On the Polymer Clay Nanocomposites for Extrusion-based Additive Manufacturing

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Abstract:

Recent advancements in the nanomaterial's have made way for the development of nanocomposites which exhibits superior material properties compared to the pristine polymer material. The prospects of the utilizing the nanomaterial's in additive manufacturing will open new directions for the development of high functional parts. With this in view the present paper focuses on the feasibility of nanoclay-based polymer composites that can be used for extrusion-based additive manufacturing. The various procedures that can be adopted for the development of the composites are addressed along with the details of the nanoclay.

Introduction:

Over the past three decades additive manufacturing formerly known as rapid prototyping has gained tremendous attention by the industries and researcher. Earlier it was used only for prototyping however, with the advancement of the technology now it is used to fabricate direct end-use products (Figure 1).

Fused deposition modelling (FDM) is an additive manufacturing (AM) process, which builds part layer by layer. It is one of the most extensively used (AM) process which can fabricate functional parts. Minimal wastage of material, safe and simple fabrication process are few of its advantages. It builds objects directly from a three dimensional computer aided design (CAD) models. The material is fed to the temperature controlled extrusion head, where it is heated to a semiliquid state. The extrusion head then deposits the material on the build platform, one layer at a time. Each layer is bonded with the previous layer. The temperature of the surrounding air is kept below the melting point of the material. Figure 2 illustrates the schematic diagram of the FDM process

However, the process have inherent problem of porosity due to which the achieved material properties decreases. Therefore, the strength of FDM parts are inferior to other polymer manufacturing technologies. Figure 3 shows the interlayer porosity in FDM build parts and the reduction in strength due to these inherent property.

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Injection molded ABS

[0^p]₁₂ Axial





+ Air Gap

0 Air Gap

- Air Gap

Figure 3 Inter layer porosity in parts build by FDM and reduction of strength due to this

Importance of Materials

Additive Manufacturing can be thought of a material dependent technology (refer figure 4). Materials are the building blocks in additive manufacturing process. Therefore, selection of material plays a critical role in additive manufacturing. However, there is scarcity of material's that can be pressed by this technology. One of the alternative way to overcome the limitation is to use the materials with enhanced mechanical properties. This could compensate the loss incurred due to porosity.



Figure 4 Impact of Materials on Parts key attributes

Material Categorization for Additive Manufacturing

Materials used in AM process can be divided into four categories (refer figure 5).

- 1. Polymers
- 2. Metals
- 3. Ceramics
- 4. Composites

However, FDM is a polymer based process. Composites can also be used in FDM process. The composites can be developed by following ways:

- i. Metal Polymer composite
- ii. Ceramic Polymer composite
- iii. Ceramic Metal composite

Also in addition to the above, macro-sized composites, nanocomposites can also be used in FDM process due to their numerous advantages.



Figure 5 Categorization of Material

Benefits of Clay

Clay is a mineral, naturally occurring in abundance. It belongs to main group of silicates with layered structure known as layered silicates (figure 6). Layered silicates are easily available and have low cost. The value added properties enhanced without the sacrificing of polymer process ability, mechanical properties and light weight, make the clays more and more important in modern polymer industry and can be used in FDM process.



Figure 6 structure of clay (Ray and Okamoto 2003)

Manipulation of Clay

The gallery in 2:1 type of clays provides the site for following three processes.

- 1. **Hydrophobic modification**: One of the ways is to exchange the cation by quaternary ammonium ions. This will make the nanoclay compatible with the polymers and enhance the possibility of formation of nanocomposite.
- 2. **Intercalation:** the structure of the nanoclay is in the form of platelets. In intercalation the polymer chains are inserted between these spacing between the clay platelets. Intercalation can also improve the performance of the polymer nanocomposites.
- Exfoliation: In this process the spacing between the clay platelets are increased by various methods. The will increase the basal spacing from 1 nanometre to around 20 nanometre. The nanocomposite with exfoliation will yield the best results in the developed nanocomposite.

Intercalation and exfoliation of the clays can be accomplished by

- i. Intercalation of polymer from solution
- ii. In situ polymerization
- iii. Melt intercalation

Natural montmorillonite modified with a quaternary ammonium **Melting point:** 3900 Degree **Basal spacing:** 1.85nm



Figure 7 Manipulation of clay platelets

Methods for Clay Manipulation

a. Intercalation of polymer from solution

Based on a solvent system. In which polymer is soluble and clay is swell able. The layered silicate is first swollen in a solvent, such as water, chloroform etc. On mixing, the polymer chains intercalate and displace the solvent within the interlayer of the silicate.

b. In situ intercalative polymerization

The layered silicate is swollen within the liquid monomer. So the polymer formation can occur between the intercalated sheets. Polymerization can be initiated by heat, Radiation and catalyst.

Upon solvent removal, the intercalated structure remains, resulting in PLS nanocomposite

c. Melt Intercalation

Involves annealing the mixture of polymer and clay. Statically under shear and above the softening point of the polymer

Advantages of melt Intercalation

Advantages of melt Intercalation over other methods care as follows:

Melt intercalation can be achieved by the common methods such as extrusion or injection moulding. Also, polymers which cannot be processed by chemical process can be extruded easily. Melt intercalation is nowadays being widely used in the industry. One of the important benefits is that the use of harmful chemicals are also avoided.

Conclusions

Fused deposition modelling process is one of the widely use polymer based additive manufacturing technology. However, due to the limited materials that can be used in the process limits its application. In this regard, development of polymer nanocomposites can serve the purpose of fabricating functional parts by the process. Nanoclay is one of the naturally occurring material and can be effectively use in the FDM process. The various methods that can be adopted to utilize the nonmaterial for developing composite that can be used in the FDM process are illustrated and it can be inferred that it possess favourable characteristics to be used for FDM process.

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