PRODUCTION OF HIGH SOLID CONTENT POLYMER/YSZ COMPOSITES AND FREE FORM YSZ FIBERS

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Abstract: With 65 wt% solid content, Polymer/YSZ composites have been produced via extruder by using of PP, PMMA and TPU. With pyrolysis process, physical stability conditions of continuous YSZ free form fibres have been investigated according to type of polymer and pre-sintering temperature. In addition to this, melt flow rate values and thermal analysis investigations of PP, PMMA, TPU, PP/YSZ, PMMA/YSZ, TPU/YSZ were determined by melt flow rate analysis and TGA. Compared to unreinforced polymers (PMMA, PP and TPU) the melt flow rate of the composites containing YSZ powder has decreased approximately 15 %. From TGA results it was also found that the contribution of the yttria stabilized zirconia changed the decomposition temperature of the polymer part.

KEYWORDS: POLYMER/YSZ COMPOSITES, MELT FLOW RATE, PYROLYSIS, FREE FORM FIBERS

1. Introduction

Polypropylene is one of the most popular thermoplastics, due to its high isotacticity, enhanced mechanical properties, narrower molecular weight distribution and increased clarity lead to a balance of physical and mechanical properties, and its environmental friendliness (recyclability) and low cost. However, with these advantages, there is also a handicap. Although its resistance to crack initiation is very high, especially at low temperatures, resistance for crack propagation of the PP matrix is very low. To optimize this behaviour, PP is usually modified with some reinforcements. PMMA is also one of the most popular thermoplastic materials with properties such as optically clear amorphous view, perfect transparency, higher impact strength. However, its application is limited at elevated temperature due to its relatively poor thermal stability [1].

Polyurethanes appear in a variety of forms: foams, elastomers, adhesives, coatings, shape memory applications, also, their elastomers (TPU) can be repeatedly melted and processed due to the absence of the chemical networks. In recent years, TPU was used in the spindle and shrink-proof processing [2-5].

In polymer matrix composites, fillers have a substantial role in developing the properties of thermoplastics and with their addition, improved mechanical properties can be obtained on polymeric materials [1].

In recent years, studies about the addition of fillers to polymers increase due to effect of fillers on composites thermal stability [6].

Yttria stabilized zirconia (YSZ) is recognized as one of the most suitable electrolyte material in solid oxide fuel cell technology (SOFC) and due to its stability in cubic structure, it can be used as fillers in applications which needs ionic conductivity and oxygen vacancies. With pyrolysis of polymers in PMC, porous materials can be obtained [7].

Porous materials are important in many industries and applications which needs high surface area, filtration ability and tendency to control over optical properties such as adsorbents, sensors and catalysts, electrodes for fuel cells [8-17].

In this study, with high solid content (65 wt%) composites free form fibers were produced with using extruder and to create continuous YSZ fibers, polymer parts of composites were pyrolyzed under an Argon atmosphere.

2. Experimental Procedure

For production of PP/YSZ, PMMA/YSZ, TPU/YSZ composites, commercial PP (Borealis), PMMA (Acrytex), TPU (Bayer Desmopan) polymers and 8-YSZ which we synthesized via high energy milling were used. To cover polymer granules with YSZ, powders and granules milled together 30 minutes in polypropylene jars with planetary mill.

With 65 wt% solid content, PMMA/YSZ, PP/YSZ, TPU/YSZ composites have been produced with two different diameters (2 and 5 mm, averagely) of cylindrical form via extruder. Amount of solid that can be feeded to the system homogenously was determined according to sustainability of product which was taken from extruder. Samples which have 2 mm diameters, pressed at 150 MPa during 2 minutes to observe physical stability of YSZ fibers after pyrolysis.

TGA investigations of PP, PMMA, TPU, PP/YSZ, PMMA/YSZ,TPU/YSZ were done in order to search out effect of YSZ on decomposition temperature of system. Effect of YSZ powders on PP, PMMA, TPU, PP/YSZ, PMMA/YSZ, TPU/YSZ systems were also investigated by melt flow rate analysis. Pyrolysis temperature was kept at 450°C and heating/cooling rate were determined at 2°C/min and 5°C/min, respectively. After pyrolysis, sintering was carried for each system at 700, 900 and 1100°C. Information about samples are given by Table 1.

With pyrolysis process, stability conditions of continuous YSZ have been investigated according to type of polymer and pre-sintering temperature.

During pyrolysis process, stability of continuous structures have been supported by alumina powder bed in a alumina crucible.

Table 1: Sample name and operations

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Raw materials</th>
<th>Diameter (mm)</th>
<th>Sintering Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA/YSZ-700(5)</td>
<td>PMMA/YSZ</td>
<td>5</td>
<td>700</td>
</tr>
<tr>
<td>PMMA/YSZ-900(5)</td>
<td>PMMA/YSZ</td>
<td>5</td>
<td>900</td>
</tr>
<tr>
<td>PMMA/YSZ-1100(5)</td>
<td>PMMA/YSZ</td>
<td>5</td>
<td>1100</td>
</tr>
<tr>
<td>PP/YSZ-700(5)</td>
<td>PP/YSZ</td>
<td>5</td>
<td>700</td>
</tr>
<tr>
<td>PP/YSZ-900(5)</td>
<td>PP/YSZ</td>
<td>5</td>
<td>900</td>
</tr>
<tr>
<td>PP/YSZ-1100(5)</td>
<td>PP/YSZ</td>
<td>5</td>
<td>1100</td>
</tr>
<tr>
<td>TPU/YSZ-700(5)</td>
<td>TPU/YSZ</td>
<td>5</td>
<td>700</td>
</tr>
<tr>
<td>TPU/YSZ-900(5)</td>
<td>TPU/YSZ</td>
<td>5</td>
<td>900</td>
</tr>
<tr>
<td>TPU/YSZ-1100(5)</td>
<td>TPU/YSZ</td>
<td>5</td>
<td>1100</td>
</tr>
<tr>
<td>PMMA/YSZ-900(2)</td>
<td>PMMA/YSZ</td>
<td>2</td>
<td>900</td>
</tr>
<tr>
<td>PP/YSZ-900(2)</td>
<td>PP/YSZ</td>
<td>2</td>
<td>900</td>
</tr>
<tr>
<td>TPU/YSZ-900(2)</td>
<td>TPU/YSZ</td>
<td>2</td>
<td>900</td>
</tr>
</tbody>
</table>
3. Results and Discussion

In Figure 1-3, TGA investigations showed that YSZ reinforcements effect on decomposition temperature of TPU, PP and PMMA. YSZ reinforcement increased decomposition temperature of PMMA and decrease decomposition temperature of PP and TPU. It is known that, high solid content gets higher heat resistance to the polymer matrix composites. But in soft polymers, when temperature gets higher, solid content comes together due to the melting of polymer part of the system. In this way, structure becomes non-homogeneous and thermal stability decrease due to the decomposition of surface which is in contact with solid part. Melt flow rates of PP, PMMA, TPU, PP/YSZ, PMMA/YSZ and TPU/YSZ are given by Table 2. Compared to unreinforced polymers (PMMA, PP and TPU), melt flow rate of the systems containing YSZ powder has decreased approximately 15% at PMMA/YSZ and PP/YSZ and TPU/YSZ systems. According to these results, it can be verified that due to filler effect of YSZ, polymer chains mobility has decreased with similar other studies.

Table 2: Melt flow rate values of samples.

<table>
<thead>
<tr>
<th></th>
<th>Melt Flow Rate (g/10 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>19.8</td>
</tr>
<tr>
<td>PMMA/YSZ</td>
<td>16.8</td>
</tr>
<tr>
<td>PP</td>
<td>20.0</td>
</tr>
<tr>
<td>PP/YSZ</td>
<td>17.2</td>
</tr>
<tr>
<td>TPU</td>
<td>17.7</td>
</tr>
<tr>
<td>TPU/YSZ</td>
<td>17.0</td>
</tr>
</tbody>
</table>

It is also determined that disc structures which pressed into disk from fibers that have 2 mm diameters and consisting of only composite fibers formed in the original shapes and in these systems, TPU/YSZ system preserved the shape of the YSZ fibers after pyrolysis. It can be clearly seen that YSZ fibers keep their structure after pyrolysis of TPU/YSZ due to elastomeric nature of TPU. In figure 4-6, it can be seen that samples which have 5 mm diameter, keep their cylindrical forms after pyrolysis. At TPU/YSZ disk, one receives that for YSZ fibers in TPU matrix were kept their continuous order after pyrolysis of TPU (Fig. 7). Some of them were formed as cylindrical tubes as same with fibers which have 5 mm diameter. Around YSZ body, spherical alumina powders can be seen obviously that used for powder bed.

Figure 1. TGA analysis of PMMA and PMMA/YSZ.

Figure 2. TGA analysis of PP and PP/YSZ.

Figure 3. TGA analysis of TPU and TPU/YSZ.

Figure 4. Stereomicroscope image of YSZ samples after pyrolysis of PMMA/YSZ-900(5).

Figure 5. Stereomicroscope image of YSZ samples after pyrolysis of TPU/YSZ-900(5).
After pyrolysis of the extruded products, YSZ system was formed as hollow cylinder or more intensive of porous cylinders depending on the polymer and their shapes dependent on both polymer type and sintering conditions which have been carried out after pyrolysis process.

Particle size, morphologies and structure which depend on polymer type and sintering temperature after pyrolysis can be seen on SEM images in Figure 8-10. Due to the elastomeric nature of TPU, particles comes together by necking mechanism, so structure is coarser than other systems. In PP/YSZ system, due to the low decomposition temperature of PP, particles keep their positions and finer structure can be seen in the system. For PMMA/YSZ, due to the lowest melt flow index of system and different mobility value of methyl and methacrylate group, coarser particles formed by joined particles that comes together and finer particles occurred by unjoined particles.

In Figure 11, SEM images of YSZ fibers after pyrolysis can be seen. YSZ fiber after pyrolysis of PP/YSZ composite fiber had averagely 200 µm diameter and from SEM image it can shown that YSZ fiber can keep its shape after pyrolysis of PP. In mid of the fiber, alumina granules can be seen around YSZ fiber.
4. Conclusion

PP/YSZ, PMMA/YSZ and TPU/YSZ composites were produced via extruder. TGA, MFR analysis was carried out to investigate the thermal and melting behaviour of YSZ on PP, PMMA and TPU’s. From TGA results and melt flow analysis, it was found that the contribution of the YSZ changed the decomposition temperature and melt flow rate of the polymer part. Melt flow rate of systems were decreased with YSZ reinforcement to the polymers. For TGA investigations, it is concluded that both for TPU and PP, decomposition temperatures were decreased although for PMMA’s was increased.

After pyrolysis, shape stability on pressed samples was seen on YSZ fibers that formed from TPU/YSZ composites. During stereo microscope studies it was observed that the prevention of initial form after pyrolysis is possible. Degree of prevention was found higher in TPU/YSZ system. YSZ fibers also kept their initial forms after pyrolysis and tube formation was observed. Although diameter of these tubes are fluctuating along to fiber axis, initial results were evaluated quite motivating for the formation of differen hollow forms having desired diameter and length.

Acknowledgement

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References