PHASE SELECTIVE LOCALIZATION OF SILICA FILLER IN POLYMETHYL METHACRYLATE/ ETHYLENE VINYL ACETATE (PMMA/EVA) COMPOSITES

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Fasa Pertempatan Terpilih Pengisi Silika Dalam Komposit Polimetil Metakrilat/Etilena Vinil Asetat (PMMA/EVA)

ABSTRAK

Penaburan pengisi dalam komposit polimer bergantung pada ketegangan antara-muka pengisi and polimer matriks, terutama bagi komposit menggunakan adunan elastomer termoplastik (TPE). Kedua-dua tegangan antara-muka, di antara pengisi dan termoplastik dan juga pengisi dan elastomer menyebabkan pengagihan dan penaburan pengisi yang berbeza dalam setiap fasa polimer. Pengisi akan memilih dan bertempat dalam fasa polimer yang mempunyai tegangan antara-muka yang lebih rendah; ini dipanggil sebagai fasa pertempatan terpilih (PSL) pengisi dalam adunan TPE. Kajian ini mengambil berat tentang PSL silika pengisi dalam komposit PMMA/EVA; yang seterusnya menentukan ciri-ciri dan sifat-sifat komposit PMMA/EVA/Si. Terdapat tiga tegangan antara-muka dalam komposit PMMA/EVA/Si seperti tegangan antara-muka PMMA/EVA, PMMA/Si, dan EVA/Si; berdasarkan persamaan Wu, nilai yang didapati ialah 7.18 mN/m, 47.99 mN/m, dan 41.24 mN/m. Ia menunjukkan bahawa silika lebih cenderung untuk bertempat dalam fasa EVA disebabkan tegangan antara-muka yang lebih rendah berbanding PMMA/Si. Di samping itu, silika dan EVA juga mempunyai nilai polariti yang serupa. Dalam usaha memaksimumkan kesan PSL Si dalam komposit PMMA/EVA/Si, tiga kaedah penyebatian yang berbeza telah dilaksanakan bagi setiap formula komposit PMMA/EVA/Si. Kaedah pertama diikuti dengan penyebatian konvensional dengan penambahan silika dalam adunan PMMA/EVA (ditandakan sebagai CON). Yang kedua adalah pra-penaburan silika dalam fasa PMMA (Si/M), yang selanjutnya dicampur dengan ekstrusi EVA untuk mendapatkan komposit akhir (ditandakan sebagai Si/M-EVA). Yang ketiga adalah pra-penaburan silika dalam fasa EVA (Si/E) dan diikuti dengan pengadunan Si/E dengan ekstrusi PMMA untuk mendapatkan komposit akhir (ditandakan sebagai Si/E-PMMA). Kajian difokuskan pada dua nisbah adunan PMMA/EVA dan kandungan silika yang berlainan. PSL diperiksa dengan mengaitkan kelikatan praktikal (diperolehi oleh rheometer kapilari) dan kelikatan teori (Model Konvensional, Model EVA, dan Model PMMA). Semua penyebatian dijalankan dengan menggunakan extruder skru berkembar. Sampel untuk ujian mekanikal dan DMA disediakan dengan menggunakan pengacuan suntikan. PSL Si kepada EVA dibuktikan dari pengiraan kelikatan praktikal dan teori Si/E-PMMA yang sepadan. Fakta dari PSL Si kepada EVA dibuktikan dengan iaitu nisbah adunan: adunan setara 50/50 PMMA/EVA dan dominasi PMMA 70/30 PMMA/EVA. Selain itu, penghijrahan silika dalam fasa PMMA ke fasa EVA dalam komposit Si/M-EVA juga dikesan dari keputusan EDX. Ia mengesahkan bahawa PSL silika lebih cenderung ke fasa EVA berbanding fasa PMMA. Oleh itu, komposit Si/E-PMMA mempamerkan sifat-sifat mekanikal, terma, dan dinamik mekanikal yang terbaik untuk komposit adunan setara. Untuk adunan dominasi PMMA komposit 70/30 PMMA/EVA/Si, Si/E-PMMA mempamerkan ciri-ciri terma yang terbaik manakala Si/M-EVA mempamerkan sifat-sifat mekanikal yang terbaik. Penemuan yang paling menarik ialah kedua-dua komposit pra-penaburan silika dalam PMMA atau EVA, telah mempamerkan sifat-sifat yang lebih baik berbanding komposit konvensional. Ini membuktikan bahawa PSL silika sangat penting kerana ia mengawalkan sifat-sifat komposit PMMA/EVA/Si.

Phase Selective Localization of Silica Filler in Polymethyl Methacrylate/ Ethylene Vinyl Acetate (PMMA/EVA) Composites

ABSTRACT

Filler dispersion in polymer composites depends on the interfacial tension of filler and polymer matrix, especially for composites using a thermoplastic elastomer blend (TPE). Both interfacial tensions, filler and thermoplastic as well as filler and elastomer, caused different distribution and dispersion of the filler in each polymer phase. The filler will select and locate in the polymer phase having low interfacial tension with; this is called as phase selective localization (PSL) of filler in TPE composites. This research concerned about PSL of silica filler in PMMA/EVA composite; which in turn decided the characteristics and properties of PMMA/EVA/Si composites. There are three interfacial tensions in PMMA/EVA/Si composite such as interfacial tensions of PMMA/EVA, PMMA/Si, and EVA/Si; based on Wu's equation, it was calculated as 7.18 mN/m, 47.99 mN/m, and 41.24 mN/m, respectively. It indicated that silica selects to locate in EVA phase because of their lower interfacial tension compared to PMMA/Si. In addition, silica and EVA also have similar polarity values. In order to maximize the effect of PSL of Si in PMMA/EVA/Si composite, three different compounding methods were implemented for each formula of PMMA/EVA/Si composite. The first method followed conventional compounding by addition of silica into melt PMMA/EVA blend (notated as CON). The second was pre-dispersion of silica into PMMA phase (Si/M), which was further blended with extruded EVA to get the final composite (notated as Si/M-EVA). The third was pre-dispersion of silica into EVA phase (Si/E) and followed by blending Si/E with extruded PMMA to get the final composite (notated as Si/E-PMMA). The investigation was focused on two PMMA/EVA blend ratios and different silica contents. PSL was examined by correlating the practical viscosity (obtained by capillary rheometer) and theoretical viscosities (Model Conventional, Model EVA, and Model PMMA). All melting compounding were conducted by using a twin-screw extruder. The samples for mechanical and DMA testing were prepared by using injection moulding. PSL of Si to EVA was proven from the well-matching of both practical and theoretical viscosity of Si/E-PMMA. The fact of PSL of Si to EVA was evident in both blend ratios: 50/50 PMMA/EVA equivalent blend and 70/30 PMMA/EVA of PMMA dominion. Moreover, migration of silica in the PMMA phase to EVA phase in Si/M-EVA composite was also detected from the EDX results. It confirmed that PSL of silica is EVA phase versus PMMA phase. Therefore, the Si/E-PMMA composite exhibited the best mechanical, thermal, and dynamic mechanical properties for the equivalent blend composites. For PMMA dominion blend of 70/30 PMMA/EVA/Si composites, Si/E-PMMA exhibited the best thermal properties while Si/M-EVA exhibited the best mechanical properties. The most interesting finding was both composites of pre-dispersion silica in PMMA or EVA, had exhibited better properties compared to the conventional composite. This proved that PSL of silica was very essential as it controlled the properties of PMMA/EVA/Si composites.

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LIST OF SYMBOLS AND ABBREVIATION

µm	Micrometer
nm	Nanometer
%	Percentage
wt %	Weight percentage
^{o}C	Degree Celsius
ASTM	American Society for Testing Material
C_{Si-P}	Concentration of filler in PMMA phase
C_{Si-E}	Concentration of filler in EVA phase
η_M	Viscosity of PMMA
η_E	Viscosity of EVA
ϕ_M	Volume fraction of PMMA
ϕ_E	Volume fraction of EVA
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimeter
EDX	Energy-dispersive X-ray spectrometer
EVA	Ethylene Vinyl Acetate
E’	Storage modulus
E”	Loss modulus
GPa	Giga Pascal
g	Gram
Si/M	Pre-dispersion of silica into PMMA
Si/E	Pre-dispersion of silica into EVA

CON	Convention method or composite
Si/M-PMMA	Pre-dispersion of Silica into PMMA method or composite
Si/E-PMMA	Pre-dispersion of Silica into EVA method or composite
50/50 PMMA/EVA	PMMA/EVA blend with weight ratio (phr) 50:50
70/30 PMMA/EVA	PMMA/EVA blend with weight ratio (phr) 70:30
Si/M(10,50)	Pre-dispersion of 10 phr silica into 50 phr PMMA
Si/M(20,50)	Pre-dispersion of 20 phr silica into 50 phr PMMA
Si/E (10,50)	Pre-dispersion of 10 phr silica into 50 phr EVA
Si/E (20,50)	Pre-dispersion of 20 phr silica into 50 phr EVA
Si/M(10,70)	Pre-dispersion of 10 phr silica into 70 phr PMMA
Si/M(20,70)	Pre-dispersion of 20 phr silica into 70 phr PMMA
Si/E (10,30)	Pre-dispersion of 10 phr silica into 30 phr EVA
Si/E (20,30)	Pre-dispersion of 20 phr silica into 30 phr EVA
CON (50,50,10)	50/50 PMMA/EVA composite with 10 phr Si prepared by CON method
CON (50,50,20)	50/50 PMMA/EVA composite with 20 phr Si prepared by CON method
CON (70,30,10)	70/30 PMMA/EVA composite with 10 phr Si prepared by CON method
CON (70,30,20)	70/30 PMMA/EVA composite with 20 phr Si prepared by CON method
Si/M-EVA (10,50-50)	50/50 PMMA/EVA composite with 10 phr Si prepared by Si/M-EVA method
Si/M-EVA (20,50-50)	50/50 PMMA/EVA composite with 20 phr Si prepared by Si/M-EVA method
Si/M-EVA (10,70-30)	70/30 PMMA/EVA composite with 10 phr Si prepared by Si/M-EVA method
Si/M-EVA (20,70-30)	70/30 PMMA/EVA composite with 20 phr Si prepared by Si/M-EVA method

Si/E-PMMA (10,50-50)	50/50 PMMA/EVA composite with 10 phr Si prepared by Si/E-PMMA method
Si/E-PMMA (20,50-50)	50/50 PMMA/EVA composite with 20 phr Si prepared by Si/E-PMMA method
Si/E-PMMA (10,30-70)	70/30 PMMA/EVA composite with 10 phr Si prepared by Si/E-PMMA method
Si/E-PMMA (20,30-70)	70/30 PMMA/EVA composite with 20 phr Si prepared by Si/E-PMMA method
MFI	Melt Flow Index
mm	Millimeter
min	Minute
MPa	Mega Pascal
phr	Part per hundred resin
PMMA	Polymethyl Methacrylate
Pa	Pascal
s	Seconds
SEM	Scanning Electron Microscope
Si	Silica
T_{onset}	Onset temperature
T_{10}	Temperature at 10 % weight loss
T_{50}	Temperature at 50 % weight loss
T_{offset}	Offset temperature
T_{max}	Maximum degradation temperature
T_m	Melting temperature
T_g	Glass transition temperature
T_c	Crystallization temperature
TGA	Thermogravimetric Analyzer

TPE	Thermoplastic Elastomer
γ_i	Surface tension
γ_i^d	Dispersion
γ_i^p	Polarity
γ_{AB}	Interfacial tension

CHAPTER 1: INTRODUCTION

1.1 Research Background

Addition of fillers to reinforce the polymeric material is a practice widely used for the production of high performances plastics (Bottazzo, 2012). In fact, a multiphase material, generally called as composite, shows advanced combined properties which are difficult to get from individual components. Reinforced fillers will improve the composite mechanical properties such as tensile and flexural strength and modulus. Moreover, advanced fillers can introduce new functional properties which are not possessed by the polymer matrix such as conductivity and magneticity (Bottazzo, 2012).

The improvement of composite properties depends strongly on the interfacial interaction between filler and polymer, which actually decides the filler dispersion in the polymer matrix. The interfacial tension could be calculated based on Wu’s equation (Sinayobye et al., 2013; Thomas et al., 2016). This factor also affects the rheological behaviour of the composite compared to the neat polymer (Arie, 1997). Rheology of particulate-filled polymers usually exhibits non-Newtonian, viscoelastic behaviour (Anne et al., 2004). Therefore, melt flow behaviour of such compounds should be studied for optimization of the processing and moulding conditions. Few variables such as shear rate, temperature, and compounds composition which affect the melt viscosity must also be examined.

Commonly, incorporation of filler into polymer blends aims to secure the blend’s modulus, especially for thermoplastic-elastomer (TPE) blends; which have a common drawback of the reduction in modulus of the blend. If a single polymer composite concerns only one interfacial tension between filler and polymer. TPE composite must consider three interfacial tensions such of the interfacial tension between polymer and elastomer, polymer and filler as well as elastomer and filler (Katbab et al., 2012).

The surface free energies of interacting components are very important since they not only dictate the strength of interaction but also control the process like the dynamics of molecular self-assembly, the stability of aqueous colloidal suspensions, spreading, wetting and adhesion. The interfacial interactions are mainly depending on the interfacial surface tensions between two phases. The surface free energy components of the solids and the characterization of the surface properties are recognized as the main key for understanding the mechanism of surface-based phenomena (Good & Van, 1992; Janczuk et al., 1993; Petra et al.,2008). For TPE composite, there is a possibility that the interfacial tension between the filler and one polymer phase is lower than that of filler and the other polymer phase. This cause the filler to select the first polymer phase to disperse rather than the second polymer phase, which is considered as phase selective localization of filler in TPE composite.

Phase selective localization of filler will occur during the compounding process and affect the filler dispersion in TPE blend; where either the thermoplastic phase or elastomer phase could have more dispersed filler than the others. This induces a rich filler domain and less filler domain, which certainly affects the composite rheology, characteristics, and properties. Ilias et al. (2011) calculated the interfacial tension (γ_{AB}) of HDPE/$CaCO_3$ and found it higher than that of EVA/$CaCO_3$ phase. Hence, the morphology of $CaCO_3$ particles-encapsulated EVA is resulted because of having the lowest free energy. Furthermore, EVA and $CaCO_3$ both have similar polarity, which also facilitated the encapsulation of $CaCO_3$ by EVA. It is worth mentioning that the final morphology of the reinforced blends will also be affected by the extent of adhesion between the $CaCO_3$/EVA under the shear forces during the melt mixing of processing.

Abdulbaset (2011) found that the morphologies of NR and LDPE as well as fillers' dispersion were strongly dependent on filler type and also mixing methods. It reported that pre-dispersion of silica into LDPE then further compounded with NR has resulted in better tensile mechanical properties compared to conventional method of adding silica into LDPE/NR blend or pre-dispersion silica into NR. This could be claimed to the phase selective localization of filler in NR and LDPE phase.

Phase selection localization is exploited in preparation of ternary rubber blend. Le et al. (2010) are one of the pioneers to investigate the phase selective localization of silica in ternary SBR/NR/EPDM rubber blend. The phase selective localization of silica is based on its polar nature and the wetting behaviour of the rubber. The different rubber-filler interaction between silica with each rubber has led to the determination of silica dispersion in the blend. Localization of silica was strongly affected by the wetting rate ratio of the blend components at the first mixing stage. While for the next stage, the rubber-filler interaction dominantly influenced the silica localization. Therefore, migration of silica from the NR phase toward the SBR phase occurred. Furthermore, a