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Synthesis of Coagent Ethylene Glycol Dimethacrylate

C. H. Chu[1]*, N. M. Hồ[1] and T. T. C. Tống[2]

[1] Institute of Chemistry and Materials, Military Institute of Science and Technology, 17 Hoang Sam St, Cau Giay Dist, Ha Noi.

[2] Lương Van Tuy Gifted High School, Ha Noi

*Corresponding author (e-mail: chienhuu62@yahoo.com)

The major application of polyolefin foams is in thermal insulation, packaging, construction and sport and leisure industries. The most widely used cross-linked polyolefin foam is based on cross-linked polyethylene. Polyethylene can be cross-linked by peroxide involving free radical generation which can result in intermolecular covalent bonding and three-dimensional network formation. Coagents are low molecular weight with two or more reactive double bonds. In cure system, coagent reacts with free radical which are generated by using peroxide, to increase the efficiency of cure to give more crosslinks. Addition of coagent reduces cure time, improves resistance to oil and fuels, improves heat aging, improves peroxide efficiency, improves flexibility and gives higher tensile strength and hardness. In this study, we investigated synthesis of coagent based on ethylene glycol dimethacrylate from ethylene glycol and methacrylic acid. The product was obtained at a temperature of 110°C, with molar ratio MA/EG: 1.1/0.5 yielded 93.5%. Structural characteristics of the product was measured by FT-IR, TG and ^{1}H-NMR. The product had a density of 1.0456 g/cm^3 (at 20°C), acidity index of 1.5 mg KOH/g, and dynamic viscosity of 5.39 cP (at 20°C).

Key words: Polyethylene; polyethylene vinylacetate foam; coagent; ethylene glycol dimethacrylate

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Foams based on polyethylene (PE), polyethylene vinylacetate (EVA) are now being used commonly as mats, insoles, thermal and sound insulators in construction industry. Main materials for producing foams include: PE resin, EVA resin, blowing agent, crosslinking agent, filler and other additives. Crosslingking agent acts to make bonds between polymer chains through direct combination between two carbon atoms or through a bridge consisting two or more carbon atoms, to help improve shaping ability, impact resistance, creep resistance, prevent the growth of microcracks, increase weather durability. Peroxides have been used for curing in industry since 50 years ago, and are now being the most common and effective method, especially for polyethylene and its blend with PP, EVA. The crosslinking process of ethylenevinyl acetate is faster than PE because of the polar groups that are easily activated in macromolecular chain. To improve the quality of crosslinking process, besides peroxide, coagents are used, for examples, triallyl cyanuarate dimethyl acrylate, and 1,3-butylene glycol dimethacrylate. They are low-weight organic compounds that contain two or more active double bonds in the molecule. They work well in resin system and activate curing process via free radical mechanism. Free radicals are formed by irradiation or peroxide, in one hand, create active sites in polymer chain, and in other hand, react with coagents to create more free radicals in the system. The mobility of the free radicals from coagents is much more than that of free radicals in the molecular chain, so collision probability for chain growth as well as crosslinking is improved substantially. Nowadays,

in industrial production of PE, EVA foams in our country, only peroxide crosslinking agents have been used. With the goal of improving the quality of the foams using crosslinking coagents, in this paper, we present the results of preparation and investigation related to coagents based on ethylene glycol dimethacrylate. The effect of the coagent ehylene glycol dimethacrylate on PE/EVA-based foams will be presented in the next paper.

EXPERIMENT

Materials and Equipment

The following were used: Ethylene glycol (EG), PA China; Methacrylic acid (MA), PA China; KOH, Na_2CO_3,H_2SO_4, PA China; flask, roughened Claisen condenser, thermometer; capillary, water remover; vacuum bump, stirrer and nitrogen.

Methods

The following was adopted:

- Fourier transform infrared spectroscopy was done on Nexus 670, US
- Nuclear magnetic resonance image was obtained on Bruker with the solvent $CDCl_3$
- Dynamic viscometry was determined according to *ASTM D445*
- Acidity index was determined according to *GOST 9439-85*; and
- Thermal analysis was done in nitrogen atmosphere with a heating rate of 10°C/min on STA 409PC/ Netzch, Germany.

RESULTS AND DISCUSSION

Preparation of Ethylene Glycol Dimethacrylate

Ethylene glycol dimethacrylate was prepared based on esterification between ethylene glycol and methacrylic acid [2, 3] with the reaction diagram presented in Figure 1. The reaction was managed in 250 ml three-necked flask with the molar ratio of the reactants as shown below:

- Methacrylic acid: 94.6 g (1.1 mol)
- Ethylene glycol: 31.0 g (0.5 mol)
- Hydroquinone: 0.25 g (0.00227 mol); and
- Sulphuric acid: 0.5%.

The reaction happened at 110°C, in nitrogen atmosphere, the reaction flask was equipped with condenser and water remover. The reaction was maintained for 6 h, after each 1 hour, a portion of the mixture was sampled to determine acidity index. The prepared product was rinsed three times, each with 50 ml of 5% Na_2CO_3 solution to neutralize excess acid and catalyst, then rinsed twice with 5% NaCl solution and finally with double-distilled water. The solution was dried with 100 g $MgSO_4$ and filtered with filter paper. It was further dried under reduced pressure at 50°C for 2 h to achieve constant weight. The gravimetric yield was then determined accordingly.

Several characteristics of the product, yield, and the change of acidity index were presented in Table 1 and Figure 2.

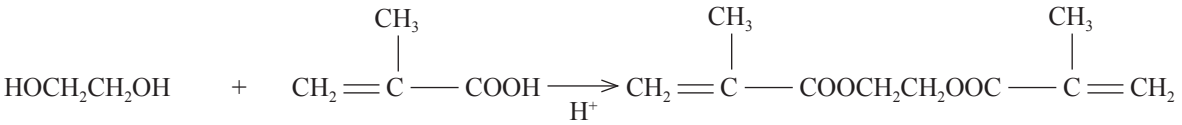

Figure 1. Preparation reaction of ethylene glycol dimethacrylate.

Table 1. Several characteristics of ethylene gylcol dimethacrylate.

Time (h)	Acidity index (mg KOH/g)	Water removed (ml)	Characteristics	Yield (%)
1	85.0	6.3	Transparent solution, the loss of water is rapid	
2	50.3	9.2	Bright yellow solution, the loss of water is rapid	
3	23.8	12.0	Bright yellow solution, large amount of lost water	
4	12.2	15.6	Bright yellow solution, the loss of water is slow	93.5
5	4.1	17.1	Bright yellow solution, the loss of water is slow	
6	1.5	18.0	Bright yellow solution, the amount of lost water is insignificant	

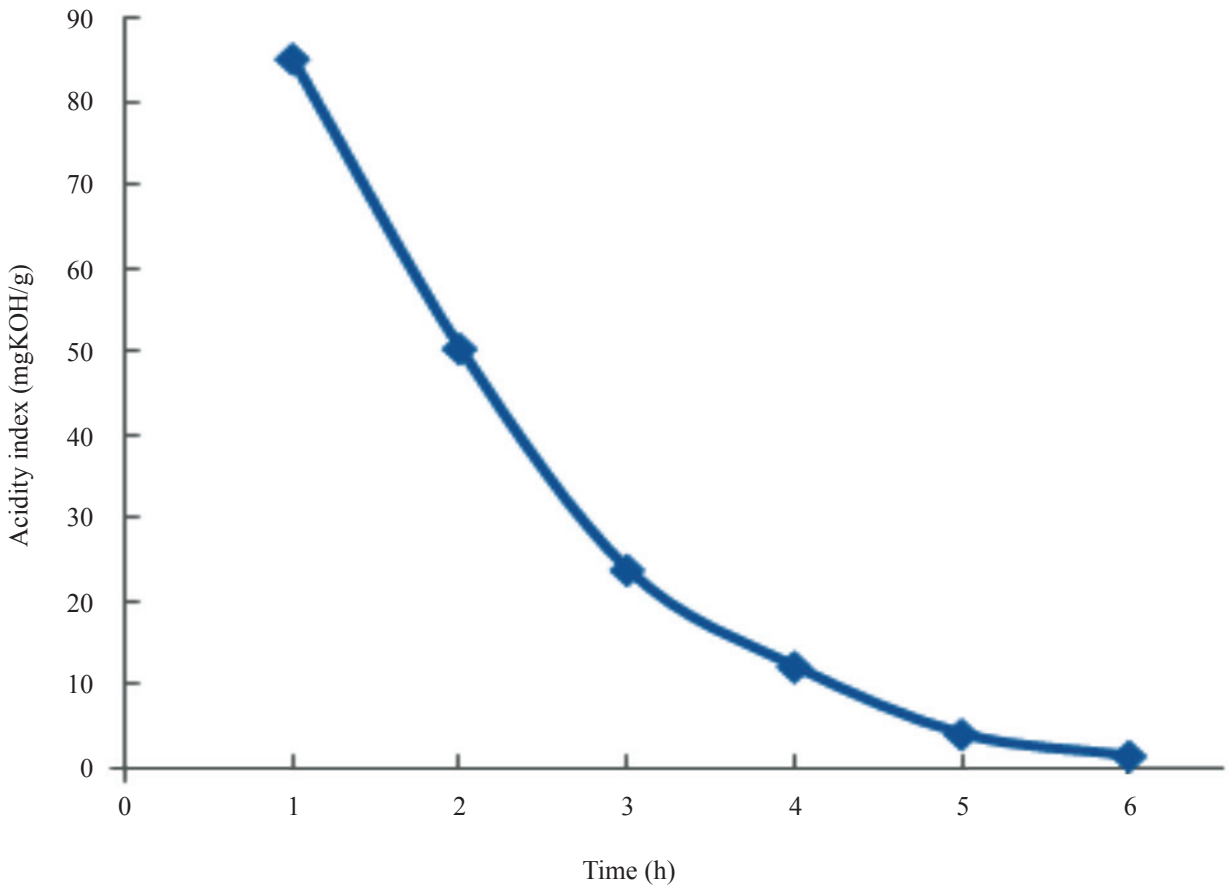

Figure 2. The change of acidity index of the reaction mixture.

Based on the amount of water loss and the change of acidity index, it was found that in the first 3 h, the acidity index of the reaction mixture decreased rapidly. The amount of the water loss was much corresponding to the formation of mono, diester product from the initial materials, in the next 2 h the acidity index changed slowly, and in the last hour, the amount of water loss was insignificant, proving that the reaction was complete. This was the time to stop the reaction and purify the product.

To affirm the obtained product, we analyzed its structure by physiochemical methods.

IR Spectrum of Obtained Ethylene Glycol Dimethacrylate

The obtained esteric product was purified, and kept for 24 h, then its IR spectrum was taken. The FTIR result is shown in Figure 3.

It was found from IR spectrum that all typical vibrations of ethylene glycol dimethacrylate were present. The absorption peak 3525.32 cm^{-1} was typical for the stretched vibration of the group –OH of trace water or materials (acid or glycol) that remained with very small amounts corresponding to weak intensity.

The absorption peak 2937.28 cm^{-1} is typical for the alkyl groups $–CH_3$; $–CH_2$ in the ethylene glycol dimethacrylate. The absorption peak 1718.99 cm^{-1} was typical for stretched vibration of carbonyl C=O in the ester with strong intensity.

The absorption peaks 1633.22 cm^{-1} and 1445.06 cm^{-1} were typical for vibration of the double bond C=C in the ester acrylate. The absorption peaks 1162.84 cm^{-1} and 949.78 cm^{-1} were typical for the stretched vibration of C–O bond in ester molecule with strong intensity.

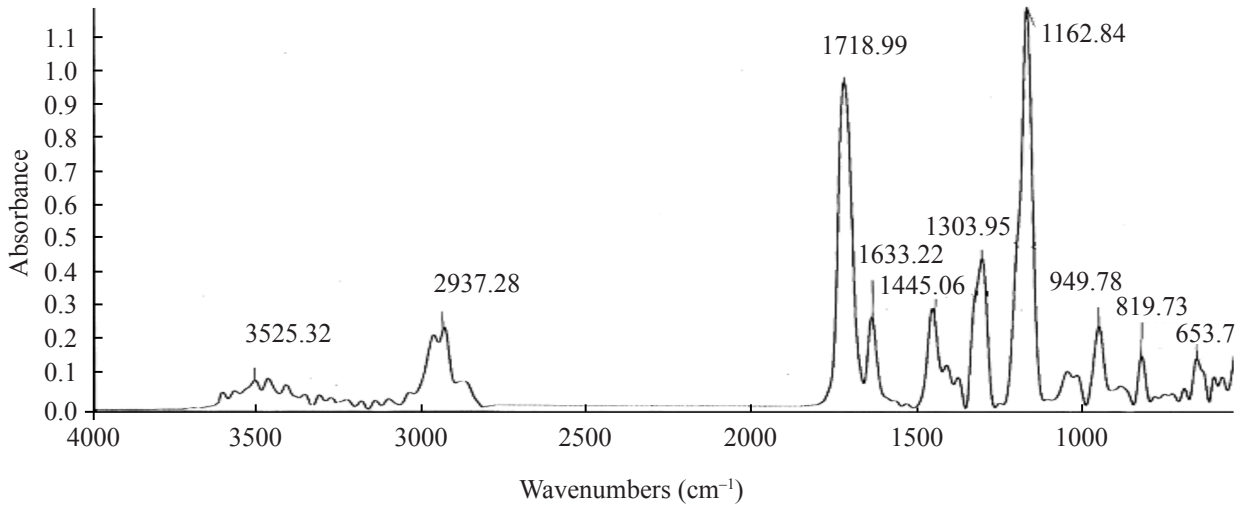

Figure 3. IR spectrum of the prepared ester product dimethacrylate.

Table 2. Assignment of NMR for the ester product.

δ (ppm)	Number of protons	Assignment
6.2	2	2 P of the group CH_2 d
5.6	2	2 P of the group CH_2 c
4.5	4	4 P of the 2 groups $–CH_2$ b
2.35	–	Trace of H_2O
1.9	6	6 P of the 2 groups $–CH_3$ a

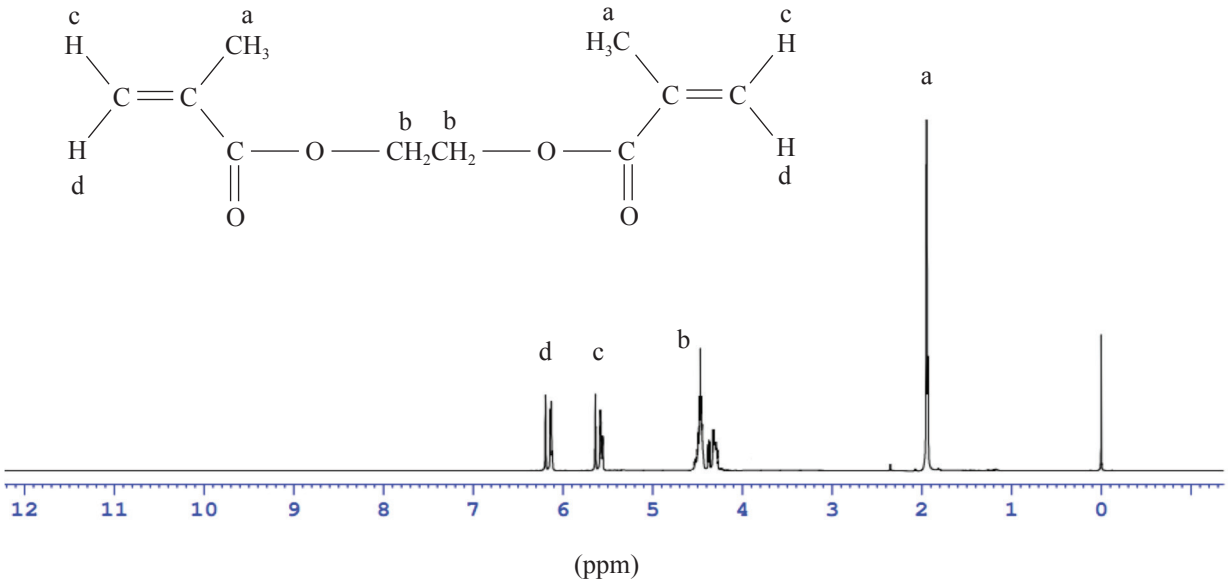

Figure 4. [1]H-NMR spectroscopy image of the ester product.

[1]H-NMR Investigation of the Product Ethylene Glycol Dimethacrylate

[1]H-NMR image of the product was taken on Bruker with the solvent $CDCl_3$ using TMS as an internal standard. The result was shown in Figure 4 and Table 2.

Based on NMR and IR results, it was found that the obtained product was completely identical to theoretical prediction and the product was relatively pure. The assignment of [1]HNMR is shown in Table 2.

Characterize Thermal Property of the Product Ethylene Glycol Dimethacrylate by Thermal Analysis

Thermal property of the product was investigated by thermal gravimetry. The result showed that the product was just a compound. There was no mass-loss peaks typical for ethylene glycol and methacrylate acid at their boiling temperatures. When heated, the weight of the sample decreased corresponding to the natural evaporation of the ester product, until the temperature of 201.5°C; there was an abrupt weight loss of 98.1% corresponding to the boiling point of the sample.

Specifications of the Product Ethylene Glycol Dimethacrylate

The obtained ester product was characterized by several parameters such as density and viscosity. The results are presented in Table 3.

CONCLUSION

The crosslinking coagent ethylene glycol dimethacrylate was successfully prepared from the raw materials with the yield of 93.5%. The structural characterization by IR and NMR showed

Table 3. Specifications of the product ethylene glycol dimethacrylate.

STT	Specification	Characterization method	Value	Product of Sigma/BASF
1	Density at 20.0°C (g/cm^3)	Measured on Anton Paar 4500 M	1.0456	1.051
2	Dynamic viscosity at 20.0°C (cP)	*ASTM D445*	5.39	–

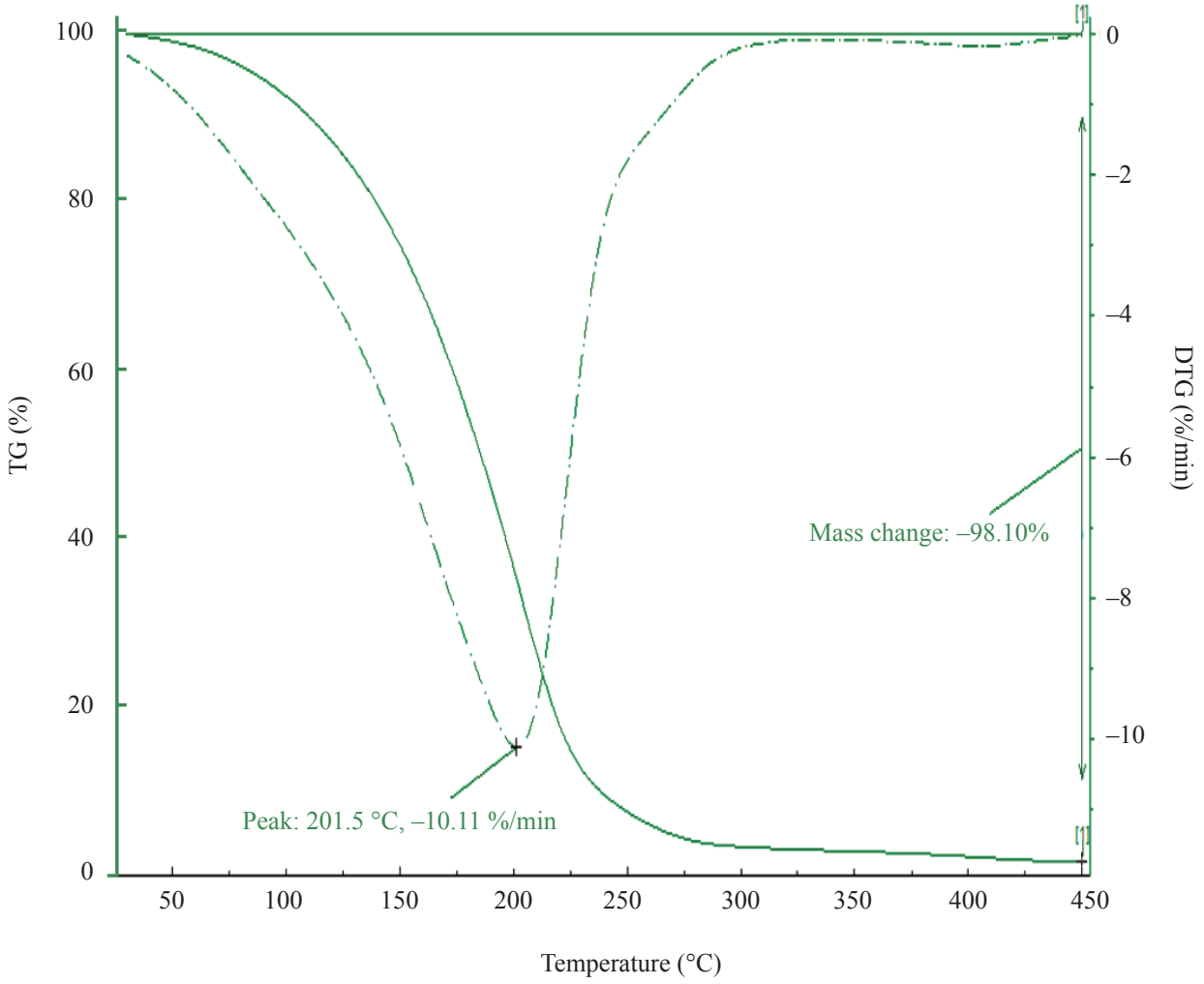

Figure 5. Thermal analysis diagram of the product ethylene glycol dimethacrylate.

that the product was of same chemical structure as the theoretical prediction. The Specifications of the product are:

- Density: 1.0456 (g/cm^3).
- Acidity index: 1.5 (mg KOH/g).
- Dynamic viscosity at 20°C: 5.39 (cP).

The product was used as the crosslinking coagent for the manufacture of PE/EVA foams with good results.

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