Preparation and Properties of Mica/Polyimide composites

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Abstract: A series of mica doped polyimide composites have been successfully prepared via the solution process. Compared to the virgin PI, the introduction of 15wt% mica leads to an increase of 15% in tensile strength. The introduction of the mica led to an increase in the temperatures at 10% weight loss (Td_{10}), it showed a 25°C increase in Td_{10} when only 10wt% of mica was added. Breakdown strength showed that the introduction of mica have certain affection on its properties.

Keywords: polyimide, mica, composites

The development polyimide has a history more than 40 years. And the researchers all over the world manage to improve its physical and functional properties by changing the structure and doping technology of the material. The electrical insulation performance, especially the corona resistance, could be increased obviously by doping mica-one kind of clays into the polyimide material, and this doped material would be widely used as electrical insulation material. In this paper, the mica/polyimide composite systems has been prepared using solution method, and thermal, mechanical and electrical properties dependent on the content of mica in the composites had been tested by means of TGA, tensile testing, and breakdown strength etc.

1. Experimental

1.1 Materials

The molecule of polyimide is composed of ODA and PMDA, the structure was shown in Fig.1, and the mica powder has a size of 1250 meshes.

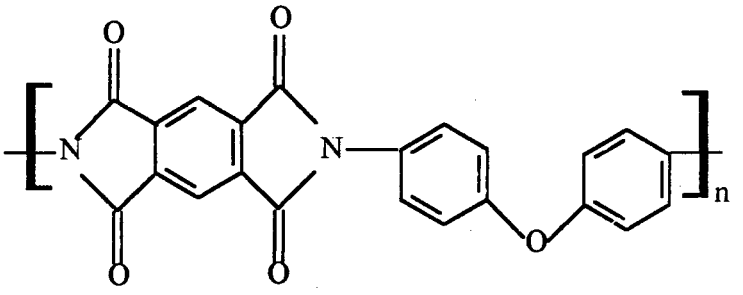

Fig. 1 Structure of polyimide

1.2 The preparation of mica powder doped polyimide films

Take 40g(0.2mol) ODA into 468g DMAc solution, and then put 42.6g(0.2mol) PMDA into the mixture, and poly(amic acid) solution could be got after several hours. Measure certain quantity of poly(amic acid), which was diluted using certain DMAc solution. Certain mica was stirred using ultrasonic wave with a coupling agent. And then put the mica mixture into poly(amic

acid) solution slowly and carefully, stirred for several hours until the mixture was homogeneous completely. The mixture solution was cast on a glass substrate, and then thermally treated consecutively by following process:

70°C(1h)→120°C(1h)→150°C(1h)→200°C(1h)→250°C(1h)→300°C(1h)

In the laboratory, 7 kinds of polyimide films with different mica content were prepared, and the components of the films were listed in Table 1.

Table 1 Composition of mica—polyimide composites

Composite system	PI-0	PI-2	PI-5	PI-10	PI-15	PI-20	PI-30
Weight ratio (PI/ Mica)	1:0	1:0.02	1:0.05	1:0.10	1:0.15	1:0.20	1:0.30

2 Results and discussion

2.1 Mechanical properties

Fig. 2 gave the relationship between tensile strength and mica content in PI/ mica composite films, it could be seen that the maximum tensile strength of the film, which was 1.15 times higher compared to the virgin polyimide, was achieved when the mica content was 15 wt%. This result was achieved mainly due to the synergetic effect between the mica powder and the polyimide resin. However, further increase in the mica content caused a decrease in the tensile strength because of the aggregation effect of the powder.

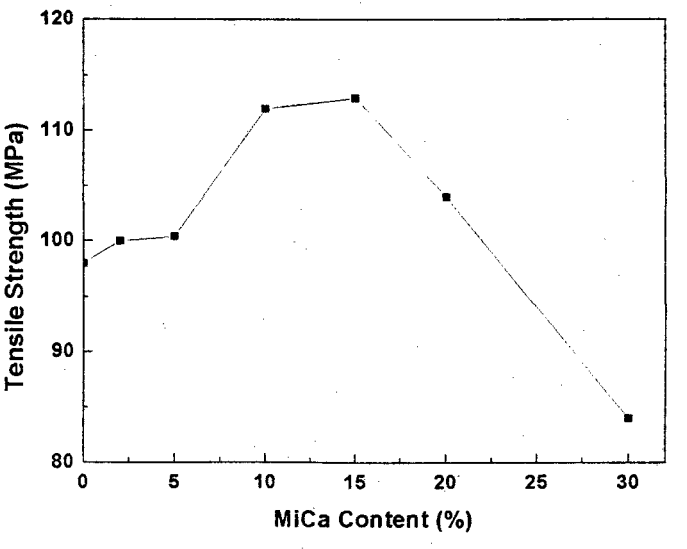

Fig.2 Relationship between tensile strength and mica content in PI/ mica composite films

2.2 Thermal property

Similarly, the decomposing temperature could be increased for the synergetic effectiveness between mica powder and polyimide molecule (see table 2).

Table 2 Thermal properties of PI/ Mica composites

Composites	PI-0	PI-2	PI-5	PI-10	PI-15	PI-20	PI-30
Td_{10}(° C)	598	614	616	623	621	615	615

2.3 Breakdown strength

Because the mica powder has a better electrical insulation performance, and the breakdown strength of composite film could be affected compared to the virgin polyimide. And some breakdown strength of the composites was listed in table 3.

Table 3. Breakdown strengths of PI/ Mica composites

Composites	PI-0	PI-2	PI-5	PI-10	PI-15	PI-20	PI-30
Breakdown strength (KV/mm)	119	159	136	96	85	77	56

From the testing results in table 3, it was found that the introduction of a small amount of mica powder leaded to an increase in the breakdown strength of the composite films due to the lower aggregation degree and the synergetic effect. But with the increase of the mica content, the breakdown strength was decreased for the higher aggregation degree. Otherwise, the composite film would be more fragile and much more defects would be generated on the surface, and the strength was decreased accordingly.

3. Conclusions

Based on above analysis, conclusions could be drawn as following:

- Mica/PI composite films with homogeneous distribution of mica power could be prepared successfully using solution method.
- The tensile strength of the composite film has a maximum value when the mica content was 15 wt%, which was 1.15 times of the virgin polyimide.
- The Td_{10} temperature was increased with the content of mica, and Td_{10} temperature was 25°C higher than that of polyimide when the mica content was 10wt%.
- The introduction of the mica would have certain influence on the breakdown strength of the composite films.

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云母掺杂聚酰亚胺复合薄膜的制备与性能研究

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摘要：通过溶液法，成功制备了 MiCa/PI 复合材料。当 Mica 含量达到 15wt%时，整个复合体系的拉伸强度最大，相对于聚酰亚胺母体提高了 15%。热性能研究结果表明，随着 Mica 含量增加，Td_{10} 也随之提高，当 Mica 的含量增加到 10wt%时，Td_{10} 提高了 25°C。击穿强度测试结果表明，Mica 的引入一定程度上影响了其性能。

关键词：聚酰亚胺，云母，复合材料

聚酰亚胺的发展已有 40 多年的历史，为了更进一步提高其物理性能，开发其功能特性，国内外的许多学者从结构、添加等各种途径对其改性，已经取得了很多可喜成果[1,2]，其中用粘土来改善性能就属于其中一类[3,4]。云母是粘土的一种，由于它具有优异的电绝缘性能，尤其是优异的耐电晕性能，目前，广泛用于各种电绝缘材料。本文通过掺杂方法将不同含量的云母粉引入到聚酰亚胺体系中，制备了多种复合材料。并用热重分析(TGA)、拉伸强度测试、击穿强度测试等方法研究了云母粉对复合体系性能的影响。

1. 实验部分

1.1 试验原料

聚酰亚胺选择的是 ODA 与 PMDA 组成的分子链，结构见图 1。云母粉尺寸为 1250 目。

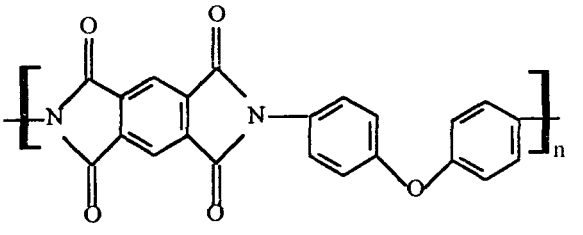

图 1 聚酰亚胺的结构示意图

Fig. 1 Structure of polyimide

1.2 云母粉掺杂聚酰亚胺复合薄膜的制备

将 40g(0.2mol) ODA 溶于 468g DMAc 中，加入 42.6g(0.2mol) PMDA，反应数小时得到聚酰胺酸溶液。分别称取定量的聚酰胺酸，用一定量的 DMAc 稀释，再称取一定比例的云母粉，用一个偶联剂在超声波中处理，然后将云母粉溶液在一边搅拌一边徐徐加入的方式倒入聚酰胺酸溶液中，搅拌数小时。将混合溶液在干净的玻璃板上涂膜，然后阶段升温处理，工艺如下：

70°C(1h)→120°C(1h)→150°C(1h)→200°C(1h)→250°C(1h)→300°C(1h)。

冷却后即得云母掺杂聚酰亚胺复合膜。

实验中制备了 7 种不同云母粉含量的聚酰亚胺复合薄膜，材料的成分组成如下表 1 所示。

表 1 云母粉聚酰亚胺物复合体系的成分组成

Table 1 Composition of mica—polyimide composites

杂化体系	PI-0	PI-2	PI-5	PI-10	PI-15	PI-20	PI-30
重量比(PI/ Mica)	1:0	1:0.02	1:0.05	1:0.10	1:0.15	1:0.20	1:0.30

2 结果与讨论

2.1 力学性能

图 2 是 Mica/PI 复合薄膜的拉伸强度与云母粉含量的关系图。由图可以看出，当云母粉含量较低时，拉伸强度随着云母粉含量的增加而增大，当云母粉含量达到 15wt%时，拉伸强度达到了最大，与聚酰亚胺母体相比，拉伸强度提高了 15%。拉伸强度的升高主要是由于 Mica 与聚酰亚胺分子之间的协同作用从而导致复合体系拉伸强度的升高。当 Mica 含量继续增高时，复合体系的拉伸强度反而降低。主要是由于 Mica 含量进一步增高导致了云母粉之间团聚加剧，造成复合体系拉伸强度降低。

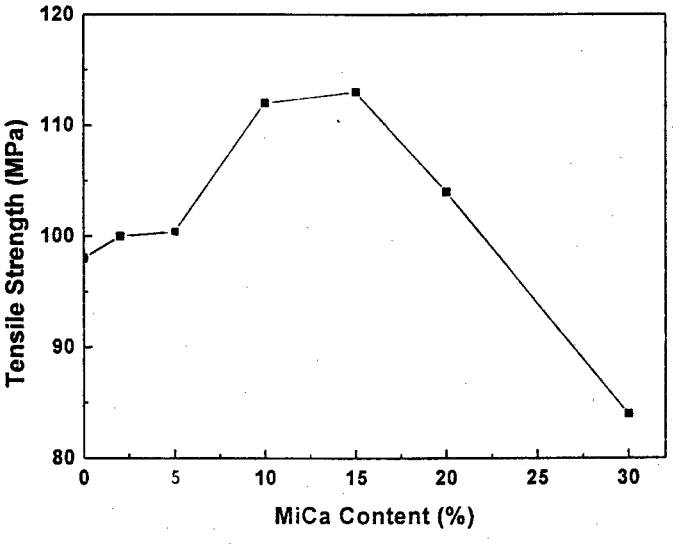

图 2 PI / Mica 复合材料的拉伸强度与 Mica 含量的关系图

Fig.2 Relationship between tensile strength and Mica content in PI/ Mica composite films

2.2 热学性能

云母粉和聚酰亚胺之间的相互作用同样也会导致复合体系热分解温度的提高(见表 2)。当云母粉含量较小时，随着云母粉含量的增加，Td_{10} 也随着提高。这也主要是由于 Mica 与聚酰亚胺分子之间的协同作用从而导致复合体系 Td_{10} 的升高。当 Mica 含量为 10wt%时，体系的 Td_{10} 较纯的树脂基体提高了 25° C。

表 2 PI / Mica 复合薄膜的热性能

Table 2 Thermal properties of PI/ Mica composites

体系	PI-0	PI-2	PI-5	PI-10	PI-15	PI-20	PI-30
Td_{10}(° C)	598	614	616	623	621	615	615

2.3 击穿强度

由于云母粉具有良好的电绝缘性能，因此它的引入也大大的影响了复合薄膜的电学性能，表 3 中列出了复合薄膜的击穿强度。

表 3 PI / Mica 复合薄膜的电击穿强度

Table 3. Breakdown strengths of PI/ Mica composites

体系	PI-0	PI-2	PI-5	PI-10	PI-15	PI-20	PI-30
击穿强度（KV/mm）	119	159	136	96	85	77	56

当云母粉含量较少时，云母粉团聚程度低，由于与聚酰亚胺之间的协同作用，因此一定程度上提高了复合薄膜的击穿强度，但是随着云母粉含量的提高，云母粉之间的团聚就会越来越厉害，导致分散均匀性降低，另外，随着云母粉含量的提高，复合薄膜变脆，质量变差，从而使复合薄膜的击穿强度降低。

3. 结论

根据以上分析结果，结论如下：

- 采用溶液法可以成功制备 Mica/PI 复合材料。
- Mica 含量达到 15wt%时，整个复合体系的拉伸强度最大，相对于聚酰亚胺母体提高了 15%。
- 随着 Mica 含量增加，Td_{10} 也随之提高，当 Mica 的含量增加到 10wt%时，Td_{10} 提高了 25°C。
- 随着 Mica 含量增加，击穿强度也有先升高后降低的趋势。

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