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Physical and Mechanical Properties of Cold Rolled PP/LCP Blends

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SUMMARY: The relation of the microstructure, the dynamic viscoelasticity, the molecule orientation and the micro hardness of the PP/LCP blends to the tensile property have been examined by rolling tests. The result shows that: (1)With the increase in the rolling ratio, □ the LCP phase of reinforcement is delayed and the distribution is improved. □The specimens is softened as the E' and the section hardness decrease. □The distribution of hardness and the molecule orientation in all specimen sections become more uniform. (2) The rolling process has improved the material property of brittle blends and their ductile property rises drastically. Especially, under the high rolling ratios such as 60% the strength and the stretch of the material have been improves greatly. (3) Thus, it is considered that the rolling processing may be an effective way to improve the microstructure, phases interface bond strength and ductile property of composite material.

KEYWORDS : High Polymer Materials, Composite Materials, Structural Analysis, Tensile Properties, Visco Elasticity, Rolling process, Molecular Orientation, Hardness

1. INTRODUCTION

From the viewpoint of the circumstance, resource protections and rubbish regeneration, it is important that designing a substitution material to the inorganic fiber reinforced plastics composite materials. Because the thermal plasticity polymer blends is easy to recycle, the improvement of the material performance is expected[1-8]. However, when the reinforcement material with hard and high strength is added to the soft matrix in the different polymer blend, the joining strength of the phase interface of blend materials influence to the improvement, and specially in decreasing in ductility. On the other hand, rolling processing could improve the property of the thermal plasticity high polymer materials that reported the probability of the improvement of the deep drawing machining[9-15]. Through Authors researched[14-16] on the injection molding by rolling machining, it was ascertained that change of inner microstructure, improvement of non-uniform structure and mechanical property in the each fracture layer, and the increase in the material strength and ductility. Therefore, it is considered that the rolling machining could improve the inner microstructure, interphase and material ductility of the blend materials.

The PP/LCP polymer blend with the excellent recycling characteristics is used to this study. The microstructure and tensile strength of this material by 10 times recycle were the same as that of the bar gin material[15-17]. The weight rate of PP/LCP=80/20 was fabricated to the blend material by injection molding in this study. The relationship of tensile and the material inner microstructure, dynamic Visco elasticity, the specimen fracture surface, the change of hard distribution by rolling was investigated.

2. EXPERIMENTAL

2.1 Materials

The pellets of PP(Asahi Chemical Co., M1700) and LCP(Unitika, Rodrun LC3000) were commercially available. They were mixed to a weight ratio of PP/LCP=80/20, and then extruded by a single-screw extruder. The blended pellets were injection molded to the dumbbell shaped specimens (JIS 1). The forming was conducted under a mold temperature at 230^{o}C and an injection rate of 22cm^{3}/sec. The gauge region, in which the length of 90mm, width of 10mm and thickness of 2mm, was cut from dumbbell-shaped specimen for the rolling. The forming condition was conducted under a cylinder nozzle temperature at 200^{o}C, a mold temperature at 40^{o}C, the injection rate of 22cm^{3}/sec.

2.2 Rolling procedure

The rolling mill of ϕ50-2 step(DDR) (OONO) was used. The direction of rolling out was the same as flow direction in injection molding. An increment in the distance between two rollers was adjusted in 100μm for one cycle in the rolling process, and the thickness 2mm was rolled to the fixed rolling reduction. The rolling condition was made in air at 20^{o}C, and rolling rate of 3m/min. The rolling ratio (ξ) was given in next Equation, indicating a reduce ratio of plate thickness.

$$\xi = \frac{H_0 - H}{H_0}$$

(H_0: Initial plate thickness, H: The plate thickness after rolling)

2.3 Microstructure observation

In order to researching the microstructure(different distribution of PP and LCP in the skin layer and core) by injection modeled specimens, the core was cut to thin pieces 10μm thick under a vertical section to the flow direction by RotationsMikrotom(Microm, HM325). Then the microstructure was observed by an optical microscope(Zeiss, Axioplan). The fracture surfaces obtained by tensile testing were observed by a scanning electron microscope(SEM, ZEISS Co.).

2.4 The dynamic viscoelasticity

The dynamic viscoelastic factors, the storage modulus E' and the loss tangent tanδ, were measured by using a dynamic viscoelastic meter (Orientec Co., Fatigueron VFA-1KNA). The tests were conducted under a fixed displacement of 25μm at frequencies of 1 and 10Hz and at temperatures ranging from -150 to 170^{o}C. The chuck distance of 40mm and the position amplify of 25μm were designed. Since different rolling ratios produce different thickness of specimen, the increasing temperature rate was set to low value of 1^{o}C/min for uniformly heating the specimens. This evaluation temperature velocity was done the same result for measuring the specimens of 5 and 1mm thickness.

2.5 The measurement of Hardness and orientation

The diamond super microhardness equipment was used to measure the specimen fracture surface hardness distribution in the skin, intermediate and core layer. The specimens were cut from the test pieces along to the flow direction and in the center of width. The hardness test in the specimen fracture surface was done to the load of 0.098N, load speed of 2.65×10^{-3}N/sec, holding time of 5sec at room temperature. The hardness was shown by $DH=\alpha P/D^2$[here: P is a load, D is a indentation depth, α=37.838(triangle indenter of 115^{o})].

In order to research the orientation distribution change in the rolling specimen fracture surface, the thin piece of 20μm was cut from the specimen center along to the flow direction by rotary micro dome. The orientation test in the specimen fracture surface was done by micro Fourier infrared ray photometer. The test was three cycle from the specimen surface to center and range section of 100×40μm. The optical strength ratio(double color ratio) was evaluated on the along to the absorption spectra direction and uprightness direction of the absorption spectra. For understanding the change in molecular orientation by rolling[18], the thin pieces of 20μm thickness were again cut in the rolling direction by the microtome. The molecular orientation was analyzed by a Fourier transformed infra-red spectrometer (FT-IR) with a microscope(Japan Spectroscopic Co., FTIR 8900μ). The measurement were done for a small area of $100\times50\mu m^2$ from surface to core regions under transmission mode. The absorption intensity of PP at the peaks of $998cm^{-1}$ and $899cm^{-1}$ was measured in the directions parallel($A_{//}$) and perpendicular($A_{\perp}$) to the flow direction. A dichroic ratio R ($R=A_{//}/A_{\perp}$) was used for evaluating the molecular orientation. The absorption at $1602cm^{-1}$ due to vibration of benzene ring was also measured for a LCP, and R was obtained.

2.6 Tensile test

A single tensile was done by computer control system autograph(Shimadzu, AG-50KN-EG). The test condition was conducted under tensile speed of 5mm/min at $30\pm1^{o}C$. Because the rolling materials produced the □□□ so that it could be grown much, the initial length of the parallel part was used for the strain calculation formula. This reason is that there is a few change of on the tensile load after the necking formed. Therefore, we could not think of the
influence of the curvature part.

3. RESULTS AND DISCUSSION

3.1 Microstructure and dynamic viscoelastic properties

The optical micrographs of blended specimens rolled to the ratios of 0 and 60% were shown in Fig.1. The observed black figure was the Matrix PP phase and the observed white figure was the LCP phase. Because the PP phase of was obviously distinguished from LCP phase of the reinforcement phase along to the injection molding direction, it is a typical non-solution system material. All the structures are broadly divided into three layers, i.e., skin, intermediate and core layers[16,19] when the resin at high temperature contacted to the model at low temperature so that the injection molding specimen surface cooled quickly. The fine and dispersion LCP phase distributed in the skin and intermediate layer(from surface about 400μm) in the blend specimen, but it would be coarsen in the core.

While that blend was rolled along to the injection direction, the increase in the rolling ratio resulted in that the LCP phase became more length. Therefore, LCP phase formed a long fiber. Specially in the rolling ratio of 60%, because LCP became a spit dumpling-shaped, LCP phase would pull out the PP phase while the external force acted to the specimen. Thus, the material mechanical strength would increase.

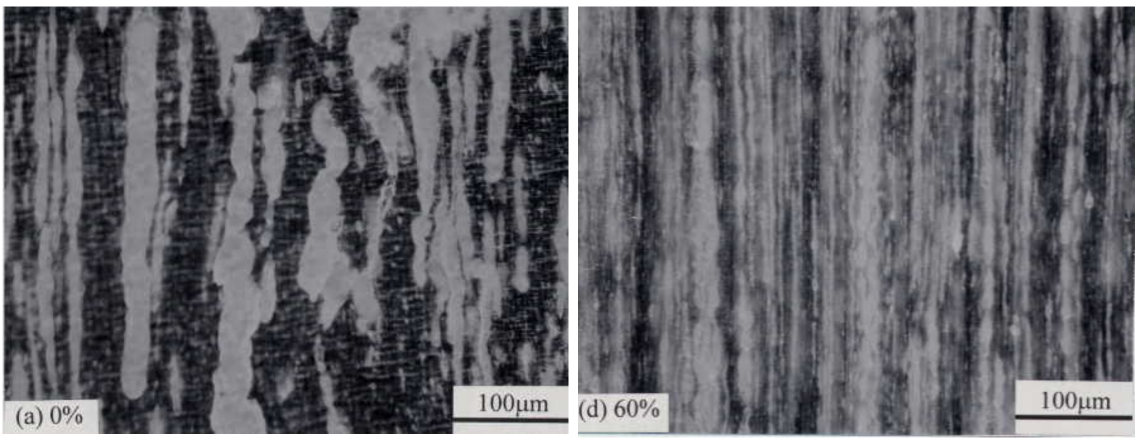

Fig.1 Polarized optical micrograph of cross section (core)

3.2 Dynamic Viscoelasticity Property

The effect of rolling on the changes of dynamic viscoelastic properties is shown in Fig.2 In order to indicating the values of tanδ and E' in the frequency of 1Hz, the temperature range were designed from –60 to 70°C. Comparing with the data of non-rolling material simple PP and LCP, the blend specimen on the change trend of tanδ and E' also showed non-rolling property as the simple PP and LCP at the temperature range. Always the middle of both simple substance materials like characteristics were shown, and it is understood that they are typical non-solution bi-phase system composite.

The material was determined to be soften on the rolling machining based on showing the decrease in E' and the increase in tanδ. This behavior remains until the rolling ratio of 40%, but it would reverse increase on the ratio of 60%. The change of tanδ for the rolling specimen of 60% became the high level at blow the glass transformation temperature of PP(-10°C), however, the rolling change would be not obviously for others non-rolling materials. But the tanδ was a simple increase companion to the increase in the rolling ratio at above –10°C, specially in it became the high level compared to the simple PP also.

According to above results the material mechanical property was influenced by rolling due to the change of the dynamic Visco-elasticity of the blend material. The decline of E' and rise of tanδ by rolling made the recycling of the low ductility blend. Because the large tanδ was a parameter that proved the capacity from the energy of the external force load to the thermal energy, it is considered that the material appeared the ductile trend.

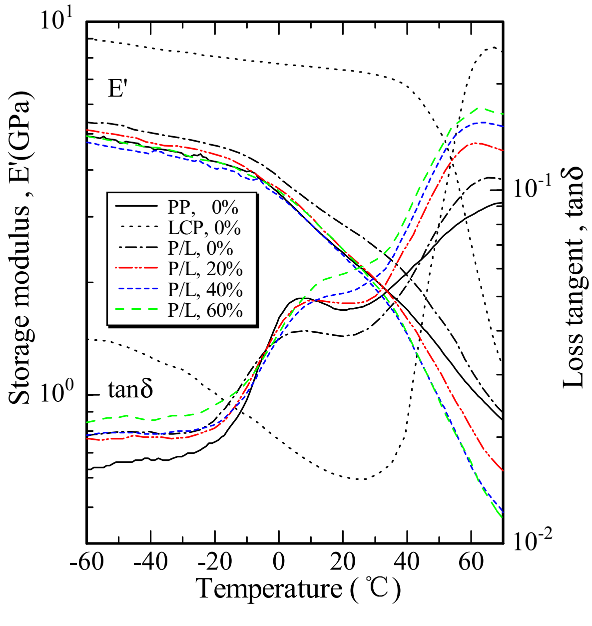

Fig.2 Effect of rolling on the Dynamic viscoelasticity

3.3 The molecular orientation

The molecular orientation distribution change of PP and LCP phase are shown in Fig.3(a)(b). The Fig. shows the sample surface in left and the center in right on the horizontal axis. Every layer(skin, intermediate, core) by each rolling ratio specimen will show a relative position in the horizontal axis. In general, the molecular orientation distributions would be increased by the increase in rolling ratio. The specimen would form the three different structures, i.e. skin, intermediate and core, by injection molding. However, the rolling may not increase the orientation on each layer.

First, the orientation change of the matrix PP phase was the same as that of the non-rolling simple PP phase by injection molding. Second, the skin orientation was low due to cooling quickly based on the structure forming mechanism for the injection-molding specimen. Because the intermediate layer flowed fast, it was acted by the strong shearing so that its orientation became the highest. Because the core soldiered at last, the crystallization would increase so that the orientation declined. Specially in the orientation in the center of core was the lowest. When rolling machining increased the rolling ratio, the orientation of core would be gradually increased. But the intermediate orientation, of which the rolling ratios are lower than 40%, was low because the residual stress was relaxed in the injection molding process. However, because there was different in between the orientation of the intermediate layer and core(about 74%) companion with decrease in increasing rolling ratio, the low orientation of the intermediate layer on the rolling ration of 60% would increase again due to re-orientation. When the rolling ratio became 60%, the different would decrease about 26%. Therefore, it resulted in increasing the surface orientation. The rolling process thus can homogenize the structure and the properties allover the specimen.

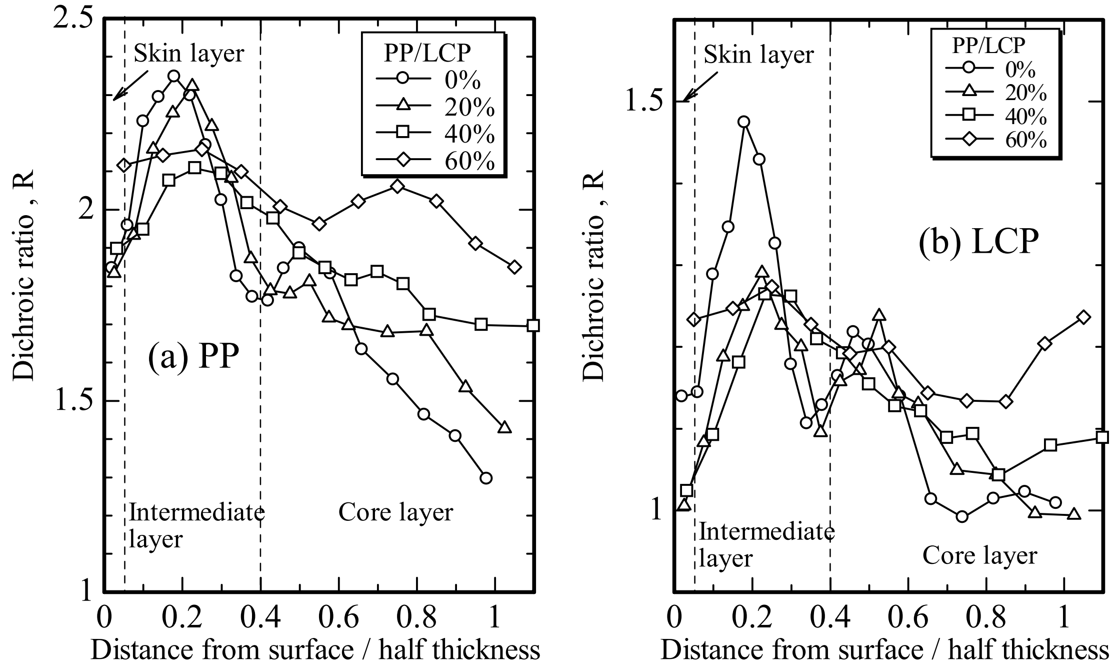

Fig.3 Distribution of molecular orientation in cross section

Moreover, companion to the orientation change of LCP phase in blend material by rolling, the core orientation increased companion to the increase in rolling ratio, it was considered that the LCP phase was enlarged. The orientation of the intermediate layer with the rolling ratio below 40% was low, however, it would increase on the rolling ratio of 60%. In the case of the rolling ratio of 20%, the orientation of the intermediate layer was lower than that of the matrix PP due to a little content of LCP phase. The joining between PP and LCP phase was low and a little content of LCP phase could not produce a strong shrinkage. Therefore, it considers that we can't expected to improve the material strength in the case of the low rolling ratio.

3.4 The microhardness of the fracture surface

The microhardness distributions on the surface of cross section of specimen rolled to various ratios are shown in Fig.4. The hardness distribution of the simple PP and LCP are used for comparing to the experimental data. The blend hardness with the addition of LCP was lower than that of a simple PP in the intermediate. It was the same as the hardness distribution of LCP phase. In other words, the hardness distribution was slowly to decline from the intermediate layer to core. Therefore, the stress concentration in the intermediate layer of a simple PP would be improved under the external force applied, and the original occurrence of the crack was reduced.

We understood that the hardness of every fracture layer was low due to specimen soften on the rolling. In the case of the rolling ratio of 20%, the hardness distribution curve level would be below that of non-rolling material. The hardness was lower when the rolling achieved to 40%. But this result except for near core produced a little different in hardness of the fracture surface because the hardness of the intermediate layer decreased greatly and the core center was small. On the other hands, the hardness of the rolling ration of 60% would be reversely and higher that of 40%. The all fracture surface(except for near core) would become to the same hardness distribution.

According to above describing, the change result of the specimen hardness on every rolling ratio is the same as that of the measurement data of the dynamic vicso elasticity. In other words, the rolling results in softening the material and improving the ductile property. Moreover, it is considered that the hardness distribution state would be improved and the un-homogenize mechanical property for the material structure would improve so that increasing the resistance to the damage on the high rolling ration(above 60%).

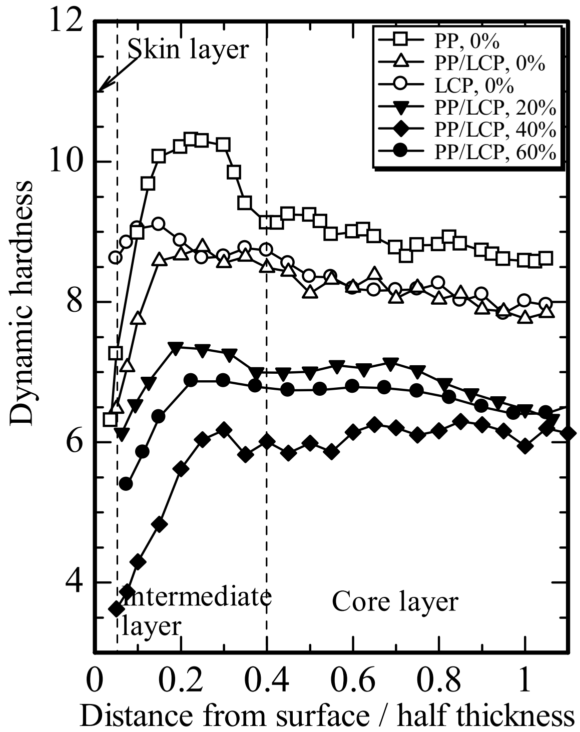

Fig.4 Distribution of hardness in cross section

3.5 Tensile fracture property

The great effect of the microstructure, morphology□material property of the blend on the rolling is above listed. The change of the material tensile property on the rolling is shown in Fig.5. The strain elongation of PP with non-rolling was more than 150% on the tensile test. PP is a typical ductile material. But the blend with the addition of 20% LCP appeared a brittle fracture within about 10%. Moreover, companion with the increase in the addition of LCP the material would lose the ductile property and become the brittle damage trend strongly.

On the other hands, the material ductility would be recycle on the rolling. The strain elongation was more than 150%. The yield stress declined on the increase in the rolling ratio up to 40%, but the yield stress would increase reversely on the rolling ratio of 60%. But the yield stress rose conversely when the rolling achieved 60%. Moreover, the observation strain of the rolling ratio of 20% occurred in the neck part due to tensile behavior, however, the observation strain would appeared in the parallel part while the rolling increased 60%.

Because the ductile matrix with the addition of the high strength reinforcement fiber form both phase separation composites, the inter-phase will influence the material strength and result in decreasing the ductile property. According to this study results, the rolling is an effective method to improve the composite strength and especially in the ductile property. In the case of the PP/LCP blend, the joining strength between both inter-phases is weakly because PP cannot solute in LCP. The crack produces in the inter-phase easily and the specimen produces the brittle damage easily. Moreover, the rolling with high rolling ratio was done: (1) the molecular orientation of PP was improved, and the LCP phase could be elongated too, (2) the un-homogenize of the structure and mechanical property in the fracture surface was improved, (3) the increase in the join strength of two inter-phase due to the increase in the compressive adhesive effect, and the material strength and ductile property were increased too.

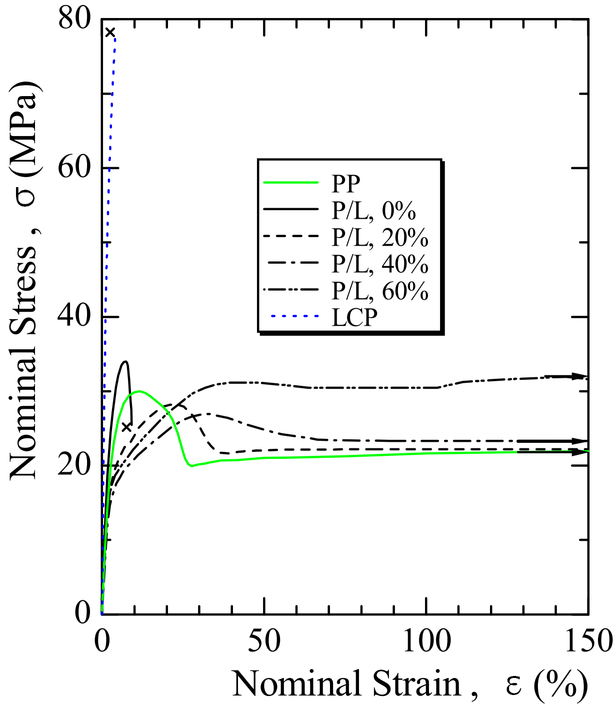

Fig.5 Nominal tensile stress-strain curves

4. CONCLUSION

(1) PP/LCP blends are a non-solution bi-phase system. The LCP phase was dispersed to fiber form along to the direction of injection molding, and would become coarsen from specimen surface to center. Because the rolling machining was done and the reinforcement of LCP phase was increased, the observed slightness trend of this blend would be increased in rolling ratio.

(2) With the increase in the rolling ratio, (a) E' and the hardness of fracture surface were low under 40%. It considers that the specimen softened. E' and hardness on the high rolling ratio of 60% would be renewed and more than it on the rolling ratio of 40%.

(3) The highest of the non-rolling material of PP phase and molecular orientation of LCP phase appeared in the intermediate layer, and they became the lowest in the center

of the core. With the increase in the rolling ratio(under 40%), the molecular orientation of the intermediate layer became lower and it increased in the core. When the molecular orientation achieved 60%, it would increase in the intermediate layer and core.

(4) High ductile property of PP single phase would lose while non-rolling ductile material of LCP phase was added to 20%. The damage was brittle fracture when the strain was less than 10%. However, the material yield stress decreased and its elongation renewed due to rolling machining. Specially, the material strength and elongation would be greatly increased on the high rolling ration of 60%. It means (a) Two phases of PP and LCP would be elongated on the rolling machining with high ductile ratio, and the molecular orientation of PP increased due to the special material elongation. (b) The mechanical property and structure uniformity on the fracture surface were improved. (c) It is considered that the increase in the join strength of two inter-phase due to the increase in the compressive adhesive effect, and the material strength and ductile property were increased too.

(5) According to the results of the composite microstructure by rolling machining, it is considered whether or not an effective method that the join strength of inter-phase and ductile property were improved.

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