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# Multi-Scale Effects on Deformation Mechanisms of Polymer Nanocomposites: Experimental Characterisation and Numerical Study

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# Abstract

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In order to make much stiffer, light weight and high performance material products, polymer nanocomposites play an emerging role in the material innovation. Unlike other thermoplastics, polymer nanocomposites are fabricated by introducing a small amount of solid nano-scale fillers (normally less than 5 wt%) such as nanoclay, carbon nanotubes or nanofibres into a plastic resin to dramatically enhance its stiffness, strength and thermal properties. The difference between nanocomposites and conventional fibre composites is that the added fillers are extremely small, only one-millionth of a millimetre thick, and provide a much larger interface area per unit volume for greatly improving the interfacial bonding effect between nanofillers and the polymer matrix.

More importantly, polypropylene (PP)/clay nanocomposites have quite a high potential to form such innovative materials and replace the conventional plastics in many automotive and packaging applications. Nevertheless, the growth of PP/clay nanocomposites faces an obstacle of hydrophobic polymer's low interactions with hydrophilic clay. Maleic anhydride (MA) grafted PP (MAPP), commonly used as a compatibiliser, has been proven to facilitate a good clay dispersion within the PP matrix through its functionalised MA groups. But despite the great attention from the manufacturers and researchers in recent years,

commercial PP/clay nanocomposites with reliable material properties are still limited in availability. The major problem stems from the complex influences of the material selection and processing methods.

The present work developed a comprehensive approach from the material formulation and processing, experimental characterisation to the numerical modelling of PP/clay nanocomposites based on the finite element analysis (FEA) of micro/nanostructures. Initially, effects of the material selection including the clay type and content, MAPP content and PP matrix viscosity were investigated for the mechanical property enhancement of PP/clay nanocomposites. These nanocomposites were prepared using twin screw extrusion and injection moulding processes with a well-known Taguchi design of experiments (DoE) method in order to statistically detect the significant factors for influencing their mechanical properties. The preferred material formulations were then determined by Pareto analysis of variance (ANOVA) with the technical and economic considerations. The fundamental material characterisation was also conducted on those formulated nanocomposites using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). Overall mechanical properties of neat PP and corresponding nanocomposites were determined by the general tensile, flexural and impact tests. Finally, computational models were established by implementing both the representative volume element (RVE) technique and innovative object-oriented finite element (OOF) analysis to predict the tensile moduli of PP/clay nanocomposites in comparison to the experimental data and available composites theoretical models.

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# Dedication

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*To*

*My parents Fengzhang Dong & Jinglan Wang*

*and*

*My wife Ruixue (Marie) Ma*

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# Nomenclatures

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$A$	Strain concentration tensor of polymer composites
$A_0$	Cross section area of 3×3 RVE domain
$A_i$	Components of Eshelby tensor ( $i=0, 1, \dots, 5$ )
$A_T$	Area of mesh triangle $T$ in shape energy function
$a$	Length of single RVE domain
$a_i(T)$	Area fraction for each mesh triangle $T$ including pixels of a given gray scale $i$ in homogeneity energy function
$B$	Stress concentration tensor of polymer composites
$b$	Width of single RVE domain
$b_0$	Width of injection moulded tensile sample
$C$	Stiffness tensor of polymer composites
$C^f$	Elastic stiffness tensor of fillers in polymer composites
$C^m$	Elastic stiffness tensor of matrix in polymer composites
$c$	Lateral distance between two clay platelets in RVE models
$D$	Screw diameter
$d$	Interlayer spacing between two layer planes in X-ray diffraction
$d_{MMT}$	Silicate layer thickness (i.e. interlayer spacing of pure MMT)
$d_i$	Galley thickness of clay silicates
$d_0$	Diameter/width of dispersed fillers in polymer composites
$d_{001}$	Interlayer spacing from (001) basal reflection peak
$E$	Total energy function parameter

$E_{11}$	Longitudinal elastic modulus of polymer composites
$E_{22}$	Transverse elastic modulus of polymer composites
$E_{33}$	Elastic modulus of polymer composites along axis 3 loading direction
$E_{MMT}$	Elastic modulus of pure MMT
$E_c$	Young's modulus of polymer composites
$E_{eff}$	Effective tensile modulus in OOF models
$E_f$	Young's modulus of fillers in polymer composites
$E_{gallery}$	Elastic modulus of the interlayer (intragallery) material in clay silicates
$E_{hom}$	Homogeneity energy function parameter
$E_m$	Young's modulus of matrix in polymer composites
$E_p$	Elastic modulus of stacks of layered intercalated clay platelets
$E_{ran-3D}^{fibres}$	Elastic modulus of fibre reinforced composites in the 3-D orientation
$E_{ran-3D}^{platelets}$	Elastic modulus of platelet reinforced composites in the 3-D orientation
$E_{shape}$	Shape energy function parameter
$E'$	Elastic (storage) modulus in DMTA
$E''$	Loss modulus in DMTA
$E_{//}$	Composite modulus parallel to the major axis of fillers
$E_{\perp}$	Composite modulus perpendicular to the major axis of fillers
$F_i$	Nodal force at node $i$
$f_s$	Staggering factor in RVE models
$g$	$g = \frac{\pi}{2}\alpha$
$\Delta H_f^0$	Heat of fusion of pure crystalline PP

$\Delta H_m$	Heat of fusion of the PP matrix
$k$	Modulus ratio of interface in Takayanagi model
$L$	Length of dispersed fillers in polymer composites
$L/D$	Screw length to diameter ratio
$L/t$ ( $L/d_0$ )	Aspect ratio of dispersed fillers in polymer composites
$L_0$	Length of injection moulded tensile sample
$L_T$	Perimeter of mesh triangle $T$ in shape energy function
$L_x$	Horizontal dimension of OOF models
$L_y$	Vertical dimension of OOF models
$\Delta L$	In-plane displacement in OOF models
$\Delta L_0$	Offset between clay platelets for the stack rows
$\Lambda$	$\Lambda = (1 - \phi_f) \left[ \frac{3(\alpha^2 + 0.25)g - 2\alpha^2}{\alpha^2 - 1} \right]$
$N$	Number of categories of the pixel selection in homogeneity energy function
$n$	Integral number in Bragg's law
$n_0$	Number of samples in each trial of Taguchi DoE
$n'$	Set number of boundary nodes under the nonzero displacement condition in OOF modelling
$S$	Average compliance of polymer composites
$S/N$	Signal to noise ratio in Taguchi DoE
$S^f$	Compliance tensor of fillers in polymer composites
$S^m$	Compliance tensor of matrix in polymer composites
$T_c$	Crystallisation temperature
$T_g$	Glass transition temperature
$T_m$	Melting temperature
$t$	Thickness of dispersed fillers in polymer composites
$t_0$	Thickness of injection moulded tensile sample
$\tan \delta$	Loss tangent in DMTA
$U_x$	Elastic strain applied on the boundaries of OOF models

	in the x direction
$U_y$	Elastic strain applied on the boundaries of OOF models in the y direction
$V$	Representative averaging volume of polymer composites
$V_f$	Volume of fillers in polymer composites
$V_m$	Volume of matrix in polymer composites
$W_f$	Clay weight fraction
$X_c$	Degree of crystallinity
$y$	Measured response value in Taguchi DoE
$\alpha$	Inverse aspect ratio of dispersed fillers in polymer composites
$\alpha, \beta$	Dimensions in the transverse and longitudinal directions for interface in Takayanagi model
$\alpha_0$	Tunable parameter in total energy function
$\varepsilon_0$	Applied strain
$\varepsilon^f$	Infinitesimal strain tensor of fillers in polymer composites
$\varepsilon^m$	Infinitesimal strain tensor of matrix in polymer composites
$\bar{\varepsilon}$	Volume-average strain of polymer composites
$\bar{\varepsilon}_f$	Volume-average strain of fillers in polymer composites
$\bar{\varepsilon}_m$	Volume-average strain of matrix in polymer composites
$\varepsilon(x)$	Strain field in polymer composites
$\varepsilon_{xx}$	Elastic tensile strain in the contour plots of OOF models
$\zeta$	Shape parameter depending on filler geometry and loading direction
$\eta$	$\eta = \frac{\frac{E_f}{E_m} - 1}{\frac{E_f}{E_m} + \zeta}$
$\theta$	Measured diffraction angle
$\lambda$	Wave length of X-ray radiation

$\lambda, \phi$	Dimensions in the transverse and longitudinal directions for dispersed phase in Takayanagi model
$\xi$	$\xi = \phi_f + \frac{E_m}{E_f - E_m} + 3(1 - \phi_f) \left[ \frac{(1 - g)\alpha^2 - \frac{g}{2}}{\alpha^2 - 1} \right]$
$\rho_f$	Density of clay particles
$\rho_m$	Density of the PP matrix
$\sigma$	Resulting axial stress
$\sigma^f$	Total stress tensor of fillers in polymer composites
$\sigma^m$	Total stress tensor of matrix in polymer composites
$\bar{\sigma}$	Volume-average stress of polymer composites
$\bar{\sigma}_f$	Volume-average stress of fillers in polymer composites
$\bar{\sigma}_m$	Volume-average stress of matrix in polymer composites
$\sigma(x)$	Stress field in polymer composites
$\sigma_{xx}$	Uniaxial stress in the contour plots of OOF models
$\tau$	Thickness of interfacial region in Takayanagi model
$\nu_{MMT}$	Poisson's ratio of pure MMT
$\nu_{gallery}$	Poisson's ratio of the interlayer (intragallery) material of clay silicates
$\nu_m$	Poisson's ratio of matrix in polymer composites
$\nu_p$	Poisson's ratio of stacks of layered intercalated clay platelets
$\phi_{MMT}$	Volume fraction of silicate layers in the stack
$\phi_f$	Volume fraction of fillers in polymer composites
$\phi_{gallery}$	Volume fraction of gallery space (i.e. interlayer area)
$\phi_m$	Volume fraction of matrix in polymer composites