Wear and Mechanical Properties of Reactive Thermotropic Liquid Crystalline Polymer/Unsaturated Polyester/Glass Fiber Hybrid Composites

Xianbao Yu,[1] Chun Wei,[1,2] Deng Xu,[1] Chihua Lu,[1] Jinhong Yu,[1,2] Shaorong Lu[1,2]

[1]*Department of Material and Chemical Engineering, Guilin University of Technology, Guilin 541004, People's Republic of China*
[2]*Key Laboratory of Nonferrous Materials and New Processing Technology, Ministry of Education, Guilin 541004, People's Republic of China*

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ABSTRACT: To improve the performance of unsaturated polyester (UP) under cold-heat alternate temperature, self-synthesized reactive thermotropic liquid crystalline polymer (TLCP)-methacryloyl copolymer (LCMC), UP, and glass fiber (GF) hybrid composites was prepared by molding technology. The apparent activation energy and crystal behavior analysis of LCMC/UP blends were investigated by Differential scanning calorimetry and X-ray diffraction (XRD), respectively, the results showed that the addition of LCMC can reduce apparent activation energy and accelerate the curing reaction of UP, the XRD analysis indicated that the crystal phase of LCMC still exist in the blends after blending with UP. The effect of LCMC content on the properties of LCMC/UP/GF hybrid composites such as impact strength, bending strength, and ring-on-block wear were also investigated through static mechanical tests and wear tests. The mechanical properties of hybrid composites increased significantly because of the addition of LCMC. The wear tests showed that LCMC can improve the wear resistance of the UP/GF/LCMC hybrid composites even though the content of LCMC was at a relatively low level (5–7.5 wt %). This makes it possible to develop novel kind of UP-based materials with good wear resistance for various applications. The Worn surface was observed by scanning electron microscopy (SEM) and the mechanism for the improvement is discussed in this paper. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3899–3906, 2007

Key words: thermotropic liquid crystalline polymer; unsaturated polyester; hybrid composites; mechanical properties; tribological property

INTRODUCTION

It is well known that thermoplastics/thermoset reinforced with either fiber [glass fiber (GF), carbon fiber, etc.] or fillers have high mechanical properties than the pure matrix, but the reinforcements can worsen processability and shorten the lifetime of equipments.[3,4] The addition of thermotropic liquid crystalline polymer (TLCP) is one possible way to ameliorate the negative factor. This is because of the low viscosity of TLCP attribute to the structure consist of linear semirigid rod-like molecules that can improve the processability of composites system and extend into fibrous structures and orient in the flow direction.[5,6] Many studies related to hybrid composites reinforced with fiber and TLCP, the matrix polymers such as polypropylene (PP),[7–9] high density polyethylene,[10] Polycarbonate (PC),[11] etc. had been done.

The properties of the fiber-matrix interface are of great importance for the macroscopic mechanical properties of composites. With a strong interface between fiber and matrix, higher mechanical property is assured.[12,13] The compatibility of reinforced TLCP and matrix plays an important part in the interfacial adhesion. Considering the compatibility of TLCP and unsaturated polyester (UP), one kind of reactive TLCP with terminal double bond group was synthesized in our laboratory. It was hoped that the double bond on the chains of TLCP might take part in the crosslinking reaction with curing system in the course of procession of hybrid composites.

In the present work, mechanical and tribological properties of TLCP/UP/GF hybrid composites are focused on investigating. The friction and wear tests using ring-block tester were carried out and the wear mechanism were studied by scanning electron microscope (SEM) observations. The wear mechanisms were discussed basing on the obtained results.

Correspondence to: C. Wei (glweichun@glite.edu.cn).
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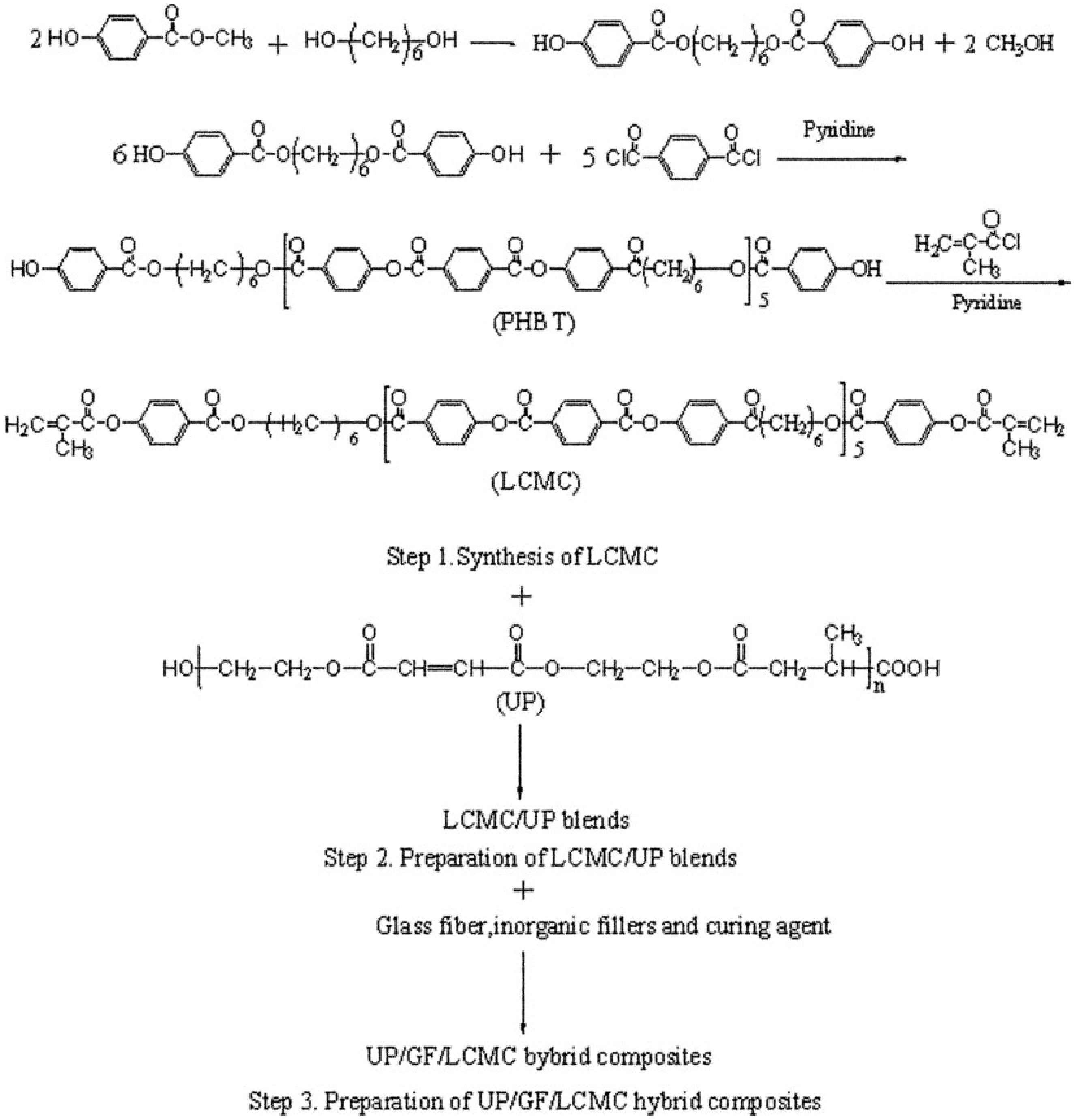
EXPERIMENTAL

Materials and measurements

The TLCP used in this work is one kind reactive polyester TLCP whose liquid crystalline polymer (LCP) phase temperature is 230–262.2°C synthesized by us (The



Scheme 1 Preparation of LCMC/UP/GF hybrid composites.

synthesis route is shown as step 1 in Scheme 1)[14,15]; UP (molecular structure see step 2 in Scheme 1), industrial products; GF (length: 5–6 mm, diameter: 10–13 μm), industrial product, curing agent (blend of styrene and peroxide), calcium carbonate, aluminum hydroxide, and zinc stearic as inorganic fillers are industrial products kindly provided by Guangdong Fuxing Materials Plant, China.

Differential scanning calorimetry (DSC) was carried out using NETZSCH DSC204 at a heating rate of 5, 10, 15, and 20 K/min under the protection of nitrogen atmosphere for determining the curing reaction. The quantity of LCMC/UP/curing agent blend powder was about 10 mg. The crystal behavior of UP, LCMC, and UP/LCMC blend was analyzed by X-ray diffractory (XRD) (model: Panalytic X′Pert Pro, Netherlands). The impact strength was measured on a tester of model JC-25, which is with no notch in the specimen. Impacting rate and impacting energy of tests are 3.5 m/s and 1 J, the dimension of specimen is 120 $\times$ 10 $\times$ 4 mm^3. The bending strength and bending modulus were examined on an electron universal testing machine (model: SHIMADZU AG-20I, Japan) at 25, 50,100,150, and 200°C, the test rate is 2 mm/min, the span is 60 mm and the specimen dimension is 120 × 10 ×4 mm^3. All the presented results are average of five specimens. The creep and stress relaxation tests were measured on an electron universal testing machine (model: SHIMADZU AG-20I, Japan), the measurement temperature is 150°C, the measurement time 5 h, and the dimension of specimen is 120 × 10 × 4 mm^3. The morphologies of impacting fracture surfaces were observed in a SEM (Model: JEOL JSM-6380 LV, Japan), the fractures were coated with a thin layer of carbon. The friction and wear tests were conducted on a ring-block tester (M-2000). The experimental parameters were shown as following: rotation speed: 180 r/min, load: 196 N, test time: 40 min, and all tests were carried out in dry friction state and at room temperature. All tests were carried out in dry friction state and room temperature. The friction coefficient,μ, was calculated by the formula: $\mu = M/(rF)$. Where M is moment of friction, reading on the tester, r is radius of ring, the value is 2 cm, F is test load. The abrasion characteristic was assessed by the wear mass, W, which was calculated by the following relationship $W = W_1 - W_2$, where W_1 and W_2 are respectively, the weight of a sample before and after its test.

Preparation of LCMC/UP/GF hybrid composites and specimens

LCMC/UP blends with different LCMC ratio (2.5, 5, 7.5, and 10 wt %) were prepared by melting mixed technology, firstly. LCMC/UP blends, GF, curing agent, and inorganic fillers were simultaneously introduced into the Mixing Plastic Mill for mixing. The preparation route was shown as Scheme 1. The smashed mixture was put into mold for compression-molding at a condition of pressure (10 MPa), temperature (160°C), and time (4 min) for consequent test.

RESULTS AND DISCUSSION

Curing kinetic of UP/LCMC blends

DSC, which measures the heat flow of the sample as a function of temperature, has extensively used to study the curing kinetics of various thermosetting polymers,[16,17] the reactive process can be described by the activation energy.

The Kissinger evaluation method induced from the Borchardt-Daniels equation[18] and Arrhenius formula with the basic assumption of DSC kinetic measurement is that the heat flow is proportional to the change in the conversion. is performed to determine the activation energy prior to identifying other kinetic parameters.[19] This method shows that the relationship between DSC peak temperature (T_p) and the heating rate ϕ is of the following form: $\ln(\phi/T_p^2) = \ln(AR/E_a - E_a/RT_p)$, where R is universal gas constant, T_p is DSC peak temperature, E_a is activation energy and A is pre-exponential factor. A plot of $\ln(\phi/T_p^2)$ versus $1/T_\mathrm{p}$ should be linear with slope $= -E_a/R$. The plots of $\ln(\phi/T_p^2)$ versus $1000/T_p$ are shown in Figure 1 and good linearity is obtained. The kinetic data derived from the plots are given in Table I.

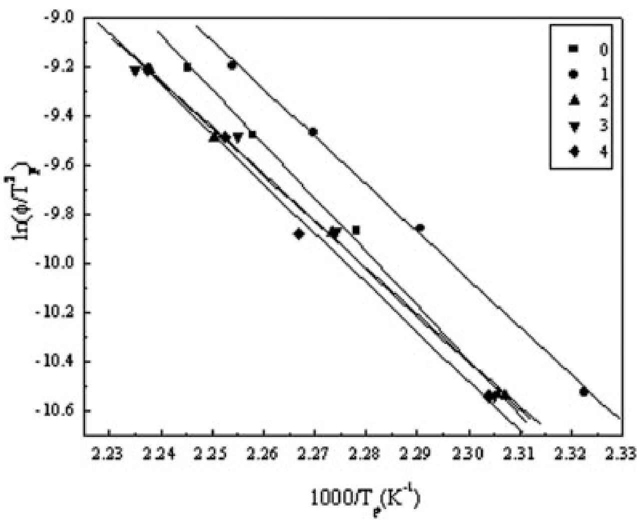


Figure 1 Plots of ln (ϕ/T_p^2) versus $1000/T_p$ for curing systems.

It can be seen from Table I that the curing activity of UP/LCMC/curing agent systems enhanced for the apparent activation energy of curing reaction decrease from 183.6 kJ/mol for the pure UP system to 150–170 kJ/mol for UP/LCMC systems. According to Lu et al.'s research,[20] these indicated that LCMC can play a role of decreasing activation energy and accelerating curing reaction, this result may be correlative with double bond on the end group of LCMC. The curing reaction mechanism of UP/LCMC/curing agent system accelerated attribute to the reaction between double bond group of LCMC and double bond group of UP under the function of curing agent, that can accelerate curing reaction.

XRD analysis of UP/LCMC blends

XRD analysis for pure UP and UP/LCMC blend are given in Figure 2. It can be seen that both LCMC/UP blend and LCMC have one group of low intensity diffraction peaks locate at the range of 19°–30°of 2θ angle, while neat UP have a broad hump peak. The y-axis values of two main peaks of LCMC are 147 cps, 81.4 cps at 19.5° and 23.3°of 2θ, the values of LCMC/UP blend are 120 cps, 76.6 cps at 19.4° and 23.2°of 2θ. These results indicated that the crystal parts of LCMC keep well in the UP/LCMC blends after blending with UP, the liquid crystal textile structure keep well in the blends, too.

TABLE I
Kinetic Data of UP/LCMC Curing Systems Determined by Kissinger Method

No.	Sample	E_a (kJ/mol)	ln A	Correction coefficient, R
0	UP/St = 100/25	183.6	50.29	−0.99863
1	UP/St/LCMC = 100/25/5	161.3	44.45	−0.99912
2	UP/St/LCMC = 100/25/10	156.7	42.90	−0.99928
3	UP/St/LCMC = 100/25/15	159.7	43.64	−0.99554
4	UP/St/LCMC = 100/25/20	167.6	45.80	−0.99682

Mechanical properties

Figure 3 shows the effect of LCMC content on impact resistance of LCMC/UP/GF composites. It can be seen that the impact strength increased at first and then decreased then increased with the increase of LCMC content. It reached the maximum when the LCMC content was about 5%, the impact strength of composite containing 5% LCMC (5.7 kJ/m^2), 114.3% higher than that of composites without LCMC. Since impact strength reflects the energy consumed before fracture, the results shown in Figure 3 demonstrated that GF can obviously induce plastic deformation of the surrounding matrix polymer to a certain extent under the condition of high strain rate after the introduction of LCMC. That indicated that the crosslinking reaction between UP and LCMC under the function of curing agent made the interaction between matrix and GF improved. The impact strength of composites decrease when LCMC content is more than 5% because of the compatibility of LCMC and UP become worse results in the interaction between matrix and GF become weaker.

The bending strengths and bending moduli of composites at different temperatures are shown as Figure 4, and the concrete values are listed in Table II. From Figure 4, it may be seen that both bending strength and modulus at anyone temperature increase with LCMC content increasing. That means that the interaction between GF/UP matrix is so strong that the GF plays a role of cooperative reinforcement. The results of experiment indicated that when the LCMC content is 5%, the bending strength (76.39 MPa) at 25°C, (66.29 MPa) at 50°C, (46.59 MPa) at 100°C, (31.66 MPa) at 150°C, (17.42 MPa) at 200°C, are 28.1, 26.1, 25.1, 55.3, and 50.2% higher than that of composites without LCMC (59.65 MPa) at 25°C, (52.56 MPa) at 50°C, (37.25 MPa) at 100°C, (20.38 MPa) at 150°C, (11.60 MPa) at 200°C, respectively. The bending modulus of composites containing 5%LCMC (9.79 GPa) at 25°C, (9.17 GPa) at 50°C, (6.35 GPa) at 100°C, (2.81 GPa) at 150°C, (1.75 GPa) at 200°C, are 14.0, 10.1, 18.5, 47.9, and 36.7% higher than that of composites have no LCMC(8.59 GPa) at 25°C, (8.33 GPa) at 50°C, (5.36 GPa) at 100°C, (1.90 GPa) at 150°C, and (1.28 GPa) at 200°C, respectively. These results indicated that the addition of LCMC is able to improve the strength and tough of composites at high temperature more effectively. The bending strength and bending muduli increase and then decrease with increase of LCMC; the values reach to the maximum when LCMC content is 5%. The bending strength and bending muduli value decreases with the increase in test temperature.

Figure 5 shows the effect of LCMC content on the creep behavior of hybrid composites, the measurement conditions as following: load: 0.03 KN, creep time 5 h, measurement temperature: 150°C. From Figure 5, it

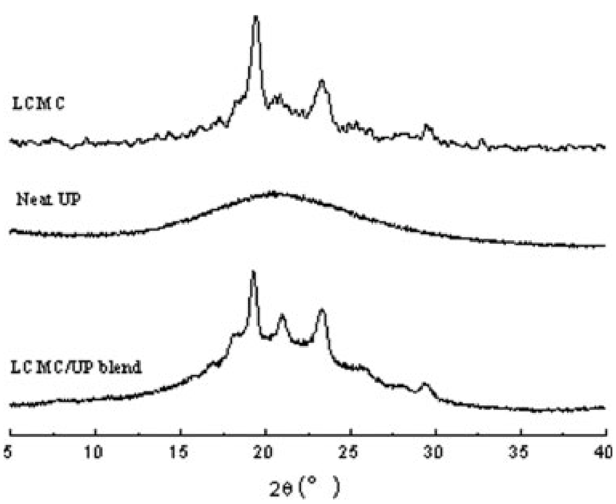


Figure 2 X-ray diffraction patterns of LCMC, neat UP, and UP/LCMC blend.

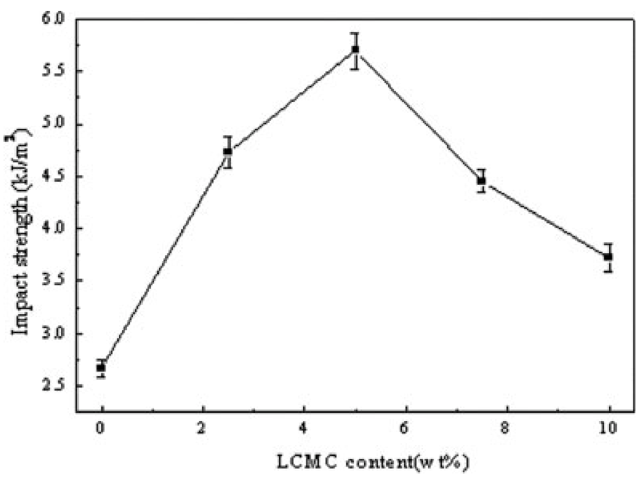


Figure 3 The relation between LCMC content and impact strengths.

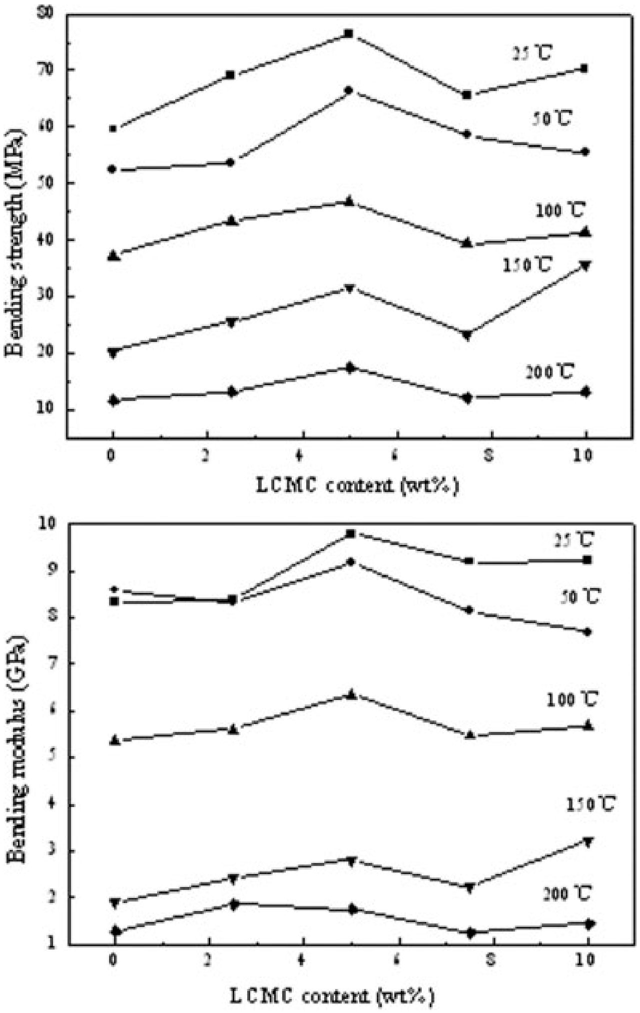


Figure 4 Effect LCMC content on bending strength and modulus of hybrid composites.

can be seen that the final creep displacement of composites decrease with the increase of LCMC content, but when the content of LCMC was 10%, the final creep displacement of composite is slightly smaller than that of composite with 5% LCMC. The results attribute to the introduction of LCMC makes the number of crosslinked points in composites increase, the chain segment length during crosslinked points decrease, so the stretches of crimped chain segments was limited, leading to the deformation of composites become smaller.

Stress relaxation behaviors of hybrid composites are shown as Figure 6. The test conditions as following: Temperature, 150; displacement, 0.6 mm; time, 5 h. From Figure 6, it can be found that the increase of LCMC content makes the stress relaxation of composites increase. It due to the crosslinked point's increase with the increase of LCMC content, the deformation of composites was difficult to occur. The result agrees well with the result of creep behavior, it also indicated also that deformation resistance and aging resistance of hybrid composites with LCMC are superior to the composite without LCMC, due to the function of crunode reinforcement of LCP.

Friction and wear performance

Figure 7 line1 shows the effect of LCMC content on the wear loss of LCMC/UP/GF hybrid composites. It can be seen that the wear loss decreases with the increasing LCMC content.

It is lower by 49% than that of hybrid composites without LCMC when LCMC content is 7.5%. This phenomenon indicates that the improvement of wear resistance of UP attribute two sides, on the one hand crosslinking reaction with LCMC are able to increase the interfacial interaction between GF and matrix, on the other hand, the matrix enhancement acts as a result of LCP self-reinforcement. The relationship between the friction coefficient and LCMC content is shown in Figure 7 line 2, the trend is almost the same with the trend of the wear loss to the LCMC content. This can be explained by the following reasons. (1) With the incorporation of LCMC into UP matrix, the propagation of the cracks into UP matrix was hindered to a certain degree by the GF. (2) The crosslinking reaction make the GF/matrix interfacial adhesion become stronger, hence the wear resistance was improved.

Morphology

The SEM morphology of worn surface of composites without LCMC and composites containing 7.5% LCMC are compared in Figure 7. From Figure 8(a) it can be seen that severe wear associated with the detachment of bulk material and left some holes on

TABLE II
Bending Strengths and Moduli of Composites with Different LCMC Content at Different Temperatures

	Bending strengths (MPa)					Bending modulus (GPa)				
Sample	25°C	50°C	100°C	150°C	200°C	25°C	50°C	100°C	150°C	200°C
0% LCMC	59.65	52.56	37.25	20.38	11.60	8.59	8.33	5.36	1.90	1.28
2.5% LCMC	69.12	53.73	43.40	25.53	13.14	8.31	8.40	5.61	2.41	1.87
5.0% LCMC	76.39	66.29	46.59	31.66	17.42	9.79	9.17	6.35	2.81	1.75
7.5% LCMC	65.57	58.47	39.33	23.42	12.09	8.14	9.19	5.47	2.23	1.26
10% LCMC	70.29	55.46	41.29	35.71	13.17	7.69	9.22	5.69	3.24	1.44

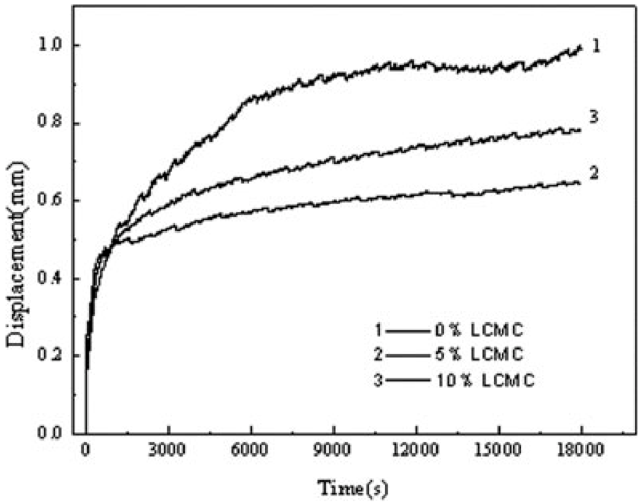


Figure 5 Effect of LCMC content on creep property of hybrid composites.

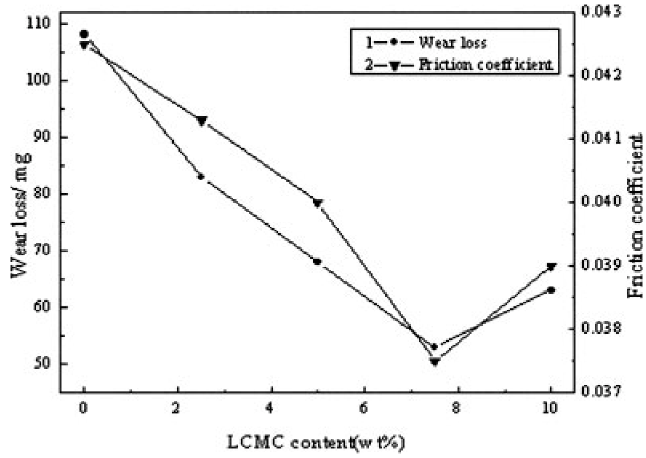


Figure 7 Effect of LCMC content on friction coefficient and wear loss.

the frictional surface. This phenomenon reflects that adhesive wear has been regarded as a main wear mechanism.

In the case of incorporating LCMC, the appearance is completely different and become rather smooth Figure 8(b). It can be concluded that the adhesive wear of composites without LCMC is replaced by fatigue wear when LCMC are introduced. So a conclusion can be draw from the above, that the friction and wear performance of UP/GF hybrid composites have been greatly improved with the addition of LCMC.

Figure 9 shows the SEM micrographs of impacting fracture surfaces of hybrid composites containing different TLCP contents. The bare appearance of GF in Figure 9(a) suggested a very weak bonding between fiber and matrix. The adhesion between GF and matrix is markedly better as shown in Figure 9(b). The fiber/matrix adhesion became even stronger in case of com-

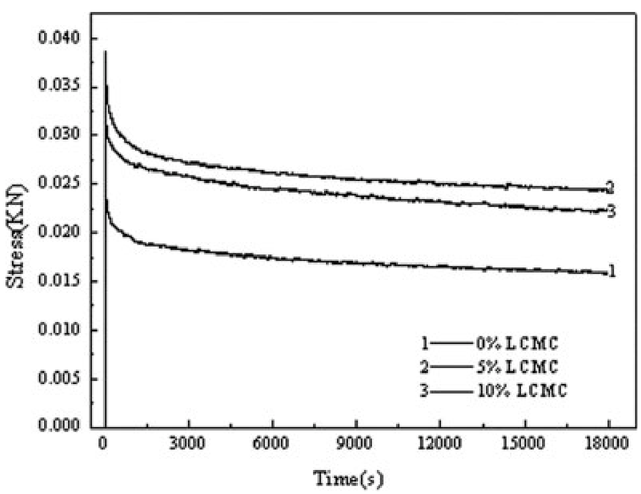


Figure 6 Effect of LCMC content on stress relaxation property of hybrid composites.

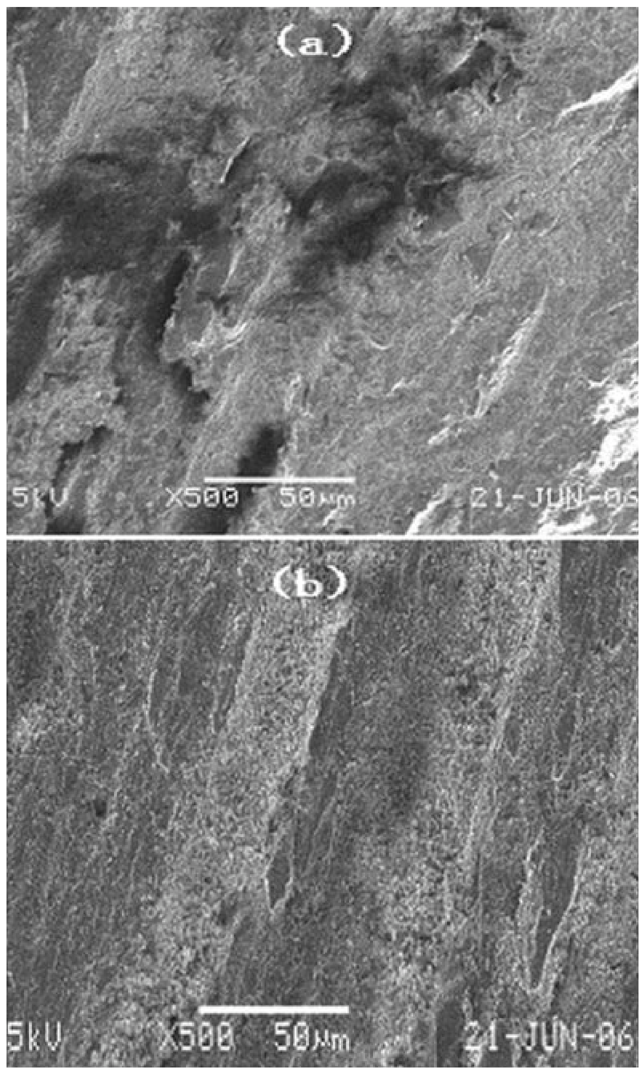


Figure 8 SEM micrographs of the worn surface of hybrid composites (a) 0%LCMC, (b) 7.5%LCMC.

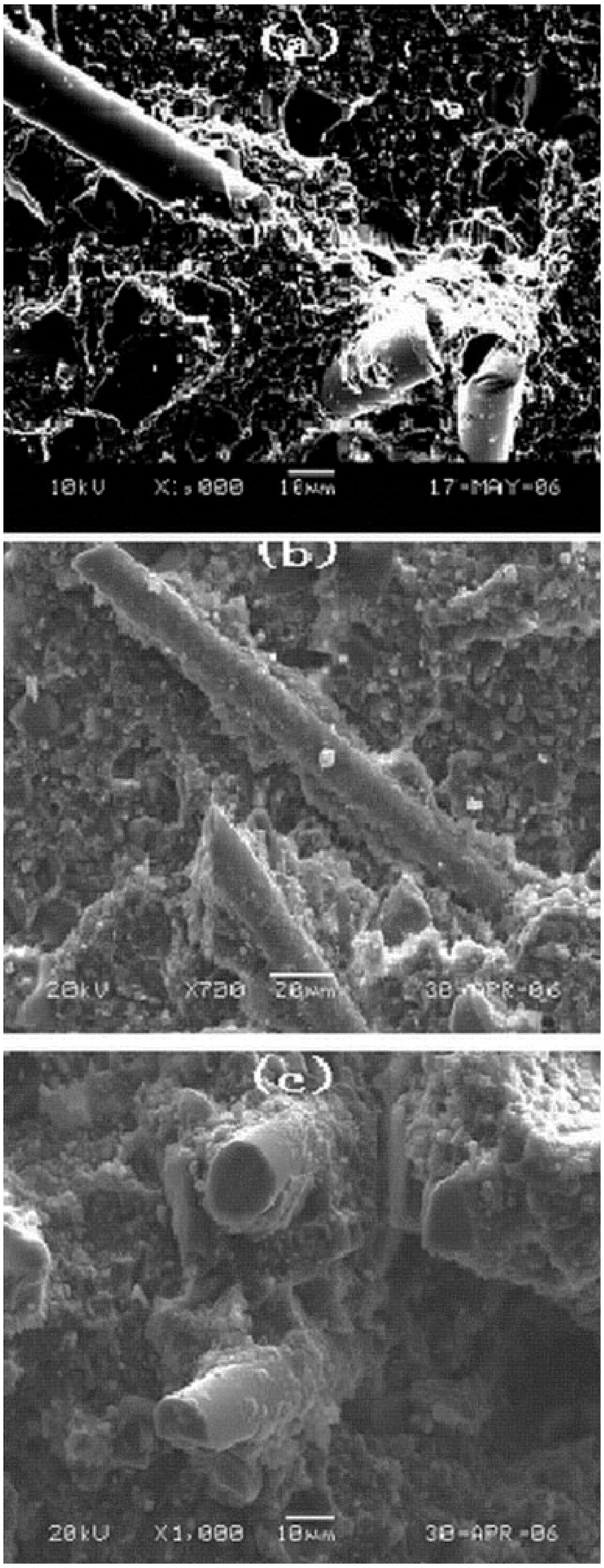


Figure 9 SEM pictures of impacting fracture surface of hybrid composites (a) 0%LCMC, (b) 2.5% LCMC, (c) 5% LCMC.

posites containing 5% LCMC as shown in Figure 9(c). The correlative researches have been reported.[4,21,22] It is very useful to compare the failure mode of the matrix in the related reinforced composites. The matrix was brittle failed without the presence of LCMC; a far tougher matrix failure can be noticed in the composites containing 5% LCMC. This is because of the possible reaction between UP matrix and LCMC under the function of curing agent, which makes the matrix/fiber interfacial adhesion increase, then makes the toughness and fracture energy of hybrid composites increase.

CONCLUSIONS

LCMC can significantly improve mechanical properties of the LCMC/UP/GF hybrid composites, which contains an optimum amount of LCMC (5 wt %). Curing kinetic results indicated that LCMC can play a role of decreasing activation energy of curing reaction and accelerating curing reaction. The impact strength is almost 1.2 times as much as that of composites without LCMC. The bending strength and modulus are higher than that of composites without LCMC, especially at the high temperature region. The mechanism for the improvement is attributed to the increase of interfacial strength between GF and matrix caused by the crosslinking reaction between UP and LCMC and to the self-reinforcement of LCMC. When the composites are subjected to an impact test, GF can induce to crack propagation and resulted in the performance of hybrid composites improved. It proves to be an effective way in lowering friction coefficient and wear loss. The wear and friction performance of hybrid composites have been greatly improved with the addition of LCMC.

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