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Effect of Silane Crosslinker on the Thermal Properties of Rice Straw/HDPE Biocomposite

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Abstract: A formulation was designed to produce silane crosslinkable rice straw/high density polyethylene (RSPE) compound suitable for injection molding process. The formulations consist of high density polyethylene (HDPE) as the base polymer, rice straw as the filler, processing aids and a mixture of crosslink chemicals. Crosslink chemicals consist of vinyltrimethoxysilane (VTMO) as crosslinking agent, dicumyl peroxide (DCP) as the initiator, dibutyltin dilaurate (DBTL) as the condensation catalyst. Lignocellulosic material, rice straw was oven dried at 70°C for 24 h, grinded and sieved. A counter rotating twin shaft high speed mixer was utilized to mix the rice straw, HDPE and the processing aids. Blends were then compounded on co-rotating and intermeshing twin screw extruder. Test specimens were prepared via injection molding process followed by oven curing at 90°C. Fourier Transform Infra Red (FTIR) was used to determine the chemical group involved in the crosslinking reaction. Degree of crosslinking in the silane crosslinked compound was measured by determining their gel content. Thermal properties were analyzed on the Differential Scanning Calorimetry (DSC) for the melt temperature, Tm, whereas Thermogravimetric (TGA) analysis for its thermal stability behavior. The degree of crosslinking in RSPE increases with an increased in VTMO and DCP concentration. The results from FTIR showed the presence of Si-O-Si bond and Si-O-C indicative of crosslinks formation. Thermal behavior of the compound illustrated that the crosslinked RSPE was more stable than the uncrosslinked RSPE and pure HDPE, while the Tm was unchanged.

Key words: Rice straw, HDPE, biocomposite, crosslinking, silane, thermal properties

INTRODUCTION

Polymer composite have been a subject of research and utilization for some decades. The need for materials having specific characteristics for specific purposes, while at the same time being non-toxic and environmentally friendly is increasing due to the lack of resources and increasing environmental pollution. All this issues have induced researchers to look for alternatives. Thus, the interest arises toward polymer composites filled with natural organic fillers. This class of composites (sometimes indicated as green composites) shows other interesting features (La Mantia and Morreale, 2006).

Industries are developing and manufacturing greener materials; government is encouraging bio-based product research, while the academicians are searching for eco-friendly materials and the public is coming to value the benefit of environment friendly products and processes, but at affordable prices. Previously, most researchers have used wood flour, rice husk and empty fruit bunch as reinforcement in the various polymers such as polyethylene, polyvinyl chloride and polypropylene (Abu Bakar et al., 2005; Chen, 2006).

In spite of all the advantages mentioned about natural fiber, there are also drawbacks in using natural fiber as reinforcement in thermoplastics. The main drawbacks are the difficulties of achieving good dispersion and strong interfacial adhesion between the hydrophilic fiber and the hydrophobic polymer (Magnus and Kristiina, 2005). Poor adhesion leads to composites with rather poor durability and toughness. This is the main reason of using silane technology in crosslinking polyethylene-rice straw composites. Silanes will be used as coupling agents to adhere fibers to a polymer matrix, stabilizing the composite material. In general, the use of this coupling agent significantly improves the mechanical properties of the composites (Magnus and Kristiina, 2005). In conjunction with the mechanical properties improvement the crosslinker is also expected to affect the rice straw/HDPE biocomposite thermal behavior. This study is carried out to analyze the effect of silane crosslinker on the thermal properties of injection grade crosslinked rice straw/HDPE biocomposite. Results are important in determining the process ability and product application limit with respect to thermal properties for crosslinked rice straw/HDPE.

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MATERIALS AND METHODS

Materials: The raw materials that are used in this research comprising rice straw and high density polyethylene injection grade, where HDPE as a matrix while rice straw as filler or fiber reinforcement in this composite. Vinyltrimethoxysilane (VTMO) is used as a crosslinking agent, dicumyl peroxide is used as radical initiator and dibutyltin dilaurate (DBTL) catalyst is used to promote hydrolysis and condensation reaction.

Methods
Filler preparation: The rice straw were placed on a pan and dried in Carbolite oven at 80°C for 24 h to eliminate the moisture content, followed by grinding process. Grinding was done on the dried straw to form fine particles. The rice straw particles were sieved to obtain the sizes of the required range 500-75 µm.

Compounding of fiber formulation: High Density Polyethylene (HDPE) and rice straw at fixed ratio 7:3 first undergo premixing process in counter rotating twin shaft high speed mixer model CL-FC-10 followed by compounding process on a co-rotating and intermeshing twin extruder model Sino PSM 30 with a screw speed of 90 rpm and temperature ranges between 180-190°C. The HDPE/rice straw pellet were then placed in dry, sealable cylindrical mixer and injected with silane chemicals liquid mixture using a syringe and blended on laboratory scale Fielder mixer for 3 min to uniformly coat the pellets. The coated pellets were allowed to rest for 2-3 h, the time necessary for complete absorption of the silane chemicals liquid mixture. The effect of varying the silane chemicals liquid mixture was studied. The VTMO concentration was varied between 0-3.5 phr, DCP between 0-0.6 phr and DBTL between 0-0.02 phr. These pellets were then injection molded on injection machine model JSW N100 BII into ASTM standard specimens for testing. Machine settings that were used are: 150°C first zones, 160°C zone two, 170°C zone three and 180°C for zone four. Cooling time was 60 sec, injection hold pressure time 3 sec, injection time 1.8 sec and injection pressure 80 kgf cm^{-2}.

Characterizations
Fourier Transform Infra-Red (FTIR): The active chemical component of rice straw/HDPE composites were identified by using FTIR spectrometer. The FTIR spectra were recorded on a spectrum 2000 GX spectrometer (Perkin-Elmer) using KBr thin (10-100 µm) disc technique for 16 scans. The resolution used was 4 cm^{-1} and the spectra scanned range was 4000-370 cm^{-1}.

Degree of crosslinking: Degree of crosslinking of the silane crosslinked RSPE sample was measured by determining their gel content after crosslinking reactions. The degree of grafting is regulated both by the silane and the peroxide concentration (Chen, 2006).

The determination of the gel content test was performed by extracting the soluble component with decahydronapthalene with refluxing at 200°C for 6 h according to ASTM D 2765-1995 Method B.

Thermal characterization
Differential scanning calorimetry: Thermal analysis of the RSPE biocomposites is carried out using Differential Scanning Calorimetry (DSC 7-Perkin Elmer) to determine the melting point, T_m. The samples were place in sealed 10 mg aluminum pans under constant nitrogen flow. DSC was performed by heating a composite sample about 5-12 mg from 30 to 250°C. The heating rate used was at 10°C min^{-1}. Melting temperature, T_m was obtained from the peak value of the endothermic graph.

Thermogravimetry analysis: Thermogravimetric (TGA) was used to characterize the decomposition and thermal stability of the RSPE biocomposites. The samples, approximately 10 mg each, were heated from 30 to 950°C at a rate 10°C min^{-1}. The material that will be molded should be thermally stable. The thermal stability of the RSPE was determined to guide processor in identifying the degradation limit of the material during processing.

RESULTS AND DISCUSSION

FTIR
Uncrosslinked RSPE: Fourier Transform Infra Red (FTIR) spectra of uncrosslinked rice straw-filled-HDPE composites injection grade are presented in Fig. 1. The spectrum shows the wave number in the region of 3746.37 cm^{-1} illustrating the presence of Si-OH chemical group coming from rice straw molecules. This shows that rice straw contain silica and that will give strength to the composites but wear and tear to the machine (Magnus and Kristiina, 2005). Peak at 2847 cm^{-1} illustrates the presence of carbonyl group that can easily absorb moisture. This moisture absorption is supported by the broad band around 3400-3600 cm^{-1} illustrating the fiber hydrophilicity. The band at 3601.44 cm^{-1} is attributed to hydroxyl group, probably originated from water absorption during sample preparation for the FTIR analysis. The stretching of aromatic carbon upon at 1638.69 cm^{-1} is assigned to C = C stretching of lignin in rice straw component.
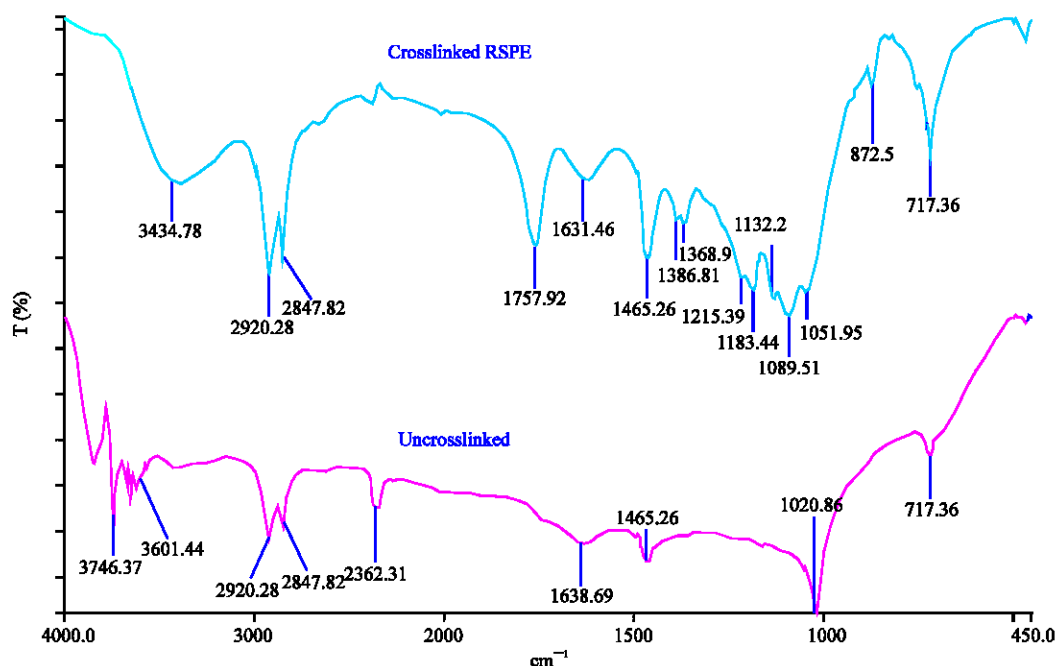
Fig. 1: FTIR spectra of uncrosslinked and crosslinked RSPE containing 1.0 phr VTMO, 0.2 phr DCP and 0.01 phr DBTL

Crosslink RSPE: Figure 1 displays the FTIR result at 1.0 phr concentration of VTMO. The band at 3434.78 cm^{-1} was attributed to hydroxyl group which also seen in uncrosslinked RSPE. The stretching of aromatic carbon bond at 1631.36 cm^{-1} is assigned to C = C and 1757.92 cm^{-1}, which is assigned to C = O stretching of lignin in rice straw component as mentioned earlier. As shown in Fig. 1, the vibrational bands at 1757.92 cm^{-1} of rice straw compositions come from the ester bonds in the cell-wall components such as hemicellulose, lignin or between those aromatic components as reported by Byung-Dae *et al.* (2004). The VTMO group gives characteristic absorption at 799, 1090 and 1192 cm^{-1} as illustrated by Toh and Chen for the crosslinked PE using VTMO (Toh, 2005; Chen, 2006). The 1089.51 cm^{-1} approximate to 1090 cm^{-1} peak observed typically can be used to determine the relative amount of the silane grafting in the biocomposite. The peak at 1192 cm^{-1} has been reported (Magnus and Kristiina, 2005; Valadez *et al.*, 1999; Abdel *et al.*, 2004) earlier to be caused by stretching of Si-O-Si and Si-O-C bonds. Thus in this study the peak shifted to 1183.44 cm^{-1} may be related to VTMO characteristic at 1192 cm^{-1} and could not only be related to polysiloxanes (Si-O-Si) but also to covalent bonding between fiber and silane (Si-O-C) (Magnus and Kristiina, 2005). This proved that silane function as a bridge to bond the rice straw fibers to the resin with a chain of primary strong bonds as similarly reported by Mohanty *et al.* (2005). The small peak at 1012 cm^{-1} is

attributed to un-reacted Si-OH groups. From Fig. 1, there is no peaks at 1100 and 1080 cm^{-1} which relate to residual unhydrolysed Si-OCH$_3$ group (Valadez *et al.*, 1999). This proved that Si-OCH$_3$ is fully hydrolysed in the samples with respect to 17.14% gel content of the RSPE composite as shown in Fig. 3 at 1.0 phr of VTMO composition. The Si-OCH$_3$ groups can originate from unhydrolysed grafted groups or from un-reacted silane in the samples. Thus this confirm that the Si-O-C at 1183 cm^{-1} is due to covalent bond between fiber and silane or Si-O-Si. Therefore RSPE incorporated with VTMO results in crosslinking occurring in PE component and also between fiber and PE.

Gel content test

Effect of VTMO silane crosslinker: The degree of crosslinking in the composites is determined by gel content measurements. Crosslinked polyethylene is in soluble in boiling decayhydronapthalin while the uncrosslinked part is soluble (Magnus *et al.*, 2007). Figure 2 shows the effect of (VTMO) concentration on the gel content of crosslinked rice straw/HDPE biocomposite. With increasing VTMO concentration, the gel content of the composite increases slowly from 17.14% to about 20.1% at low crosslinker concentrations (1 to 2 phr) and the gel percentage increases rapidly at high crosslinker concentrations (2.5 to 3 phr). From previous study with silane grafted HDPE, it was shown that fiber could be incorporated in the crosslink network since the silanol groups could react with hydroxyl groups in fiber as well
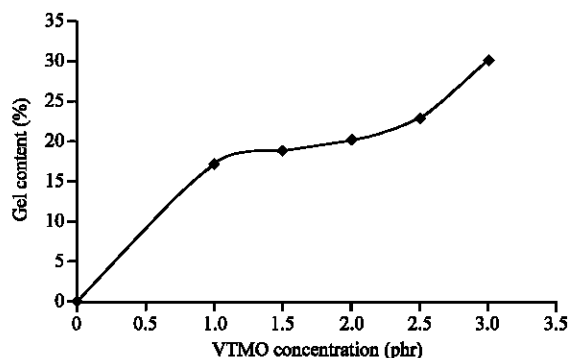
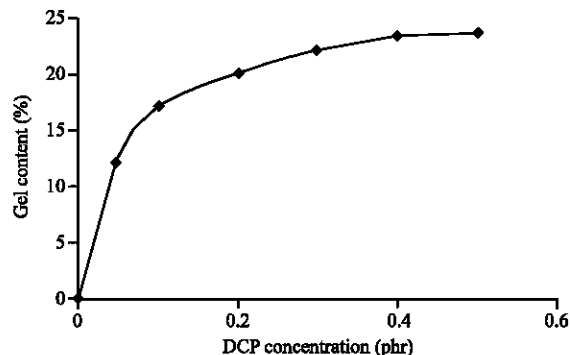Fig. 2: Effect of VTMO concentration on gel content of RSPE biocomposite

Fig. 3: Effect of DCP concentration on gel content of RSPE biocomposite

as with other hydroxyl groups grafted on the polyethylene backbone (Magnus and Kristiina, 2005). This can be proved from FTIR result that shows peak at 1183.44 cm^{-1} which represent the covalent bonding between fiber and silane (Si-O-C). As shown from Fig. 2, no gel was formed in the composites where no silane solution was added. A dosage of low crosslinker concentration does not significantly improve the crosslinking results.

Effect of DCP initiator: In order to iniatiate the crosslinking reaction, dicumyl peroxide (DCP) is used in this study. Vinyl silanes can be grafted onto the polyethylene backbone by the use of small amount of peroxide. The degree of crosslinking of crosslinked RSPE biocomposite increases with increasing concentration of DCP initiator. It was observed that, gel content increases with an increased in DCP initiator concentration. Figure 3 showed that gel content reached highest gel value at 0.4 to 0.5 phr of DCP concentration. When the amount of DCP was less than 0.1 phr, the silane grafting did not proceed sufficiently. In crosslinking reactions, peroxide initiates the reaction at elevated temperature and form free radicals. Free radicals of peroxide will abstract hydrogen from the polyethylene molecules, thus creating unstable carbon. After which, silane is grafted onto the carbon to form a copolymer and the remaining free radical on the copolymer branch will continue to abstract a hydrogen atom from other polyethylene molecule to become stable.

Thermal characterization
Thermogravimetric analysis
Effect of VTMO silane crosslinker: The thermogravimetry analysis curves for the uncrosslinked and crosslinked RSPE biocomposite samples with various amount of VTMO (vinylmethoxysilane) are shown in Fig. 4. Thermal stability for the decomposition temperature from TGA analysis improved as expected for crosslinked

RSPE biocomposite. However, these changes were small to be considered as a significant effect. This behavior was almost similar for all samples, uncrosslinked and crosslinked RSPE biocomposites. The results showed that the thermal stability of crosslinked RSPE slightly increased with VTMO crosslinker concentration. This is a logical consequence of the thermal stability of the vinylsilane in term of bonds strength. In the silane system the crosslinking reactions form a very stable siloxane bond, Si-O-Si which shown in Fig. 1 and the vibrational band Si-O-C is at 1183.44 cm^{-1}. For RSPE biocomposites prepared at 30% fiber loading, it was verified that the degradation temperature was shifted to a lower temperature 350°C showing that the presence of the rice straw lowered the thermal stability of the polymer (Fei *et al.*, 2008; Nachtigall *et al.*, 2007). An initial slight weight loss at temperature about 100-120°C for RSPE biocomposite could be related to the elimination of light volatiles present in the rice straw component. The weight loss referred to the decomposition of the fibers, starts as low as 150°C with the decomposition of pectin, lignin and nonstructural hemicellulose component present in fibers. This proof that rice straw fiber is suitable to be processed with polymer that have melt temperature below 200°C such as polyolefin that is Polyethylene or Polypropylene. A major weight loss, starts at 460°C which end approximately at 500°C depending on VTMO composition. It is the main degradation occurred to the structure of crosslinked and uncrosslinked RSPE biocomposite indicating the initiation of a second reaction zone. A slow further loss of weight occurred until 900°C, indicating that there is further reaction involving the char. Mansaray and Ghaly (1998) reported that three major constituents of lignocellulosic materials (hemicellulose, cellulose and lignin) are chemically active and decomposes thermo mechanically in the temperature range of 150-500°C (hemicellulose decomposes mainly between 150-350°C, cellulose decomposes between 275-350°C and lignin
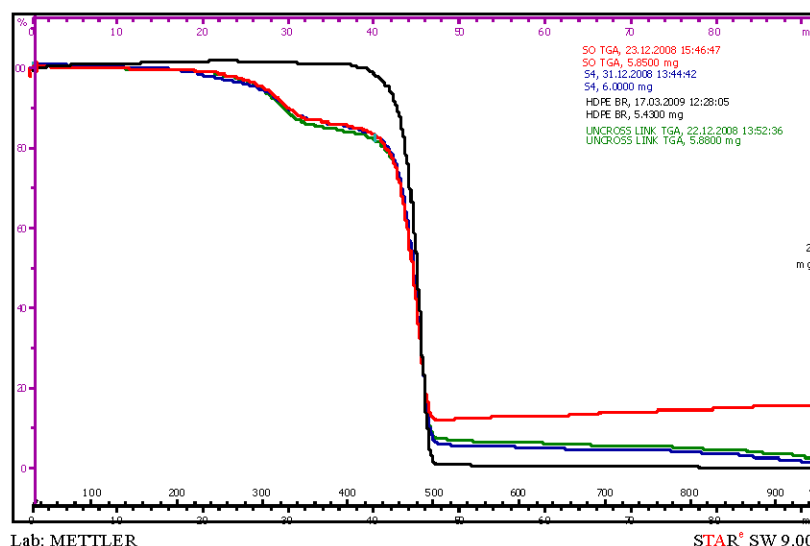
Fig. 4: TGA thermogram for decomposition temperature of crosslinked RSPE at various VTMO concentration. (S0) 2.0 phr, (S4) 3.0 phr
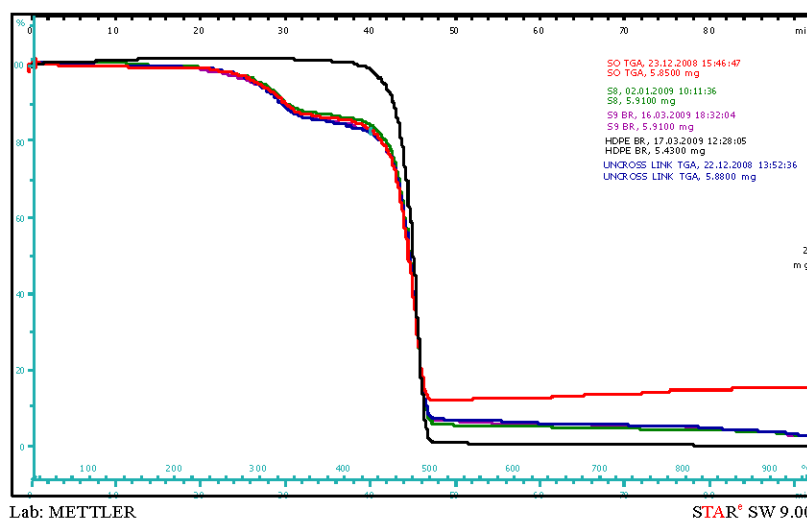

Fig. 5: TGA thermogram of decomposition temperature of crosslinked RSPE at various DCP concentration. (S0) 0.2 phr, (S8) 0.1 phr, (S) 0.3 phr

undergoes gradual decomposition between 250-500°C) (Mansaray and Ghaly, 1998). From the analysis it shows that the most suitable processing temperature for HDPE/rice straw before the fiber degrade is below 200°C.

Effect of DCP initiator: In order to iniatiate the crosslinking reaction, dicumyl peroxide (DCP) is used in this study. Vinyl silanes can be grafted onto the polyethylene backbone by the use of small amount of peroxide. It is can be seen in Fig. 5 that the thermal

decomposition temperature of crosslinked RSPE improved compared to uncrosslinked RSPE. Thermal stability of the crosslinked RSPE increases with DCP concentration, lower concentration of dicumyl peroxide used in the formulation led to less peroxide undergoing crosslinking with HDPE molecules during the silane grafting reactions and thus led to lower decomposition temperature. This indicated that the thermal stability of the crosslinked RSPE is dependent on the degree of crosslinking (gel content).
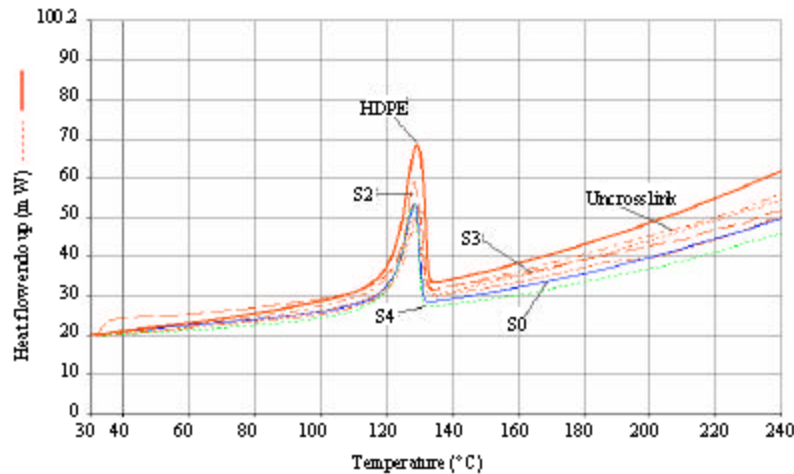
Fig. 6: DSC thermogram of of crosslinked RSPE at various VTMO concentration. (S0) 2.0 phr, (S2) 1.5 phr, (S3) 2.5 phr, (S4) 3.0 phr
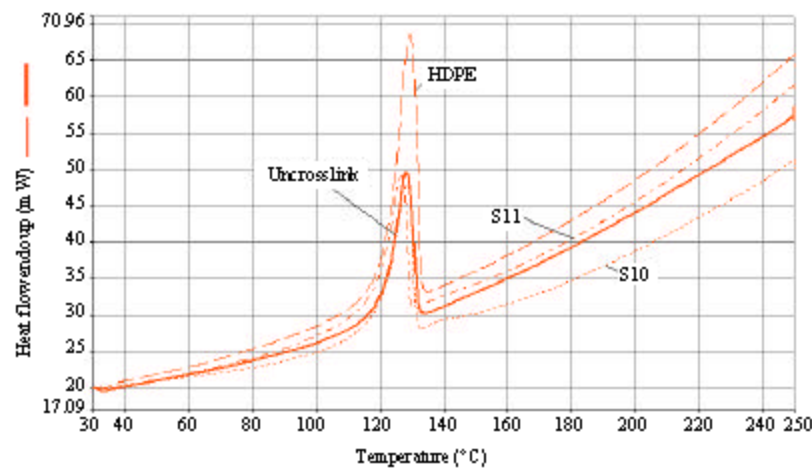

Fig. 7: DSC thermogram of of crosslinked RSPE at various DCP concentration. (S10) 0.4 phr, (S11) 0.5 phr

DSC

Effect of VTMO: Differential Scanning Calorimetric (DSC) was applied to determine the melting peak and specific melting enthalpies (endotherms) of uncrosslinked and crosslinked RSPE biocomposite. The obtained melting peak temperatures as a function of VTMO crosslinker concentration (1.5 phr to 3 phr) were shown in Fig. 6. In the case of the VTMO as crosslinker it appeared, that the melting property of the RSPE was hardly influenced by the crosslinking process since the melting temperatures remaining basically unchanged in all crosslinked and uncrosslinked RSPE biocomposite. The result also showed that introducing rice straw fiber to HDPE matrix did not change the characteristic peak position but led to the reduced peak heat flow rate (Fei *et al.*, 2008). The melting temperature is related to the crystal size, while the entalphy of fusion (area under the curve) is related to the total amount of crystallites.

The melting temperature of pure HDPE injection grade is 132°C. From the figure T_m of pure HDPE is only depressed by about 1-3°C by the addition of rice straw. This indicates that rice straw slightly disturb the arrangement of the HDPE chain thus the crystalline region is probably reduced slightly and therefore shows insufficient effect on the amorphous region in the composite. This probably due to the synergistic effect of crosslinking that occur both between PE and also rice straws, result in minimal changes in the PE crystalline region. Since, rice straw filler was not deformed by the thermal transition and behave as an inert material and only reacted at degradation point of temperature (Naurah, 2005).

Effect of DCP: As can be seen in Fig. 7, the peak temperatures for crosslinked RSPE shift to lower values compared with virgin HDPE and uncrosslinked RSPE with the addition of a small amount of DCP initiator (0.4 phr to 0.5 phr). This indicates that crosslinking had a direct influence on the process of crosslinked RSPE melt temperature biocomposite. Crosslinking causes formation of new chemical bonds between the macromolecular chain and this hinders the crystal growth which means reduce the crystallinity of HDPE (Magnus and Kristiina, 2005; Krupa and Luyt, 2001; Magnus and Thomas, 1999). The gel content test which was shown in Fig. 3 proof that crosslinking occur with the gel content value is 17 to 24%. However, the effect of DCP concentration only has slight influences on the T_m on the crosslinked RSPE. Only a slight shift towards the lower end occurs in the melting peak as DCP is increased. This behavior similar to that observed in effect of VTMO. Melting peak is derived from PE alone whereas rice straw only reacted during degradation process.

CONCLUSION

Silane crosslinked composites were successfully produced by injection molding process. Silane is grafted onto both polyethylene and fiber thereby creating a crosslinked network in the matrix with chemical bonds (covalent and hydrogen bonding) to fiber. The degree of crosslinking of crosslinked RSPE increased with increasing of VTMO and DCP concentration. Thermal behavior of the compound illustrated that the crosslinked RSPE was more stable than the uncrosslinked RSPE and pure HDPE and increased with VTMO and DCP concentrations. The T_m experienced mild changes at various concentration of VTMO and DCP.

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