Clay Polyimide Composite Film with Low CTE and High Water Vapor Barrier Property

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ABSTRACT

A new clay polymer composite film (TP film) developed in this work was prepared by mixing specially processed talc, a kind of non-swelling clay, and polyimide at an optimal ratio. TP film is with the excellent properties of talc and the good handling property of polyimide. TP film combines low coefficient of thermal expansion (CTE) from 10 to 15 ppm/K in the wide range of tempearture, shrinkage of 0.04 %, water vapor barrier property that can be used as a PV back sheet. We established a process and conditions for a roll film production. Some other usage of TP film such as printable electronics substrate film, coating layer of thermal interface material, and so on, were proposed.

Keywords: Clay, Polyimide, Water vapor barrier, Coefficient of thermal expansion, Thermal conductivity

1 INTRODUCTION

Phyllosilicate (clay) has been used as a filler to improve thermal stability and gas barrier property of plastic films. Clay is heat-resistant, and it is superior at resistively for chemicals, and safe for human body, and can be used at reasonable cost. However, it is difficult to lift the loading so much so that molding characteristics of the composite become poor if the clay loading is too high. Therefore there has been a few film-preparation-trial using clays as a main component. The thermal stability and the gas barrier performance could be improved drastically if the layered clay crystals are highly ordered parallel to the film surface [1-3]. Realizing the structure, it is favorable if delaminated plate-like clay crystals are mixed in a plastic matrix in a nano-composite material of clay and plastic, and the fundamental requirement is the polarity matching of the clay and the plastic.

These clay-based-films named “Claist” are heat-resistant, and they have a high gas barrier property against various gases such as hydrogen and oxygen in the wide range of temperatures [4-11]. Its flexibility is similar to that of ordinary copying paper. Moreover, the CTE is smaller than 10 ppm/K in the wide range of temperature. However, the films were mechanically weak and they were with poor handling; therefore it was necessary to improve its fragility [12]. Another problem is that the paste containing the swelling clay needs long time to dry due to the high liquid content, which makes continuous production of thick film difficult.

TP film developed in this work was prepared by mixing specially processed talc, a kind of non-swelling clay and polyimide at an optimal ratio. Talc is non-polar, so it would not have a good affinity with polyimide, a polar plastic, but because of an improved mixing technique, etc., we were able to realize a uniformly mixed film material with the excellent properties of talc and the good handling property of polyimide.

2 PREPARATION OF TP FILM

TP film was produced by casting an organic solvent based paste containing talc and polyimic acid, then drying the solvent and subsequently heat-curing the dried material. Clay films have been prepared with many different combinations of clay and plastic, since there is no particular limitation on the kind of clay and plastic used. The results indicate that mixing talc and polyimide at an optimal ratio yields a mechanically strong film with improved fragility. The paste was prepared by dispersing specially processed talc in polar solvents such as DMAc or NMP in which polyimic acid is dissolved. In the case of swelling clay, it needs to be dilute to prepare uniform hydrous paste because of its high gelling property. However, the use of talc made it possible to reduce the amount of solvent. The solid content of the paste is around 20 wt% or over, which is extremely high comparing the one using swelling clay and the high solid content enable to prepare a thick film. Typically, the talc loading was 70 % to the total dry weight. Fragility of TP film becomes more noticeable when talc loading is more than this. On the other hand, improvement of the characteristics is less effective when the talc loading is less. Trials carried out repeatedly using a production equipment with a furnace capable of heating up to 350 °C, establishing a production method and conditions for a roll-film up to 57 cm wide with thicknesses from 30 to 120 μm (Fig. 1).

Figure 1: A 57cm wide TP film.

3 MICROSTRUCTURE OF TP FILM

TP film is superior in thermal stability, gas barrier property, and flexibility because of the high talc loading. TP film can be cut in desired shape and size by a pair of scissors or a paper cutter easily. The film thickness can be controlled by adjusting quantity of raw materials or the coating thickness. Microstructure of the TP film was analyzed by SEM. From the SEM image, it is observed randomly arranged talc particles dispersed in polyimide matrix. The matrix may brought the toughness of TP film.

4 PROPERTIES OF TP FILM

TP film showed very little difference in size before and after a heat treatment and a markedly improved water vapor barrier property.

4.1 Heat Durability

A TG-DTA analysis of TP film of 70 wt% talc loading was conducted. A TG decline is observed between 550 to 650℃ due to decomposition of polyimide. There is no significant change observed until 500℃ in both TG and DTA curves.

4.2 Water Vapor Barrier Property

TP film has lower moisture absorbency compare to polyimide and the measured values for 60 and 80% talc loading samples were 0.8 and 0.5%, respectively. TP film has a water vapor barrier permeability of 0.5 g/ m^2 day which is sufficient for use as a back sheet of crystalline silicon solar cells. We also succeeded in aligning the clay crystals parallel to the film surface and further improving the water vapor barrier property in nearly two orders of magnitude by adding certain amount of swelling clay. Water vapor barrier property of TP film can be controlled between from 1.0 to 0.01 g/m^2 day standardized to 100 micrometer thick. The SEM observation shows that the orientation of the clay is improved as the addition of the swelling clay.

4.3 Coefficient of Thermal Expansion

CTE of TP film is measured up to 350℃ by repeated heating to evaluate the dimensional stability,. TP film showed very little shrinkage (0.04%) after the first heating from room temperature to 350°C. Additionally, TP film has a constant low CTE from 10 to 15 ppm/K throughout the temperature range.

4.4 Electric Insulation

TP film has the same level of electrical insulation as polyimide has, and TP film has an excellent breakdown voltage of about 70 kV/mm showing better performance than conventional plastics.

4.5 Thermal Conductivity

TP film has horizontal and vertical thermal conductivity of from1.5 to 3 W/mK, and 7 W/mKw, respectively.

4.6 Flame Retandancy

TP film has VTM-0 flammability on UL-94 rating. Additionally, TP film is evaluated as a non-combustible material by cone calorimeter test.

4.7 Flexibility

TP film around 100 micrometers thick has flexibility in the range from 1 to 3 mm by mandrel bending test.

4.8 Long Term Durability

To evaluate long-term durability of TP film, we conducted a dump heat tests aiming to use it for a solar cell material. They say 3,000 hours of durability is requested under 85 ℃, 85 % of relative humidity. Even after 6,000 hours, noticeable change in water vapor barrier property of TP film was not found (Fig. 2). In addition, the infrared absorption spectrum was acquired; no significant difference observed even after 6,500 hours, indicating there is no degradation of TP film occur also on the level of the molecular bond.

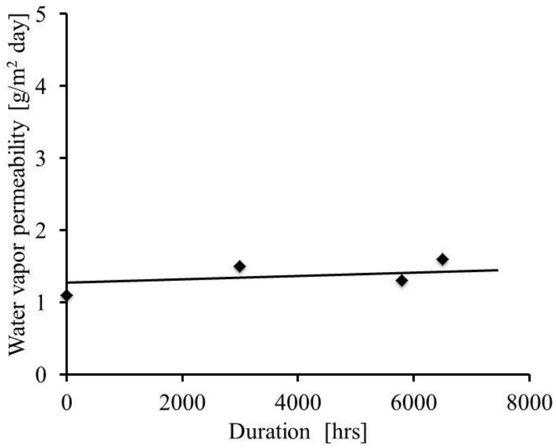

Figure 2: Time course change in water vapor permeability of TP film; Dump heat condition 85℃, 85%RH; WVP measurement at 40℃, 90%RH.

4.9 Radiation Durability

Exposure test was conducted using 10 MeV electron gun facility. Total irradiation of 300KGy didn’t cause any change in outlook and texture of TP film.

5 APPLICATIONS

As described above, TP film has many excellent properties, so that it is a promising material for many applications. The proposed structure of the solar cell back sheet using TP film is shown in Figure 3. In the case of typical back sheet, from the side exposed to ambient air, it is composed of weather-durable layer, water vapor barrier layer, and electric insulation layer. These layers adhere by adhesive agents. Therefore, if any of the constituent layers or adhesives deteriorates, some problems such as peeling of the elemental layer may occur. On the other hand, TP film combines all the properties such as weather resistance, water vapor barrier, and electric insulation, therefore TP film can be used as a single layer back sheet. From the simple sheet structure, high durability and reliability is expected. Adhesion strength to EVA obtained was sufficient for the practical use. The target of this material as a back sheet is to elongate the life span of crystalline silicon solar cells from the current 20 to 40, and even 50 years.

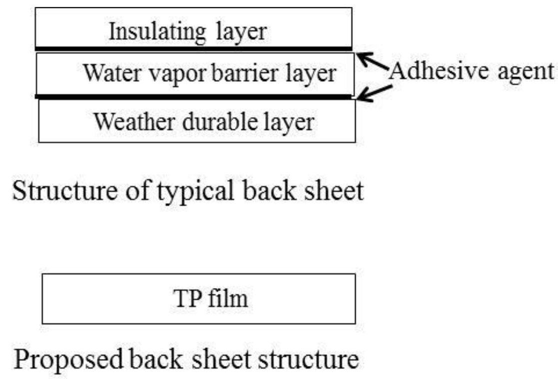

Figure 3: Proposed back sheet structure.

Conductive inks with Ag or Cu nanoparticles will introduce into electric circuits production used in mobile terminals on a large scale, offering a tremendous savings in production. We successfully print patterns on TP film by a printing method using Ag and Cu nanoparticle-inks (Fig. 4). Print appropriateness to the film surface was fine. TP film is suitable for calcinations of the Cu ink at elevated temperature as 350℃ due to its small shrinkage and CTE. Also it is a promising material for flexible display substrate such as TFT because repeted heating is applied on the production process. TP film is also a candiate material as substrate material for displays and lightings [13, 14].

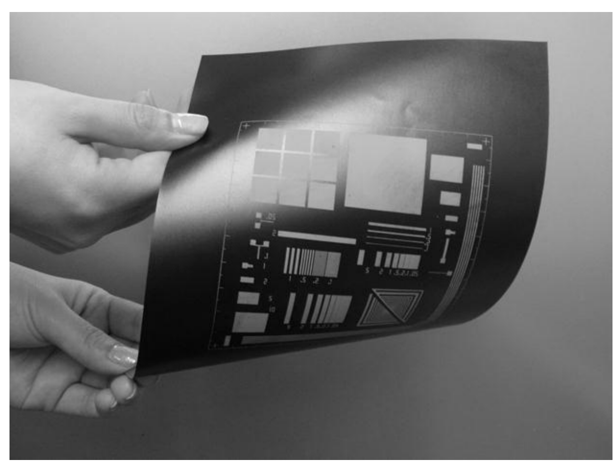

Figure 4: TP film with printed patterns by a nanoink.

Electric conductive thermal interface materials, graphite or aluminum sheet, are normally coated by PET,

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even PET's thermal conductivity is as low as 0.25W / m K. TP film has relatively high thermal conductivity from 1.5 to 7 W/mK, so it will be a good candidate of the coating layer of the thermal insulation material especially for displays, LEDs, and so on (Fig. 5).

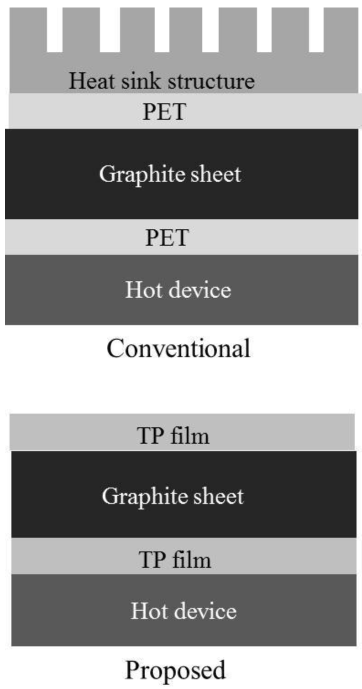

Figure 5: Proposed structure of heat insulation using TP film.

Non-flammable TP film is promising as an insulating material for lithium-ion batteries, high voltage cables, energy storage media, and so on reducing the risk of fire. Furthermore, since polyimide and clay both are with excellent resistance to radiation, it is expected as an aerospace material.

SUMMARY

We developed an unique talc polyimide composite film. The developed film is with the excellent properties of talc and the good handling property of polyimide. TP film combines low CTE and high water vapor barrier property. We established a process and conditions for the roll film production. We are conductiong further evaluation on the applicability of individual purpose for the next step.

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