.
A cautious comparison with injection molded PEEK shows comparable results between VICTREX AM™ 200 specimens made from LMPAEK™ PEEK-based copolymer and PEEK. Tests were carried out at high temperatures when possible. High testing temperature generally makes things worse for the chemical resistance of a polymer. Therefore, if the chemical resistance of a polymer is good at high temperature, it will be the same if not better at any use temperature below the test conditions.
More chemicals and conditions will be tested in the future.

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