

Improvement of Impact Properties of Polypropylene by Modification with Very Low-Density Polyethylene

Eung Soo Kim, Jae Hun Shim,* Ji Yoon Woo, Keun Young Lee, Jin-San Yoon

Department of Polymer Science and Engineering, Inha University, Incheon 402-751, Korea

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ABSTRACT: Very low-density polyethylene (VLDPE) was compounded with polypropylene (PP) to improve its impact strength. VLDPE was modified by grafting 3-(trimethoxysilyl) propyl methacrylate silane (MS) to VLDPE to prepare mVLDPE. PP was melt-mixed either with VLDPE or mVLDPE together with Cloisite®20A (C20A). The composites exhibited a phase-separated morphology, irrespective of whether the VLDPE had been modified with the silane compounds or not. Incorporation of C20A decreased the domain size of the dispersed phases of both PP/VLDPE and PP/mVLDPE blends. The tensile strength and elongation at break of PP/VLDPE and PP/mVLDPE

were improved by the addition of C20A. In contrast, their impact strengths were reduced by the clay. However, the decrease in impact strength was less significant in PP/mVLDPE/C20A than in PP/VLDPE/C20A. The superior mechanical properties of PP/mVLDPE/C20A over PP/VLDPE/C20A were attributed to enhanced interfacial interactions originating from chemical reactions between silane residues on mVLDPE and the silanol groups of C20A. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 3547–3552, 2011

Key words: morphology; blends; strength

INTRODUCTION

Most polymers are seldom miscible with each other because of insufficient interaction between them and the negligible gain in mixing entropy due to their high molecular weights.^{1–3} Therefore, material properties of the blends are usually governed by interfacial interactions and the sizes of the dispersed phases that are determined by processing conditions or additives.^{4,5} When a polymer blend is subjected to melt mixing, the mixing shear breaks up the dispersed phase into smaller domains, deforming it into the final morphology. As the concentration of the dispersed phase increases, the final size of the dispersed phase is determined by the competition between coalescence and breakup.⁶ Flocculation and aggregation are largely governed by the interfacial energy between the polymer matrix and the clay.⁷ The effective introduction of additives can reduce the size of the dispersed phase by lowering interfacial tension. Ray and Bousmina reported that clay modified with an organic compound reduced the domain sizes of the dispersed phase in PC/PMMA blends,⁸ attributable to the enhancement of compatibility by the clay layers. The adsorption energy of

polymer chains to the clay surface may induce the compatibility enhancement in immiscible polymer blends.

Polypropylene (PP) is one of the most widely used commodity plastics. Improvement of its properties and versatility has been extensively explored through the incorporation of clay and toughening agents,^{9–19} with Kawasumi et al.,⁹ Manias et al.,¹⁰ and Maiti et al.¹¹ having studied the fabrication and characterization of PP/clay composites.

This work reports very low-density polyethylene (VLDPE) modification by the grafting of a silane compound. The resulting modified VLDPE (mVLDPE) was then compounded with PP and clay by melt mixing with a corotating twin-screw extruder. The trimethoxy silane groups introduced to the mVLDPE were anticipated to react with silanol groups on the silicate surface of the clay, which would then increase interactions between the clay and the mVLDPE and increase the durability of the PP/mVLDPE/clay composites. The morphologies and mechanical properties of the resulting composites were examined.

EXPERIMENTAL

Materials

The clay was Cloisite®20A (C20A), obtained from Southern Clay Co. (SC). C20A was embedded with 38 wt % of 2M2HT [dimethyl, dehydrogenated

*Present address: CNC Division, Kukdo Chemical, Seoul 153-802, Korea

Correspondence to: J.-S. Yoon (jsyoon@inha.ac.kr).

TABLE I
Composition of the PP/VLDPE Composites

	PP/VLDPE	PP/mVLDPE	PP/VLDPE/C20A	PP/mVLDPE/C20A
PP	85	85	85	85
VLDPE	15	–	15	–
mVLDPE	–	15	–	15
C20A (phr)	–	–	2	2

tallow, quaternary ammonium salt, where HT is hydrogenated tallow (ca. 65% C18; ca. 30% C16; ca. 5% C14)] in the interlayer. 3-(trimethoxysilyl)propyl methacrylate (MS) (Aldrich Chem., MO) was of reagent grade and used without further purification. Homo-PP was obtained from Korea Petrochemical (YUHWA POLYPRO®4017, Korea, melt index: 8.5 g/10 min). VLDPE was purchased from Dow Chemical Company. (DOW™ VLDPE DFDA, MI, melt index: 1.3 g/10 min).

Characterization

Fourier transform infrared (FTIR) spectroscopy was undertaken on an FTIR VERTEX 80V (Bruker Optics, Ettlingen, Germany). FTIR spectra were recorded at wave numbers between 4000 and 40 cm^{-1} . Changes in the interlayer distances of the clay in the composites were assessed by wide-angle X-ray scattering (WAXS; DMAX 2500, Rigaku, Japan) with a Cu K α radiation source operated at 40 kV and 40 mA. The patterns were recorded by monitoring diffraction peaks at $2\theta = 2^\circ\text{--}10^\circ$ with a scanning rate of $2^\circ/\text{min}$. Cross-sectional morphologies of the PP/VLDPE composites were observed by scanning electron microscopy (SEM, Hitachi, S-4300, Japan). Impact tests were performed according to the ASTM D 256 Izod impact method (CEAST, 6545/000, Pianezza, Italy). At least five tests were averaged to determine the notched impact energy. The tensile properties of the composites were measured using a universal testing machine (UTM, Hounsfield, H 10KS-0061, Surrey, UK). The internal micromorphology of the composites was examined by transmission electron microscopy (TEM, Philips, CM200, Netherlands) with an acceleration voltage of 100 kV. Ultrathin sections (<100 nm) were microtomed using a diamond knife (MT-X, Leica, Switzerland) and observed without staining.

Preparation and compounding of the mVLDPE

Neat VLDPE was tumble-mixed with a solution of MS and dicumyl peroxide in a sealed pack. The mixture was immediately introduced into the hopper of the twin-screw extruder. The contents of the silane compound and dicumyl peroxide were fixed at 5 and 0.1 wt %, respectively. VLDPE was modified

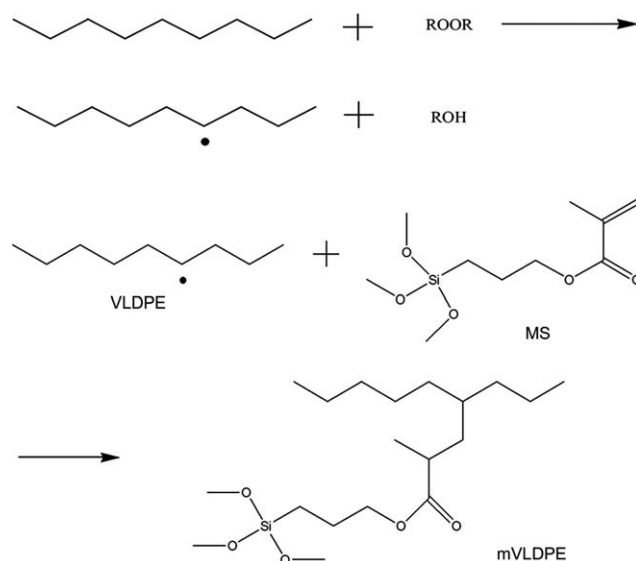
with MS using the twin-screw extruder at 200 rpm at 180–200°C. All ingredients were dried in a vacuum oven at 60°C for 1 day before processing. PP/VLDPE (15 wt %)/clay (2 wt %) composites were prepared by compounding the VLDPEs for 10 min using the twin-screw extruder at 200°C and screw speed of 200 rpm. Table I lists compositions of the composites.

RESULTS AND DISCUSSION

Modification of VLDPE and C20A

VLDPE was modified with the silane compound as per Scheme 1. The radicals produced from dicumyl peroxide could form radicals on the VLDPE chains during melt mixing in the twin extruder. These radicals could then react with the methacrylate groups of MS.

FTIR spectra of neat and MS-modified VLDPE are shown in Figure 1. Peaks corresponding to symmetric C–H stretching vibration, asymmetric C–H stretching and C–H bending due to methyl and methylene groups were clearly observed in the FTIR spectrum of neat VLDPE at 1460, 1376, and 899 cm^{-1} , respectively. The peak at 1194 cm^{-1} in the spectra of mVLDPE was assigned to the CH₃ rocking vibration of methoxysilane groups (Si–O–CH₃).



Scheme 1 Modification of VLDPE with 3-(trimethoxysilyl)propyl methacrylate.

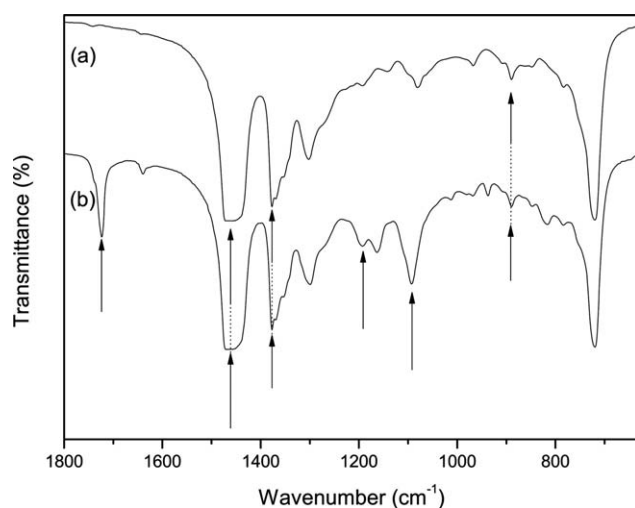


Figure 1 FTIR spectra of (a) VLDPE and (b) mVLDPE.

The peak at 1095 cm^{-1} was more intense in mVLDPE than in neat VLDPE. The strong peak at 1725 cm^{-1} of the mVLDPE spectrum originated from the carbonyl group of the MS residue. The spectra provide clear evidence of the successful incorporation of MS into the VLDPE.

To verify the occurrence of chemical reactions between VLDPE and the methacrylate residues on the surface of C20A, VLDPE/C20A, and mVLDPE/C20A composites were subjected to soxhlet extraction with toluene for 1 week. This would remove from the composites VLDPE and mVLDPE molecules not chemically bound to C20A. Figure 2 shows FTIR spectra of the VLDPE/C20A and mVLDPE/C20A composites after the soxhlet extraction. After the extraction, the C=O peak at $1700\text{--}1740\text{ cm}^{-1}$ was observed in spectra of residue from mVLDPE/

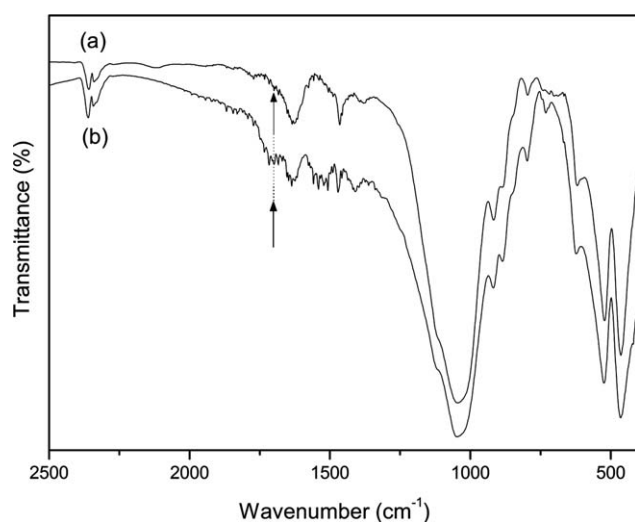


Figure 2 FTIR spectra of (a) VLDPE/C20A and (b) mVLDPE/C20A residues after the soxhlet extraction for 1 week with toluene.

C20A but not from VLDPE/C20A. This indicates that some mVLDPE molecules were chemically bound to C20A, but unmodified VLDPE molecules were not chemically bound to C20A in the neat VLDPE/C20A composite.

Morphology of the composites

Layered, nanometer structures of clays are typically observed by WAXD and TEM. WAXD provides indirect evidence of intercalation of polymer chains into the clay galleries. TEM offers a qualitative understanding of the clay structure through direct visualization.

Figure 3 shows WAXD patterns of C20A, PP/VLDPE/C20A, and PP/mVLDPE/C20A composites in the $2\theta = 2\text{--}10^\circ$ range. The interlayer spacing (d_{001}) of the (001) plane of C20A was 2.58 nm and those of the PP/VLDPE/C20A and PP/mVLDPE/C20A composites were 3.10 nm and 3.23 nm, respectively, indicating that the C20A layers were intercalated with the polymers. The d_{001} spacing of the latter composite was larger than that of the former due to the stronger interaction between the mVLDPE and the C20A layers.

Figure 4 presents typical TEM images of the composites. Figure 4(a) shows regions of individual dispersions of partially delaminated sheets in the

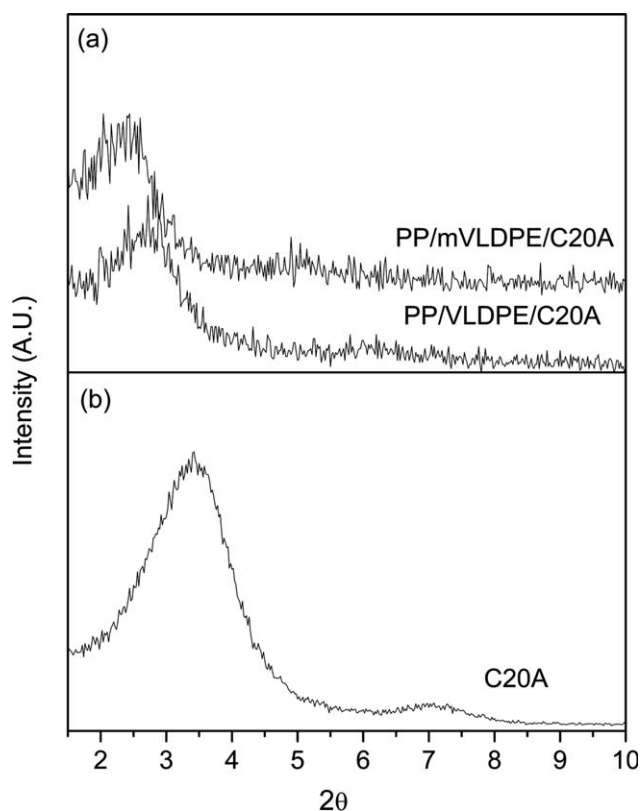


Figure 3 WAXD patterns of (a) PP/neat VLDPE/C20A, PP/mVLDPE/C20A and (b) C20A.

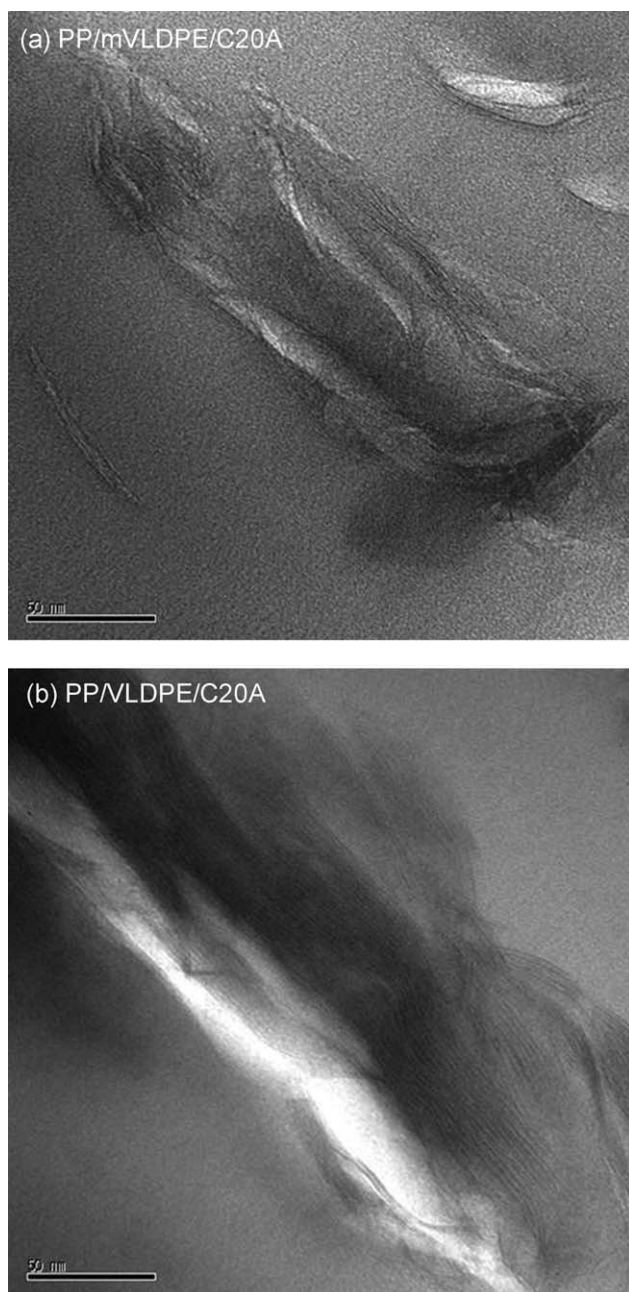


Figure 4 TEM images of the PP/mVLDPE/C20A (a) and PP/VLDPE/C20A (b) nanocomposites.

matrix as well as regions where the regular stacking of the clay sheets was preserved. There were considerably fewer individually dispersed silicate layers in PP/VLDPE/C20A than in PP/mVLDPE/C20A [Fig. 4(b)]. Therefore, the incorporation of mVLDPE effectively aided the dispersion of silicate layers in the composites.

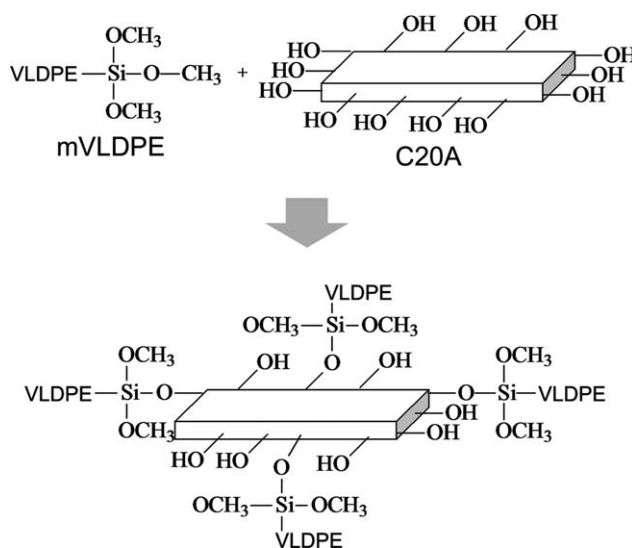
Scheme 2 shows a plausible chemical reaction between mVLDPE and the silicate layers of C20A. Trialkoxysilyl residues react with the silanol groups of C20A, and the chemically bound VLDPE enhances interactions between the two components, aiding

the dispersion of the silicate layers in the polymer blend matrix.

Figure 5 shows cryogenically fractured surfaces of the composites. The VLDPE domains were phase-separated and embedded in the PP matrix in the PP/VLDPE blend. The domains of mVLDPE in PP/mVLDPE were larger than those of VLDPE in PP/VLDPE [Fig. 5(a,b)]. This is because mVLDPE is more hydrophilic than VLDPE due to the hydrophilic MS residue grafted to the mVLDPE. The hydrophobic polymer, PP, would then have less affinity toward mVLDPE than VLDPE. There were more dispersed domains in PP/mVLDPE than in PP/VLDPE. As cryogenic fractures normally propagate through weak points, PP was shown to interact with mVLDPE less strongly than with VLDPE.

The VLDPE domains in PP/VLDPE/C20A were smaller than in PP/VLDPE. The same was also true for the PP/mVLDPE blends, with smaller mVLDPE domains observed in PP/mVLDPE/C20A than in PP/mVLDPE. Mean domain sizes were calculated from SEM images, with results shown in Figure 6. The dispersed domains sizes in PP/VLDPE and PP/mVLDPE were reduced by 60.0 and 77.8%, respectively upon C20A incorporation.

Ray and Bousmina suggested the potential reasons for the different domain size of the dispersed phase as a result of the clay incorporation. Domain sizes may decrease because of the increase in the melt viscosity of the clay-rich phase and the resulting decrease in difference between the shear viscosities of the polymeric components. The second reason is the reduction of the interfacial tension between the components due to the clay incorporation.⁸ The third explanation is related to the anisotropic appearance of clay. The platelet structure of the clay layers may



Scheme 2 Proposed chemical reaction between the silicate layers and mVLDPE.

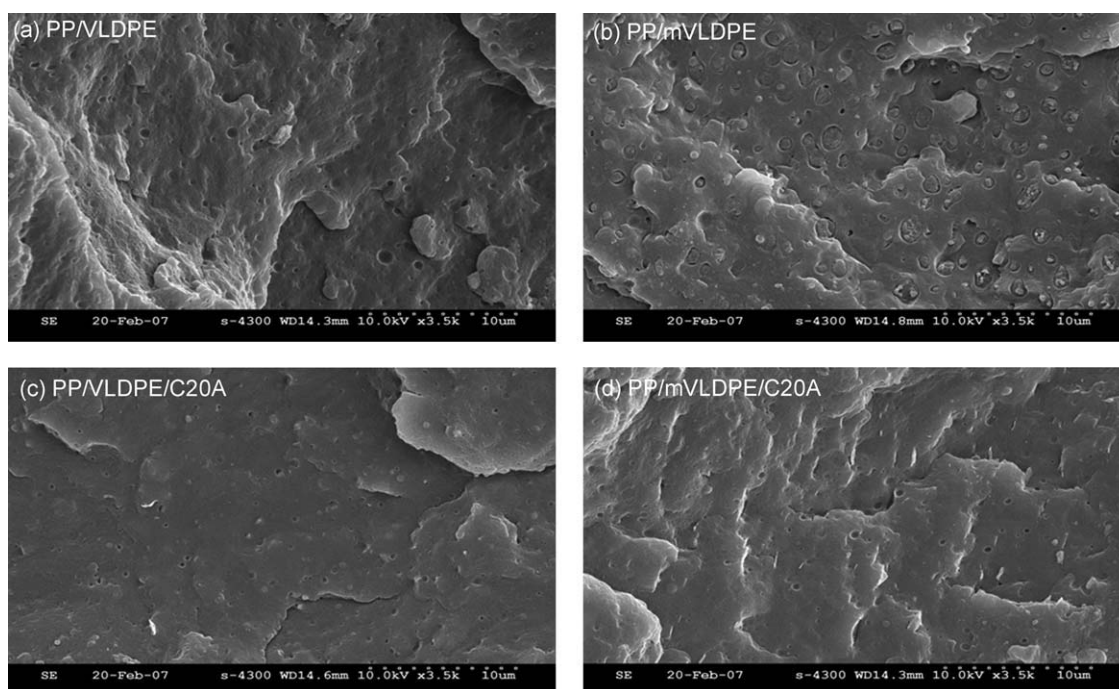


Figure 5 SEM images of the PP/VLDPE (a), PP/mVLDPE (b), PP/VLDPE/C20A (c), and PP/mVLDPE/C20A (d) nanocomposites.

hinder the coalescence of the phases to lead to smaller dispersed phase.

The more pronounced decrease of domain size in PP/mVLDPE/C20A compared with PP/VLDPE/C20A with C20A incorporation may be imputable to the stronger interaction of C20A with mVLDPE than with VLDPE. Chen et al.²⁰ observed that the incorporation of C25A into poly(L-lactide) (PLLA)/poly (butylenes succinate) (PBS) 75/25 blend did not decrease the domain size of the PBS phase. Moreover, the PLLA/PBS/C25A composite was extremely brittle. In contrast, C25A treated with (glycidoxypropyl) trimethoxy silane (C25A-GPS) considerably

decreased the PBS domain size and greatly strengthened the blend. Because the epoxy groups of the GPS residue in C25A-GPS can react with the end groups of the aliphatic polyesters, the increased toughness and decrease in dispersed domain size were attributed to chemical reactions that enhanced interfacial interactions.

Mechanical properties of composites

Table II lists the tensile properties of PP/VLDPE blends and PP/VLDPE/C20A composites. The incorporation of VLDPE decreased the tensile strength and elongation at break of PP considerably. The addition of C20A to the PP/VLDPE blends increased the elongation at break slightly, whereas tensile strength remained almost unchanged. In contrast, incorporation of mVLDPE instead of VLDPE significantly improved the tensile strength and the elongation at break. The improved tensile properties of the PP/mVLDPE/clay composites were attributed to the higher degree of dispersion, attributable to enhanced

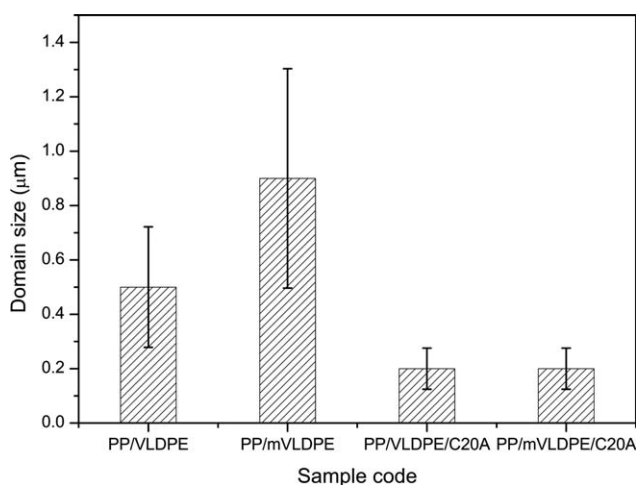


Figure 6 Domain size of the PP/VLDPE, PP/mVLDPE, PP/VLDPE/C20A, and PP/mVLDPE/C20A nanocomposites.

TABLE II
Tensile Properties of PP/VLDPE and PP/VLDPE/Clay

	Tensile strength (MPa)	Elongation at break (%)
PP	36.0 (±0.6)	500.0 (±67)
PP/VLDPE	25.2 (±0.4)	158.6 (±20)
PP/mVLDPE	24.9 (±0.8)	185.6 (±26)
PP/VLDPE/C20A	25.6 (±0.9)	188.8 (±45)
PP/mVLDPE/C20A	27.8 (±1.5)	355.6 (±37)

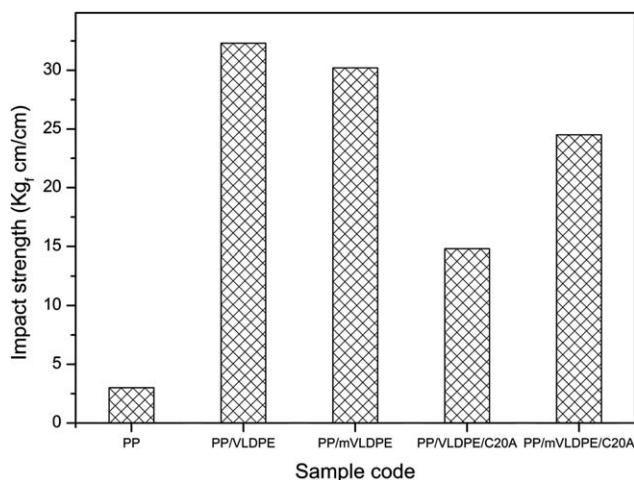


Figure 7 Impact strength of the PP, PP/VLDPE, PP/mVLDPE, PP/VLDPE/C20A, and PP/mVLDPE/C20A composites.

interaction between the components through chemical reactions between the mVLDPE and the silanol groups of C20A.

Figure 7 shows the impact strengths of the composites. PP had an impact strength of 3 kg_f·cm/cm, whereas that of PP/VLDPE blend was higher than 30 kg_f·cm/cm, indicating that VLDPE effectively toughened the PP. However, as shown in Figure 7 and Table II, the impact and tensile strengths of PP/mVLDPE were slightly lower than those of PP/VLDPE, again due to the lower affinity of PP toward mVLDPE than toward VLDPE.

The impact strengths of PP/VLDPE/C20A and PP/mVLDPE/C20A were lower than those of PP/VLDPE and PP/mVLDPE, respectively; with the decrease of impact strength less significant in PP/mVLDPE/C20A than in PP/VLDPE/C20A. Incorporation of C20A into PP/VLDPE and PP/mVLDPE did not discernibly affect tensile strength. The elongation at break of PP/mVLDPE/C20A was higher than those of PP/VLDPE, PP/mVLDPE and PP/VLDPE/C20A (Table II). The increased interfacial interaction due to the chemical reaction of mVLDPE and C20A was likely responsible for the higher impact strength of PP/mVLDPE/C20A compared with that of PP/VLDPE/C20A. Therefore, the PP/mVLDPE/C20A composite could ameliorate the fragile impact strength of PP without any significant sacrifice of tensile properties.

CONCLUSIONS

VLDPE was found to toughen PP, with the PP/VLDPE blend exhibiting about 10 times higher

impact strength than neat PP. However, the tensile strength and elongation at break of PP decreased considerably due to the incorporation of rubbery VLDPE. The dispersed domain size in PP/VLDPE was reduced by 60% as a result of the incorporation of 2 phr C20A. The decrease in domain size of the dispersed phase was more pronounced when VLDPE modified with 3-(trimethoxysilyl) propyl methacrylate silane (mVLDPE) was compounded into the composite instead of neat VLDPE. The impact strength and tensile properties of PP/mVLDPE/C20A were superior to those of PP/VLDPE/C20A. PP/mVLDPE/C20A exhibited 8 times higher impact strength than neat PP while maintaining a tensile strength and an elongation at break similar to those of PP.

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