Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 23 Aug 2006

To cite this article: Sung Woo Kim, Don Keun Lee, Young Soo Kang & Yong Joo Kim (2006): Preparation of Heat Insulating Nanocomposite Film with MPS (Mercaptopropyl Trimethoxysilane) Coated-Nanoparticles, Molecular Crystals and Liquid Crystals, 445:1, 81/[371]-92/[382]

To link to this article: http://dx.doi.org/10.1080/15421400500367058

Mol. Cryst. Liq. Cryst., Vol. 445, pp. 81/[371]–92/[382], 2006

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500367058

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To improve the heat insulating property of plastic films, SiO_2 nanoparticles as inorganic insulating filler were prepared from sodium metasilicate by emulsion method in reverse micelle. MgO, Al_2O_3 and CaO nanoparticles were also prepared. Surface modifications of synthesized heat insulating nanoparticles were accomplished with MPS (mercaptopropyl trimethoxysilane) coating to maximize homogeneous distribution and compatibility between obtained heat insulating nanoparticles and EVA (ethylene vinylacetate). Finally heat insulating films were prepared with MPS coated-heat insulating nanoparticles at the ratio of 2 wt% and EVA. The insulating capacity was tested by IR spectroscopy and light transmission was observed by UV-vis spectroscopy. The mechanical properties such as tensile strength, elongation, impact strength, tear strength, clarity and haze were also studied.

Keywords: EVA (ethylene vinylacetate); heat insulating film

This research was supported by the Program for the Training of Graduate Students in Regional Innovation which was conducted by the Ministry of Commerce, Industry and Energy of the Korean Government. Y. J. Kim acknowledges the financial support from Regional Research Center at Hanbat National University.

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INTRODUCTION

Commercial applications of rubbers and plastics often require the use of particulate fillers to obtain the desired reinforcement. In the rubber industry, besides carbon blacks, silicas are the other reinforcing filler used to impart specific properties to rubber compounds [1]. Extensive work has also been carried out on structural development in silica/rubber composites [2]. The surface functional environment of silica particles is quite different from that of carbon blacks due to the existence of silanol groups in the particles. Thus, the primary discussion on the structural development in the silica/rubber system is focused on the interactions between silica particles and rubber molecules [3]. To maximize the interactions between silica and rubber, various methods used to modify the surface properties of the silicas are largely introduced in terms of thermal, chemical, electrochemical, and coupling agent treatments. A silane coupling agent contains functional groups that can react with the rubber and the silicas. In this way, the rubber-silica adhesion is increased and consequently the reinforcing effect of the silicas is enhanced [4,5]. Al_2O_3, MgO and CaO nanoparticles were prepared from different precursors to the corresponding metal oxide that are insulating materials during thermal treatment was studied extensively in the past [6–10]. In the light of these studies, we applied silane coupling agent modified-inorganic fillers (silicas, Al_2O_3, MgO and CaO) to filler-polymer nanocomposites as the reinforcing fillers which can improve mechanical properties and heat insulating ability in the insulating wavelength range (700–1400 nm) of EVA (ethylene vinylacetate) film.

EXPERIMENTS

1. Materials and Analytical Methods

Calcium (98.5%) from BDH Laboratory Supplies Poole, magnesium (98%), aluminium sec-butylate (97%), sodium meta-silicate ($Na_2O{\cdot}SiO_2{\cdot}9H_2O$, Aldrich) and cyclohexane ($>99.5\%$) from Aldrich, polyoxyethylene nonylphenol ether (NP-5) and (NP-9) from IlChil Chemicals, were used as received. Ammonia solution (NH_4OH, Junsei), hydrochloric acid (HCl, Aldrich), MPS ($C_6H_{16}O_3SSi$, Aldrich) and EVA (ethylene vinylacetate), EF-443 from Hyundai Petrochemical Co. were used in their commercial form. Transmission electron microscopy (TEM) images were obtained by using a HITACHI, H-7500. X-ray powder diffraction (XRD) was obtained with a Philps, X'Pert-MPD system. Fourier Transform Infrared Spectroscopy (FTIR)

spectra were obtained by using PERKIN ELMER SPECTRUM 2000. The tensile strength and elongation were measured with SHIMADZU, AG-10TG.

2. Synthesis of Heat Insulating Nanoparticles by Emulsion Method

Two types of inverse microemulsions for nanosized-SiO_2, designated as microemulsion A (MA) and microemulsion B (MB), were first prepared separately. Both MA and MB contained two common components, i.e., a non-ionic surfactant mixture of NP-9 and NP-5 in a weight ratio of 2/3 and cyclohexane. The only difference was that MA consisted of an aqueous solution of sodium meta-silicate with a concentration 0.05 M, while MB contained an aqueous solution of hydrochloric acid (0.05 M). MA contains cyclohexane of 68.10 wt%, NP-9/NP-5 (2/3) of 17.10 wt% and an aqueous solution of sodium meta-silicate of 14.96 wt%. On the other hand, MB contains the same amount of cyclohexane and NP-9/NP-5 with MA except the aqueous solution of hydrochloric acid of 15.18 wt%. Equal amounts of the MA and MB microemulsions of those compositions were then mixed with continuous stirring at room temperature for about 2 hrs. The resulting mixed microemulsion was then destabilized by heating it up to about 80°C. On cooling, it was separated into clear and turbid phases. The fine silica particles were recovered from the turbid phase by centrifugation. The particles were washed with acetone six times to remove residual surfactants. The silica particles were then dried at 100°C in a vacuum oven. We synthesized microsized-SiO_2 nanoparticles from sodium metasilicate by relatively simple method [11,12].

3. Synthesis of Al_2O_3, MgO, and CaO Nanoparticles

The principle of the preparation of alumina xerogels from aluminium alcoholates is known from the work of Adkins [8]. In order to apply to alumina aerogels a method similar to that proposed for silica, we selected aluminium sec-butylate, a commercially available compound, which is soluble in sec-butanol [9–10]. The precipitation starts immediately after the first addition of water. Alumina aerogels were prepared from a 10% (by weight) solution in sec-butanol of aluminium sec-butylate hydrolyzed by various quantities of water, the solvent being evacuated in the autoclave. General procedures are described below for MgO and CaO [9,10]. In a three-necked 2 L round bottom flask equipped with a mechanical stirrer, water cooled-condenser, and argon inlet with a three-way stopcock was placed 300 mL of

toluene. In another flask, 2.4 g (0.10 mol) of Mg turnings was allowed to react with 100 mL of CH_3OH under Ar. Then 4 mL (0.22 mol) of distilled water was added dropwise from a syringe over a 30 min period. This solution was stirred at room temperature for 6 hrs under Ar. The resultant slightly milky solution (gel-like) was placed in an autoclave, heated to 200°C, vented, and thus converted to a $Mg(OH)_2$ aerogel as previously described. This fine white powder was heat treated (dehydrated) for 12 hrs under vacuum about 200°C, and maintained at 500°C in the electric furnace for overnight. CaO nanoparticle was prepared as the same procedure as described for MgO nanoparticle by using calcium metal.

4. Surface Modification of Heat Insulating Nanoparticles

Surface modification of the heat insulating nanoparticles was done by MPS (mercaptopropyl trimethoxysilane) to enhance dispersive property and stability of nanoparticles in the polymer matrices [13,14]. The synthesized heat insulating nanoparticles were kept in 0.1 M HCl overnight. Ammonium hydroxide and deionized water were mixed in ethanol at the molar ratio of 0.5 M and MPS was dissolved in ethanol with stirring. After the silane coupling agents (MPS) were hydrolyzed for 1 hr, heat insulating nanoparticles that were pretreated with HCl was added. The solution was put into autoclavable bottle and heated to 300°C for 6 hrs. After 6 hrs, solvent was evaporated, washed with ethanol and dried at room temperature. Finally, MPS coated-nanoparticles were obtained.

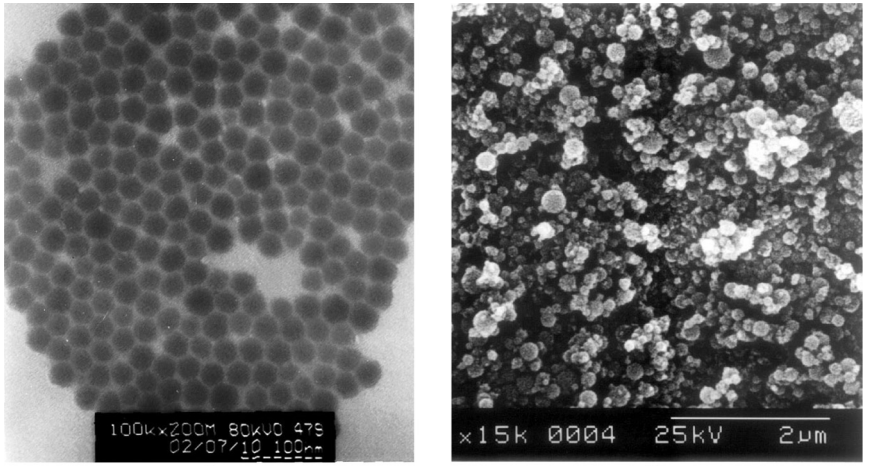
5. Preparation of EVA/Heat Insulating Nanoparticle Nanocomposite and EVA Film with Heat Insulating Ability by Inserting Surface Modified-Nanoparticles into EVA

EVA and surface modified-heat insulating nanoparticles which were added at the ratio of 2 wt% were well kneaded in Buss-Kneader. In this step, nanoparticles can be perfectly encapsulated by EVA, therefore nanoparticles were dispersed separately without aggregation and strongly attached to EVA. Because MPS coated on nanoparticles avoided reversible aggregation of particles and maximized compatibility between nanoparticles and EVA. The kneaded composites were reformed as pellet type master batch by pelletizer and extruder. The insulating master batch was transferred into Blow Film Extruder in order to prepare heat insulating EVA film. Thickness of final film was controlled to obtain 60 μm.

RESULTS AND DISCUSSIONS

Size of SiO_2 nanoparticles was determined as 20–30 nm by TEM image (Fig. 1A). The particles are monodispersed and spherical which have narrow size distribution. The particles show spherical shape that may represent the simplest form that a colloidal particle can easily adopt during the nucleation or growth process, as driven by minimization of interfacial energy [15,16]. In microsized-SiO_2, the obtained particles were large and aggregated (Fig. 1B). To achieve monodispersity, nucleation and growth stages must be strictly separated and nucleation should be avoided during the period of growth. In a closed system, the monomer (usually exists as a complex or a solid precursor) must be added or released slowly at a well-controlled rate in order to keep it from passing the critical supersaturation levels during the growth period [17,18]. According to TEM image (Fig. 2A), the shape of Al_2O_3 nanoparticle is either spherical or oval with particle size of 10–20 nm. MgO nanoparticles show wide size distribution as 5–20 nm and are almost spherical (Fig. 2B). In TEM image (Fig. 2C), the particles were neither monodispersed nor regular shape. Therefore, these particles have restrictions on applying to EVA films because these aggregated particles may reduce light transparency.

To be used as heat insulating filler for EVA film, it should absorb radiated heat which has wavelength range 7 μm–10 μm from ground



A B

FIGURE 1 TEM images of nanosized-SiO_2 (A) and microsized-SiO_2 (B) particles.

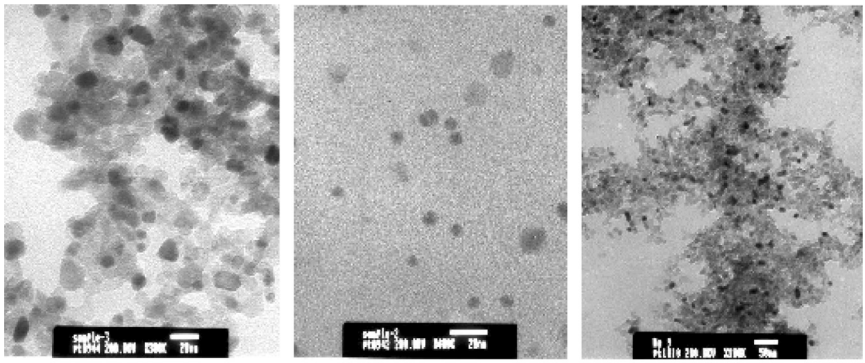


FIGURE 2 TEM images of Al_2O_3 (A), MgO (B) and CaO (C) nanoparticles.

during night time. The wavelength range of 7 μm–10 μm can be converted into the wavenumber range of 700 cm^{-1}–1400 cm^{-1} which indicates radiated heat. Therefore, heat insulating property of surface modified-nanoparticles can be indirectly measured by FT-IT spectra in the wavenumber range of 700 cm^{-1}–1400 cm^{-1}. In Figure 3, MgO and

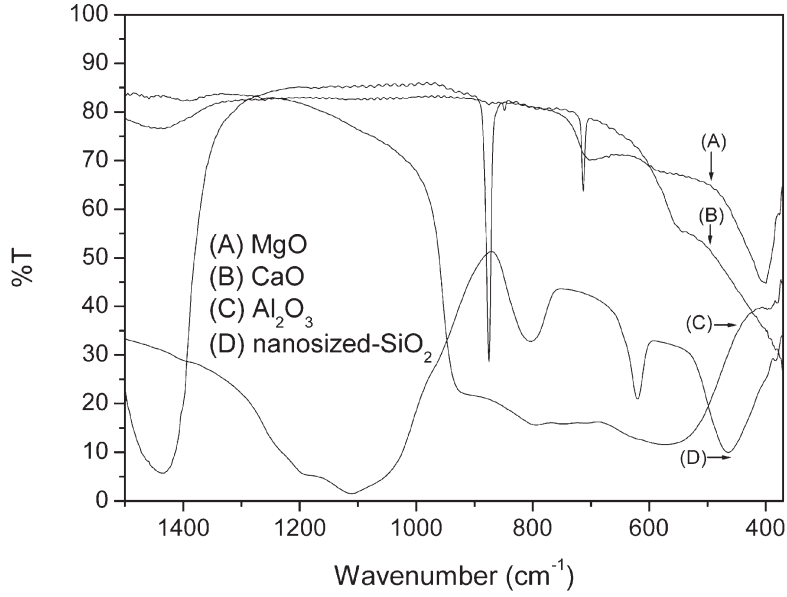


FIGURE 3 FT-IR spectra of heat insulating nanoparticles.

CaO nanoparticles rarely absorbed the range of radiated heat, so it is concluded that they are not efficient heat insulating materials. On the other hand, Al_2O_3 and SiO_2 nanoparticles absorb the wavenumber range which is assumed as the same range of radiated heat. Al_2O_3 shows heat insulating ability only at the range between 700–950 cm^{-1} however the value is negligible because of narrow range available. SiO_2 nanoparticles which absorb the radiated heat throughout the range of 700 cm^{-1}–1400 cm^{-1} have the best heat insulating ability among the samples. The efficiency of heat insulating ability decreases according to the order of $SiO_2 > Al_2O_3 > CaO > MgO$.

To investigate dispersibility of surface modified-nanoparticles in EVA, the images were obtained with optical microscope. In raw EVA film (Fig. 4A), any alien substances were not observed however the films which contain heat insulating nanoparticles show some different things which is definitely surface modified-particles. EVA/Al_2O_3-MPS film represents film of 60 μm thickness that is nanocomposite of EVA and MPS modified-Al_2O_3 nanoparticles. The other samples can be also described as the same manner for each heat insulating nanoparticles respectively. EVA/Al_2O_3-MPS film, EVA/CaO-MPS film and EVA/SiO_2-MPS(micro) film (Fig. 4 – B, C, F) rarely show particles. Only few particles were observed and they even formed agglomerations. These results exactly correspond to their TEM images that show not monodispersed but aggregated particles. On the other hand, EVA/MgO-MPS film and EVA/SiO_2-MPS(nano) film (Fig. 4 – D, E) show excellent dispersibility of nanoparticles into EVA. In EVA/MgO-MPS film, MPS modified-MgO particles were relatively well dispersed into EVA during preparing procedures of film with the exception of few agglomerations. EVA/SiO_2-MPS(nano) film show the best dispersibility without any agglomeration and as competitively low contents of 2 wt%, particles equally dispersed throughout EVA. Homogeneous distribution of nanosized-SiO_2 particles resulted from MPS coating onto silica surface. Nanosized-SiO_2 particles were monodispersed even before MPS modification. By coating MPS onto silica surface, reversible aggregation of particles was prevented and functional group, which can maximize compatibility between particles and EVA, attached to silica particles to make particles perfectly encapsulated in EVA. Therefore, we can conclude that successful MPS coating onto silica surface can lead to excellent EVA film with homogeneously monodispersed nanoparticles.

In addition to heat insulating property, one of the required fundamental properties of agricultural plastic film is light transparency in the daytime. Light which is useful at crop growth has the wavenumber range of 400–700 nm. Therefore, we can simply measure light

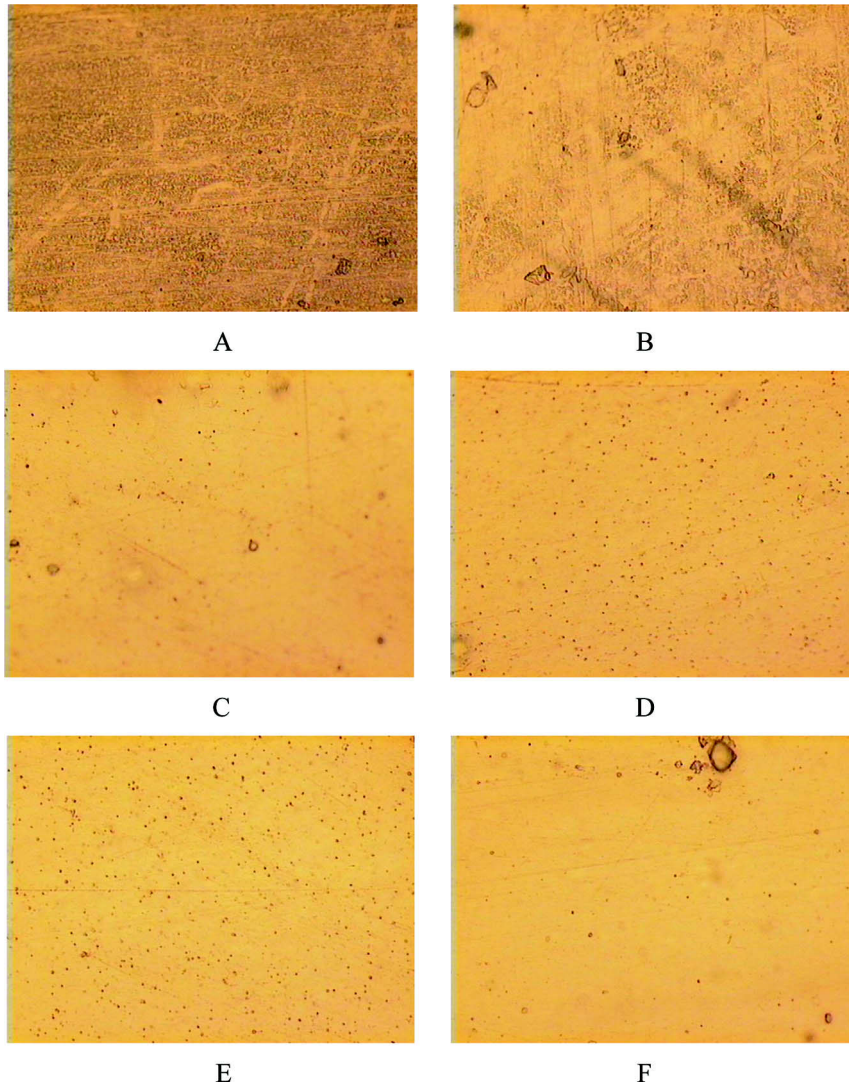


FIGURE 4 Optical microscope images of (A) EVA film, (B) EVA/Al_2O_3-MPS film, (C) EVA/CaO-MPS film, (D) EVA/MgO-MPS film, (E) EVA/SiO_2-MPS(nano) film, (F) EVA/SiO_2-MPS(micro) film.

transparency of plastic films with UV-vis spectra. In Figure 5, 3 layered-EVA film which was receive from Il- Shin Chemical Co. in commercial form were used to compare it with the other prepared films. All

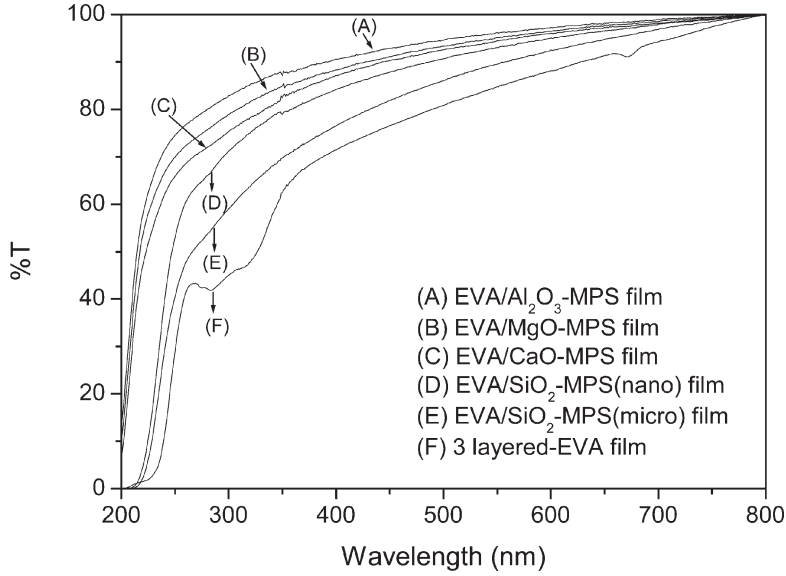


FIGURE 5 UV-vis spectra of EVA/nanoparticles EVA film.

of the prepared films in this study show better light transparency compared with 3 layered-EVA. Vinyl films that include nanosized-particles have distinguished light transparency over 80% at the range of 400–700 nm because of low contents (2 wt%) of heat insulating filler and homogeneous distribution. Microsized-particle dispersed film shows inferior property to in case of nanoparticles due to the lots of large agglomerations.

Heat insulating ability of plastic films was indirectly investigated by FT-IR spectra (Fig. 6). The plastic films which include MgO, CaO and Al_2O_3 nanoparticles have low absorption ability as negligible value. These three films are not possible to be used as heat insulating film. 3 layered-EVA film, EVA/SiO_2-MPS(micro) film and EVA/SiO_2-MPS(nano) film show distinguished absorption ability over 50%. Especially, EVA/SiO_2-MPS(nano) film has the best heat insulating ability as 60%. It may act as efficient heat insulating film for agriculture. The efficiency of heat insulating ability increases according to the order of EVA/MgO-MPS film < EVA/CaO-MPS film < EVA/Al_2O_3-MPS film < 3 layered-EVA film < EVA/SiO_2-MPS (micro) film < EVA/SiO_2-MPS (nano) film.

We investigated mechanical properties of EVA/nanoparticles film in order to find out whether defect of mechanical properties might

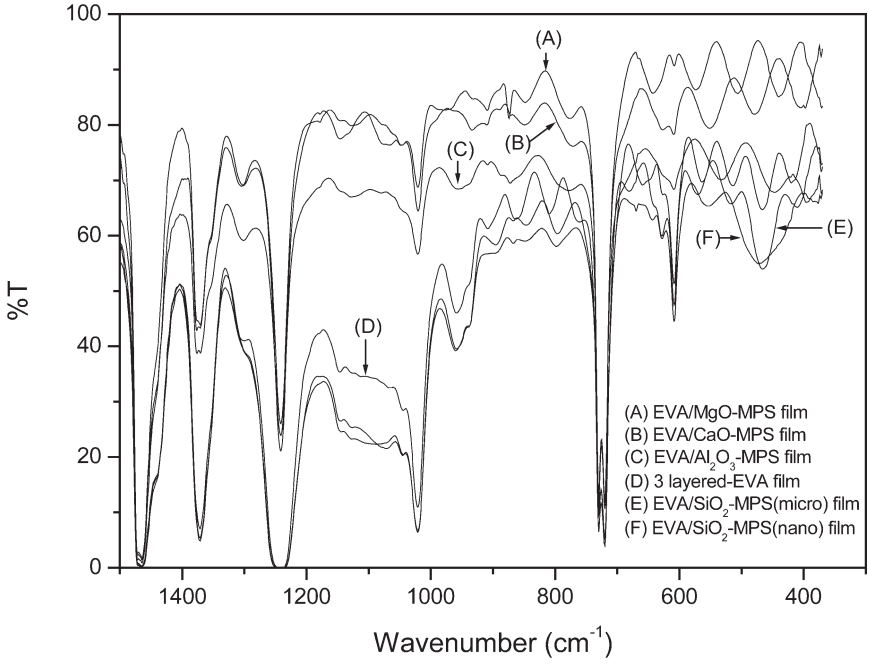


FIGURE 6 FT-IR spectra of EVA/nanoparticles EVA film.

be occurred when nanoparticles were inserted into EVA. For this reason, the prepared nanocomposite EVA films were compared with raw EVA. We focus on making mention about nanocomposite films that contain SiO_2 nanoparticles because EVA/SiO_2-MPS(micro) film and

TABLE 1 Mechanical Property Test for EVA/Nanoparticles Nanocomposite Films

	Thickness (μm)	Tensile strength (kgf/cm^2)		Elongation (%)		Tear strength (kgf/cm^2)		Haze (%)	
		TD	MD	TD	MD	TD	MD	Clarity	Haze
EVA(EF-443)	60	270	250	600	300	160	130		3.4
EVA/SiO_2-MPS(micro) film	60	272	236	658	513	118	93	92.5	10.6
EVA/SiO_2-MPS(nano) film	60	285	294	695	406	115	96	93.3	7.1

TABLE 2 Quality Standards for Heat Insulating Film

	Thickness (mm)			
	0.060	0.070	0.080	0.100
Tensile strength (kgf/cm^2)	over 160	over 170	over 170	over 180
Elongation (%)	over 220	over 220	over 220	over 270
Eear strength (kgf/cm^2)	over 60	over 60	over 60	over 70
Haze (%)	below 25			

EVA/SiO_2-MPS(nano) film showed excellent efficiency in heat insulating property and light transparency. From the measurement of tensile strength (Table 1), EVA/SiO_2-MPS(nano) indicated superior tensile strength to raw EVA film and the balance between TD and MD was also excellent. EVA/SiO_2-MPS(micro) film has the equal value of tensile strength compared with raw EVA film. In the elongation measurement, by inserting MPS modified-SiO_2 nanoparticles into EVA, the value of elongation was remarkably improved. However, inserted nanoparticles had a bad influence upon tear strength, clarity and haze but the decreased value was little as it can be negligible. Furthermore, in spite of decrease, the values were even over Quality Standards for heat insulating film (Table 2). It is prescribed in the quality standards for heat insulating film that tear strength should be satisfied over 60 kgf/cm^2 and the value of haze should meet below 25%. From these results, we can conclude that MPS coating on silica surface has definitely positive effect on mechanical property with negligible decrease in clarity between silica and EVA by maximizing compatibility because the EVA-silica adhesion is increased and consequently the reinforcing effect of the silica is enhanced [4,5].

CONCLUSION

Nanoparticles such as SiO_2, MgO, CaO and Al_2O_3 which have absorbing ability of radiated heat between 800 and 1400 nm range were successfully prepared. Surface modification of obtained insulating inorganic fillers was conducted by MPS (mercaptopropyl trimethoxysilane) that is a kind of silane coupling agents in order to enhance compatibility between EVA and inorganic fillers and attain perfect encapsulation of nanoparticles with EVA. All of the prepared nanocomposite films that include nanosized-particles have distinguished light transparency over 80% at the range of 400–700 nm because of low contents (2 wt%) of heat insulating filler and homogeneous

distribution. Microsized-particle dispersed-film shows inferior property to those of nanoparticles due to the lots of large agglomerations. The efficiency of heat insulating ability increases according to the order of EVA/MgO-MPS film < EVA/CaO-MPS film < EVA/Al_2O_3-MPS film < 3 layered-EVA film < EVA/SiO_2-MPS(micro) film < EVA/SiO_2-MPS(nano) film.

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